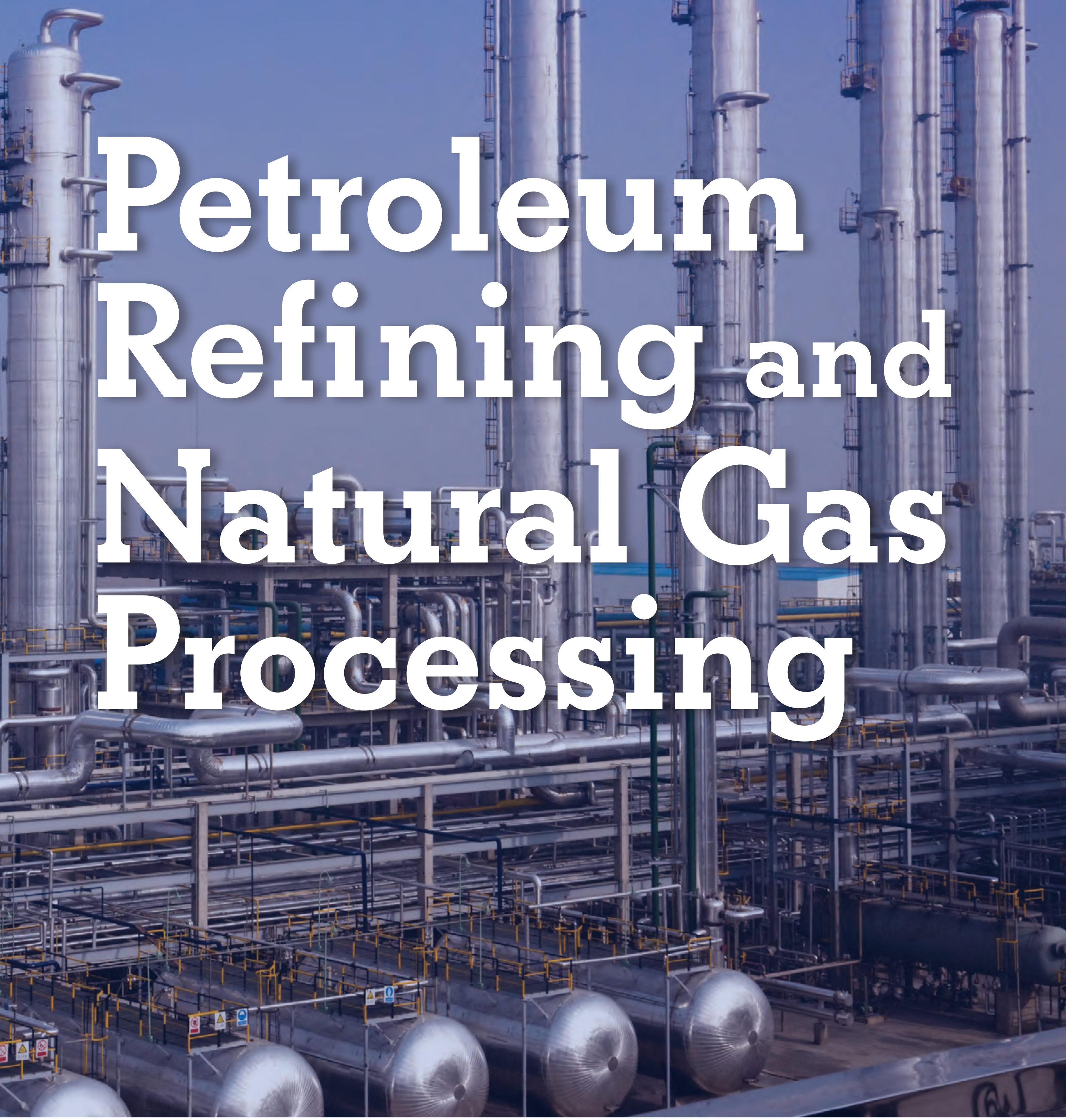
Petroleum Refining and Natural Gas Processing



M.R. Riazi, S. Eser, S.S. Agrawal, J.L. Peña Díez, editors

ASTM
INTERNATIONAL
Standards Worldwide

Petroleum Refining and Natural Gas Processing

M.R. Riazi, Semih Eser, Suresh S. Agrawal, and José Luis Peña Díez, Editors

ASTM Stock Number: MNL58

ASTM International
100 Barr Harbor Drive
PO Box C700
West Conshohocken, PA 19428-2959

Printed in U.S.A.

Library of Congress Cataloging-in-Publication Data

Petroleum refining and natural gas processing / M.R. Riazi ... [et al.].
p. cm. — ([ASTM manual series] ; MNL 58)
Includes bibliographical references and index.
ISBN 978-0-8031-7022-3 (alk. paper)
1. Petroleum—Refining. 2. Natural gas. I. Riazi, M. R.
TP690.P4728 2011
665.5'3—dc23 **2011027593**

Printed in
2013

Foreword

THIS PUBLICATION, *Petroleum Refining and Natural Gas Processing,* was sponsored by Committee D02 on Petroleum Products and Lubricants. This is Manual 58 in ASTM International's manual series.

To
Our families

Preface

Oil and gas have been the main sources of energy the world over for the past century and will remain important sources of energy for the first half of this century, and possibly beyond. Currently, more than 60 % of the world's energy is produced from oil and gas, and energy needs are increasing. In addition, oil and gas provide the main feedstocks for the petrochemical industry. World population is expected to increase to eight billion by 2030, which will demand an increase in energy of 40 % in the next two decades. With these increases in energy consumption it is becoming necessary to consider unconventional types of oils. Such oils, which are heavier, require more rigorous processing and treatment. The evolution of petroleum refining began with the birth of modern oil production in Pennsylvania in the nineteenth century. Current refineries are much more complex than those of a few decades ago and there is significant research concerning the development of more economical uses of available hydrocarbon resources.

In the past few decades there has been an increase in the number of publications that report advancements in the petroleum industry. *Petroleum Refining and Natural Gas Processing* is a continuation of those efforts and attempts to bring together the most recent advances in various areas of petroleum downstream activities, with an emphasis on economic and environmental considerations, heavy-oil processing, and new developments in oil and gas processing.

The primary goal of this book is to provide a comprehensive reference that covers the latest developments in all aspects of petroleum and natural gas processing in the downstream sector of the petroleum industry. It includes topics on economy and marketing, scheduling and planning, modeling and simulation, design and operation, inspection and maintenance, corrosion, environment, safety, storage and transportation, quality and process control, products specifications, management, biofuel processing and production, as well as other issues related to these topics. Every attempt has been made to avoid overlap between chapters, however, there are some topics that have been included in more than one chapter when relevant to both chapters. Another objective of this book is to describe the latest technology available to those working in the petroleum industry, especially designers, researchers, operators, managers, decision-makers, business people, and government officials. The petroleum industry is a diverse and complex industry and it is almost impossible to include all aspects of it in a single book. However, we tried to cover the most vital issues and we believe this is the most comprehensive resource published to date for use by people involved in this worldwide industry. We hope this contribution will be useful to them. In writing this book we benefited from the published works of many researchers, which are cited at the end of each chapter. We welcome comments and suggestions from readers.

More than 40 scientists, experts, and professionals from both academia and industry have cooperated and contributed to the 33 chapters in this book. Authors with years of experience made unique contributions not available in any similar publications. We are grateful to all of them for their efforts in bringing this book to fruition.

We also thank the large number of anonymous reviewers who went through lengthy manuscripts and provided us with their constructive comments and suggestions, which greatly enhanced the quality of the manual. Many publishers, organizations, and companies provided us with permission to use their published data, graphs, and figures and we thank them for their cooperation in supporting this publication effort.

We are also thankful to ASTM International for sponsoring publication of this book, especially to Kathy Dernoga, Monica Siperko, Marsha Firman, and other ASTM staff involved in this project. Kathy Dernoga's review and encouragement were essential to the completion of this work. The support and encouragement of Dr. George E. Totten, ASTM's Committee on Publications representative for this manual, is also appreciated. The reviewing process was managed and conducted by Christine Urso of the American Institute of Physics (AIP) and she was extremely cooperative in uploading the manuscripts to the online reviewing site, inviting reviewers, and handling of all manuscripts submitted for this manual. Also, many thanks to Rebecca L. Edwards, senior project manager at Cenveo Publisher Services for copyediting and production.

Finally, and most importantly, we thank our families for their patience, understanding, cooperation, and moral support, which were essential throughout this process.

M. R. Riazi—Kuwait University, Kuwait
Semih Eser—The Pennsylvania State University, University Park, PA, USA
Suresh S. Agrawal—Offsite Management Systems, Houston, TX, USA
José Luis Peña Díez—Repsol, Madrid, Spain

Contents

1

Introduction

M.R. Riazi[1], Semih Eser[2], José Luis Peña Díez[3], and Suresh S. Agrawal[4]

ABBREVIATIONS

APC	Advanced process control
API	American Petroleum Institute
DAO	Deasphalted oil
DEG	Diethylene glycol
EIA	Energy Information Administration
EPA	U.S. Environmental Protection Agency
FCC	Fluid catalytic cracking
FO	Fuel oil
GOR	Gas-to-oil ratio
GTL	Gas-to-liquid
H-Oil	Heavy oil
HDS	Hydrodesulfurization
LCO	Light cycle oil
LPG	Liquefied petroleum gas
MDEA	Monodiethanol amine
MEA	Monoethanol amine
NGL	Natural gas liquid
OSHA	Occupational Safety and Health Administration
PSA	Pressure sewing adsorption
RON	Research octane number
TEG	Triethylene glycol
ULSD	Ultralow sulfur diesel
VGO	Vacuum gas oil
VRDS	Vacuum residue desulfurization

1.1 PETROLEUM FLUIDS, REFINERY FEEDSTOCKS, AND PRODUCTS

Petroleum was first used in 1546 by the German mineralogist George Bauer and was reported as a naturally occurring flammable liquid found in rocks that contain various types of hydrocarbons. Petroleum and natural gas play an important role in providing energy and the production of petrochemicals. The word "petroleum" comes from the Latin words of *petra* (rock) and *oleum*, which refers to a special type of oil [1]. Petroleum is a complex mixture of hundreds of hydrocarbons comprising mainly paraffins, naphthenes, and aromatics. The lightest hydrocarbon component of petroleum is methane, which is the main element of natural gas, and the heaviest components include asphaltenes, with molecular weights higher than 1000 that are found in heavy oils. These complex high-molecular-weight structures also contain heteroatoms such as nitrogen (N) and sulfur (S). In addition, small quantities of hydrogen and some metals are present in most crude oils as will be discussed later. In today's terminology, crude oil is referred to as the liquid type of petroleum that is processed in petroleum refineries, and natural gas is a mixture of light hydrocarbons produced from petroleum and gas reservoirs.

There are several theories on the formation process of petroleum and hydrocarbons. It is generally believed that the petroleum is derived from aquatic plants and animals through conversion of organic compounds into hydrocarbons. These organisms and plants under aquatic conditions have converted inorganic compounds dissolved in water (such as carbon dioxide) to organic compounds through the energy provided by the sun,

$$6CO_2 + 6H_2O + \text{energy} \rightarrow 6O_2 + C_6H_{12}O_6 \tag{1.1}$$

in which $C_6H_{12}O_6$ (a carbohydrate) is an organic compound. Formed organic compounds may be decomposed into hydrocarbons under certain conditions of temperature and pressure,

$$(CH_2O)_n \rightarrow xCO_2 + yCH_z \tag{1.2}$$

in which n, x, y and z are integer numbers and yCH_z is the closed formula for the produced hydrocarbon compound. Conversion of such organic materials to hydrocarbons occurs under heat (~210–250°F), pressure (~2500 psi), and radioactive rays. Catalysts for such reactions are vanadium (V) and nickel (Ni), and for this reason some of these metals are found in small quantities in petroleum fluids. A geologic time of approximately 1 million years is required for completion of such reactions. In some other theories it is suggested that calcium carbonate ($CaCO_3$), an inorganic compound, can be converted to calcium carbide (CaC_2), which reacts with water (H_2O) to make acetylene (C_2H_2), a hydrocarbon. Either way, an aquatic environment is required for the formation of petroleum and that could be a good reason why major oil reservoirs are located in the vicinity of seas and oceans, and major oil fields are found at the seabeds of the Gulf of Mexico or the Persian Gulf in the Middle East.

Hydrocarbons produced from organic materials gradually migrate through porous rocks and form a petroleum reservoir when a nonporous or seal rock is found. A series of reservoirs within a common rock form an oil field. Hydrocarbons found in different fields and reservoirs vary depending on their source and the maturity of the formation process, and this leads to the production of different kinds of reservoir fluids. Figure 1.1 shows seven kinds of

---

[1] Kuwait University, Kuwait
[2] The Pennsylvania State University, University Park, PA, USA
[3] Repsol, Madrid, Spain
[4] Offsite Management Systems LLC, Sugar Land, TX, USA

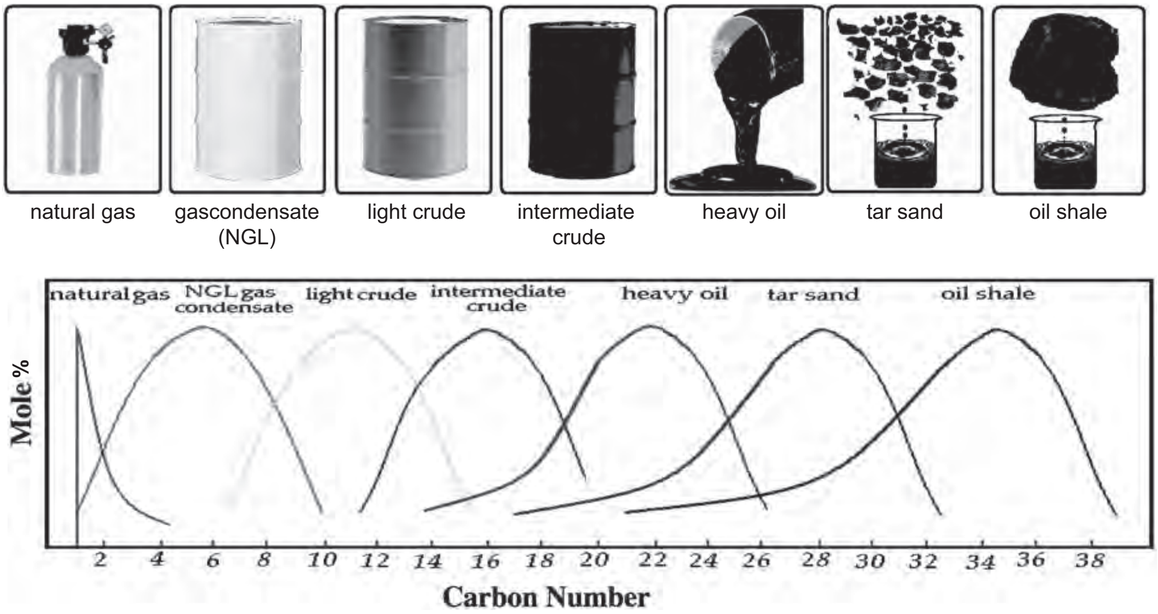


Figure 1.1—Various categories of natural gas and liquid and naturally occurring petroleum fluids and their approximate hydrocarbon molecular weight distributions according to their carbon numbers [2,3].

reservoir fluids from natural gas to tar sand and oil shale. Heavy oil refers to crudes having an API gravity of less than 20 (or specific gravity > 0.93), whereas extra heavy oils, tar sands, oil shale, and bitumen are considered extra-heavy oil (API gravity < 10 or specific gravity > 1). These heavy fluids usually do not flow naturally (except in hot reservoirs), need artificial heating or enhanced recovery technologies for their extraction, and are considered as unconventional oils. Further specifications of these types of petroleum fluids are given in Chapter 2.

Reservoir fluids can also be characterized by their gas-to-oil ratio (GOR) when they are brought to atmospheric conditions. Dry gases contain more than 90 % methane, and upon production at the surface have a GOR of 100,000 (scf/bbl) or more whereas oils with a GOR of less than 1000 (scf/bbl) contain less than 50 % methane and the produced crude oil has an API gravity of less than 40. Separation of oil and gas and production of crude oil from a reservoir fluid occurs at the surface facilities under field processing [3]. The water content of reservoir fluid is separated through a gravity-type separator, and the pressure of a reservoir fluid at the wellhead is gradually reduced to 1 atm in two- or three-stage gas-liquid separators, as shown in Figure 1.2 [4]. In this figure, the pressure of a reservoir fluid with a GOR of 853 scf/bbl is reduced from 164.5 to 1.01 bar in three stages. The liquid produced from the last stage is called crude oil and contains small concentrations of dissolved light gases. Table 1.1 gives a typical composition of a reservoir fluid and the produced crude oil and gases. Gas produced by this method is called associated gas to distinguish it from natural gas produced directly from a gas reservoir. Produced crude oil is then transferred to an export terminal or to a local refinery for processing. In the case of natural gas, water can be separated through the glycol dehydration process, as discussed in Chapter 11.

In addition to the above forms of naturally occurring hydrocarbons, there are huge amounts of hydrates under the sea and at the bottom of oceans. Hydrates are ice-like crystalline structures formed under high pressures and low temperatures where light hydrocarbons (i.e., C_1, C_2, C_3, or C_4) are surrounded by water molecules. When hydrates are moved outside of the thermodynamic stability conditions they decompose into water and hydrocarbons, releasing large amounts of natural gas. However, current technologies do not allow their commercial exploitation, and there is an intense work of research facing the challenge of making them a usable source of energy.

In general, the distribution of elements present in a typical crude oil vary within fairly narrow limits, and on weight basis they are 83–87 % carbon, 10–14 % hydrogen, 0.1–2 % nitrogen, 0.05–1.5 % oxygen, 0.05–6 % sulfur, and less than 0.1 % metals such as vanadium, nickel, and copper [1]. The quality of crude oils is determined by their API gravity and sulfur contents. A lower carbon-to-hydrogen

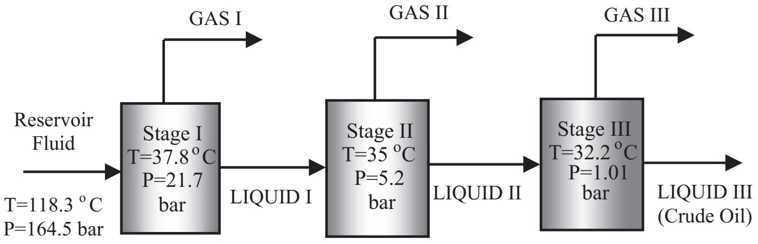


Figure 1.2—Schematic of a three-stage separator in a Middle East production field [4].

TABLE 1.1—Calculated Composition (in mol %) of Crude Product from a Three-Stage Separator [4]

No.	Component	Feed	First-Stage Gas	Second-Stage Gas	Third-Stage Gas	Third-Stage Liquid
1	N_2	0.09	0.54	0.12	0.05	0.00
2	CO_2	2.09	3.91	4.09	1.44	0.02
3	H_2S	1.89	1.47	4.38	5.06	0.14
4	H_2O	0.00	0.00	0.00	0.00	0.00
5	C_1	29.18	64.10	32.12	5.68	0.03
6	C_2	13.60	19.62	32.65	25.41	0.38
7	C_3	9.20	7.41	18.24	35.47	3.05
8	nC_4	4.30	1.48	4.56	13.92	4.38
9	iC_4	0.95	0.41	1.23	3.47	0.78
10	nC_5	2.60	0.36	1.01	3.98	4.81
11	iC_6	1.38	0.24	0.68	2.61	2.37
12	C_6	4.32	0.27	0.61	2.22	9.01
13	C_{7+}	30.40	0.19	0.31	0.69	75.03
Specific gravity at 60°F						0.8105
Temperature, °F		245	105	100	90	90
Pressure, psia		2197	315	75	15	15
GOR, scf/bbl		853	580	156	117	

ratio of crude indicates a better quality and a higher heating value. General characteristics of various oils are given in Table 1.2 and some specifications of petroleum products and their boiling ranges are presented in Table 1.3 [5]. Products from an Alaskan crude oil with their respective boiling range, carbon number, and yields are presented in Figure 1.3. Product specifications related to the quality of fuels are changing with time as demonstrated in Table 1.4 [5]. Further information about the quality and properties of petroleum crude oils and products are discussed in Chapter 4.

1.2 STATUS OF WORLD ENERGY SUPPLY AND DEMAND

Various forms of energy sources can be divided into two groups of nonrenewable and renewable forms. Nonrenewable forms of energy, which refer to resources that cannot be replaced after consumption, comprise mainly fossil fuels, such as oil, natural gas, and coal. Renewable forms of energy include biomass, solar, wind, hydro (water), and geothermal energy. In addition, nuclear energy, which is produced from the nuclear fission of uranium, is considered nonrenewable because of the limited uranium resources, but a potential future nuclear fusion technology could make it be considered as an inexhaustible resource. According to the Energy Information Administration (EIA) [6], world energy consumption in 2007 was 38 % oil, 23 % gas, 26 % coal, 6 % nuclear, 6 % hydro, and 1 % other renewable forms of energy. This indicates that oil and gas provide more than 60 % of the world energy supply. In addition, oil and gas are the main source of feedstocks for petrochemical plants that are eventually converted into many industrial chemicals and materials, such as polymers and plastics, dyes, synthetic fertilizers, insecticides, and pharmaceuticals.

The total proved oil reserves in 2007 amount to 1238 billion bbl, with the Middle East share of 61 %, North and South America account for 15 %, Europe and Euro-Asia 12 %, Africa approximately 10 %, and the Asia Pacific region 3 % of the total proved reserves. The estimated oil reserves in 2008 were 1342 billion bbl up by 8 % from the previous year's estimate. This is mainly due to the inclusion of Canada's heavy-oil sand reserves in the 2008 estimate [7]. In addition, there are huge unconventional oil resources distributed in Canada, South America, Russia, and China, where the production could be economically feasible if the oil price maintains above $80/bbl. With the addition of unconventional oil reserves, the total world oil reserves could reach approximately 10 trillion bbl. As of January 1, 2009, the proved world natural gas reserves were estimated at 6254 trillion ft^3, of which 40 % are located in the Middle

TABLE 1.2—Properties of Light, Heavy, and Extra-Heavy Crudes and Residue

Classification	Definition
Extra light	High API gravity, low S, N, and negligible asphaltene and metals
Light crude	Medium-range API gravity, low S, N, metals, and moderate asphaltene
Heavy crude	Medium-range API gravity, high S, N, high metals, and asphaltene
Extra heavy/residue	Low API gravity and very high contaminants (S, N, metals, and asphaltenes)

TABLE 1.3—Main Products Obtained during the Refining Processes along with Their Boiling Point and Their Final Product Use [5]

Refinery Streams	Boiling Range, °C	Number of Carbons	Processing	Final Product(s)
LPG	–40 to 0	1–4	Sweetener	Propane fuel (bottled gas)
Light naphtha	39–85	~8	Hydrotreater	Gasoline (fuel for cars)
Heavy naphtha	85–200	~10	Catalytic reformer	Gasoline, aromatics (chemicals and plastics)
Kerosine	170–270	~15	Hydrotreater	Jet fuel, no. 1 diesel (fuel for aeroplanes)
Gas oil	180–343	~20	Hydrotreater	Heating oil, no. 2 diesel (fuel for car and transportation)
Atmospheric residue	343+		Hydrotreater	Fuel oil
Vacuum gas oil	340–566	~35	FCC hydrotreater lubricating plant hydrocracker	Gasoline, LCO, gases fuel oil, FCC feed lubricating basestock gasoline, jet, diesel, FCC feed, lubricating basestock
Vacuum residue	540+	40+	Coker visbreaker asphalt unit hydrotreater	Coke, coker gas oil visbreaker gas oil, resid deasphalted oil, asphalt FCC feed road surfacing

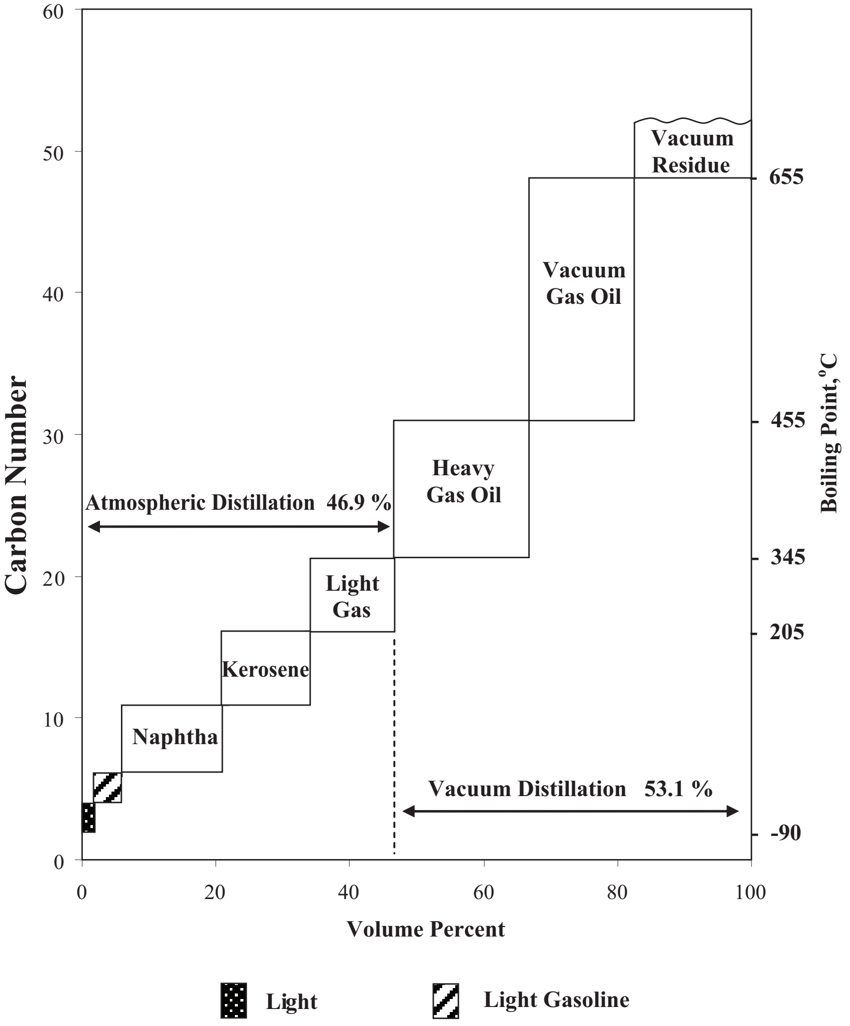


Figure 1.3—Products of atmospheric distillation oil for a typical Alaskan crude oil [4].

TABLE 1.4—Finished Product Specifications and Future Worldwide Restrictions[a]

Fuel/Properties	Situation in 1990s	Situation in 2010	Foreseeable Trend 2010–2020
Gasoline			
Clear RON	89–94	95–98	98
Clear MON	80–84	85–88	92
Benzene, vol %	3–5	1–2	<0.5
Aromatics, vol %	30–50	20–30	<30
Olefins, vol %	10–20	5–10	<10
Sulfur, ppm	300–500	50–100	<10
Diesel oil			
Sulfur, ppm	2000–5000	50	<10
Cetane number	45–50	50–53	>52
Aromatics, vol %	25–35	10–20	<10
Fuel oil (LS FO)			
Sulfur, wt %	3–4	0.5–1	<0.5
Nitrogen, wt %	0.5–0.7	0.3–.0.5	

[a]On average based on European standards from several studies [5].

East [6]. The production of natural gas in the world in 2006 reached 104 trillion ft^3, and it is projected to increase to 153 trillion ft^3 in 2030 [7].

There is a general confidence that is based on existing reserves data on hydrocarbon availability for the next decades, although the lower quality of the fluids and the exploitation of more difficult reservoirs will have an effect on market price. The development of unconventional oil and specialty gas (shale gas) is also starting to play an important role in changing energy markets. On the other side, the progressive implementation of laws with focus on carbon policies and energy efficiency may result in significantly different future consumption scenarios. Further discussion on oil and natural gas reserves and the projections of energy supply and consumption are presented in Chapter 3.

Coal is another important fossil fuel in addition to oil and gas and provides a significant share of the total energy used in the world. A current status of coal production and consumption in the world is presented in Figure 1.4. The estimated production peaks for oil, gas, and coal in the world are shown in Figure 1.5 [8]. Various estimates indicate that the world oil peak would occur sometime between 2015 and 2020. It would be followed by peak gas and then peak coal. The United States and China are the major producers of coal in the world, and China consumes more than twice the amount that the United States does because more than 83 % of China's electricity is produced by coal-burning power plants. Coal can also be converted into gaseous or liquid fuels through gasification and (direct or indirect) liquefaction processes, although coal liquids produced by direct liquefaction have lower heating values than those of conventional oils and tend to contain more sulfur and other heteroatoms than found in oil. Because coal has a higher carbon-to-hydrogen ratio than that of oil, burning or conversion of coal produces large quantities of carbon dioxide that need to be mitigated because of the global warming problem.

The contribution of different sources to the energy production in recent years as presented above is expected to change during this century. By the end of the 21st century, the contribution of alternative sources of energy such as solar, wind, or nuclear energy could exceed that of oil and gas. According to the U.S. Department of Energy, the supply for oil will begin to decrease by 2020, and the demand for natural gas will peak around 2050. These projections are obviously speculative and vary substantially

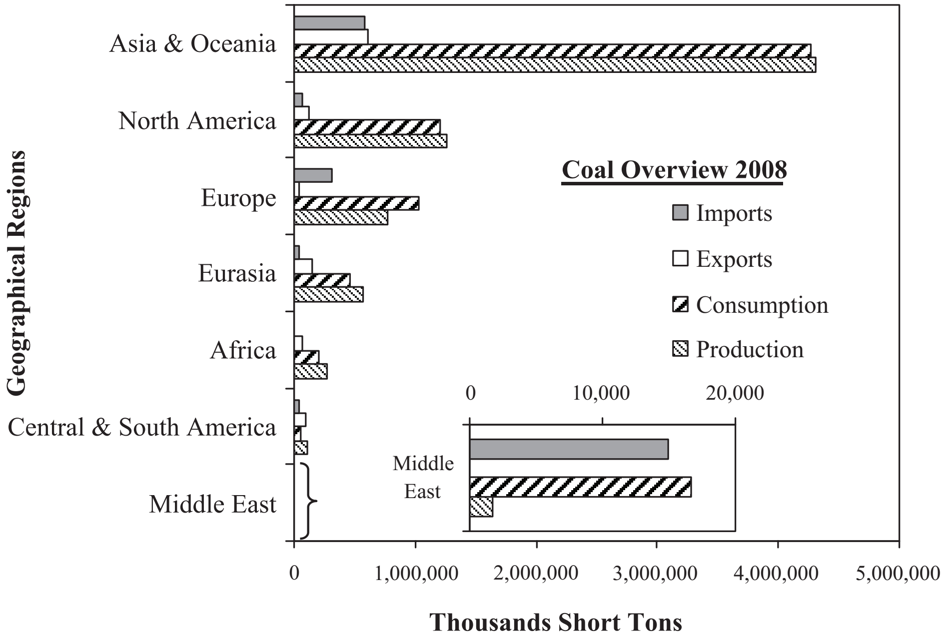


Figure 1.4—An overview of coal as a function of geographical region (2008).

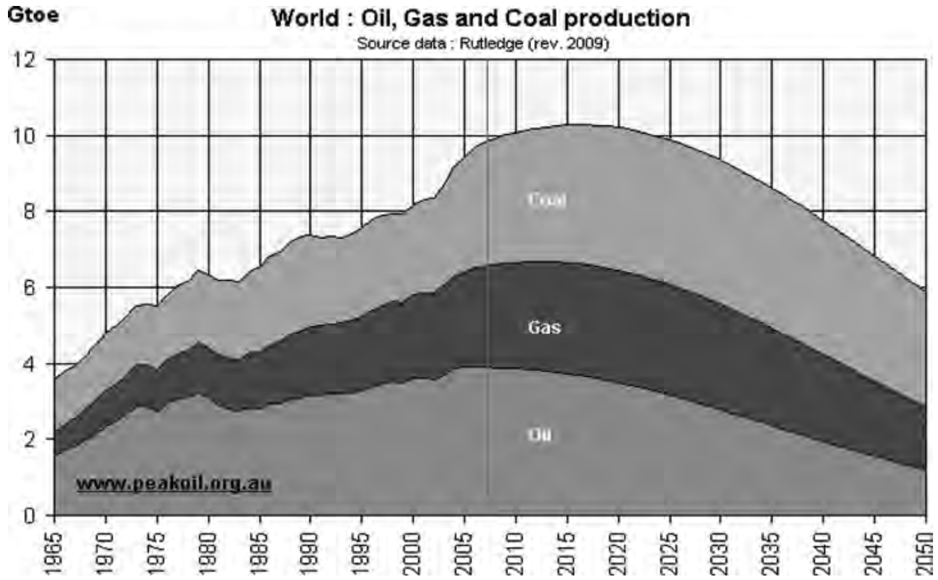


Figure 1.5—Occurrence of peak oil, gas, and coal [8].

from one source to another. However, as the production of energy from conventional and nonrenewable sources decreases, there will be more attempts to produce energy from unconventional oil and gas and renewable energy sources such as biomass and solar energy, as discussed in Chapter 3. Worldwide petroleum refineries and natural gas processing plant distribution as well as statistical data on refining capacities and expansion trends are also discussed in Chapter 3.

1.3 PETROLEUM REFINING

Refining is a series of physical and chemical processes in which petroleum is converted into several products for direct use or to provide feedstocks for petrochemical industries. Petroleum was first distilled by M.Z. Razi, a Persian chemist, who produced kerosine in the 9th century for use in kerosine lamps and for paving the streets of Baghdad with tar.

The first process of petroleum refining is desalting, in which the salt content of oil is reduced to 1–10 PTB (pound equivalent NaCl per thousand barrel of crude). Desalted oil then enters a distillation unit that operates at atmospheric pressure. In this unit, crude oil is separated according to boiling point range into distillate fractions such as liquefied petroleum gas (LPG), naphtha, kerosine, and light- and heavy-gas oils. Figure 1.3 shows the distribution of distillation fractions for a typical Alaskan crude oil along with the boiling point and carbon number ranges for the constituent hydrocarbons. Atmospheric residue (composing 54 % of a typical Alaskan crude as seen Figure 1.3) is further fractionated in a vacuum distillation unit (at 40–50 mmHg) to produce vacuum gas oils and vacuum residue. Straight-run products from atmospheric distillation generally undergo only finishing processes such as hydrotreatment to remove heteroatoms (e.g., S and N) and blending to achieve the mandated specification before they are sold as final products. Vacuum distillation generates intermediate streams (i.e., vacuum gas oils and vacuum residue) that go through a series of conversion and finishing processes to produce light- and middle-distillate fuels, such as gasoline, jet fuel, diesel fuel, fuel oil, and non-fuel products such as lubricating oils. Table 1.3 lists the main products obtained during the refining processes along with their boiling point ranges and final use. An overview of refinery processes as well as feedstocks and products is given in Table 1.5 [9]. Applications and specifications of all fuels and materials obtained from crude oil refining are discussed in Chapters 2 and 4.

One of the main characteristics of today's modern refineries is the capability to convert heavy crude oil into light and middle distillates without producing heavy residues. In today's refineries, more than 44 % of a typical crude oil can be converted into gasoline with less than 9 % ending up as heavy residues and carbon, compared with a gasoline yield of only 3 % from a simple batch distillation in the 19th century. A brief history of the refinery evolution is given in Table 1.6. This advancement of petroleum refining is due to the development of many new processes for refining and upgrading the conventional and heavy oils, as discussed in Chapters 5–10.

Chapter 5 gives an overview of the objectives of petroleum refining, overall refinery flow, and the major processes used for refining crude oil are divided into four categories: separation, conversion, finishing, and supporting processes. Separation processes make use of the differences in the physical properties of crude oil components to separate groups of hydrocarbon compounds or inorganic impurities, whereas conversion processes cause chemical changes in the hydrocarbon composition of crude oils. Finishing processes involve hydrotreating to remove heteroatoms (S, N, and metals) and product blending to produce fuels and materials with desired specifications and in compliance with environmental and government regulations. Finally, supporting processes provide the recovery of the removed heteroatoms or hetoroatom compounds, production of the hydrogen necessary for conversion and hydrotreating processes, and effluent water treatment systems.

One of the main processes used in petroleum refineries to crack heavy oils and residues into light- and middle-distillate products is fluid catalytic cracking (FCC). FCC is a

TABLE 1.5—An Overview of Refining Processes and Their Feedstock and Valuable Products [9]

Process Name	Reactions (Type)	Feedstock(s)	Product(s)
Fractionation processes			
Atmospheric distillation	Separation (thermal)	Desalted crude oil	Gas, gas oil, distillate, residual
Vacuum distillation	Separation (thermal)	Atmospheric tower residual	Gas oil, lubricating stock, residual
Conversion processes-decomposition			
Catalytic cracking	Alteration (catalytic)	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Coking	Polymerize (thermal)	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Hydrocracking	Hydrogenate (catalytic)	Gas oil, cracked oil, residual	Lighter, higher quality products
Hydrogen steam reforming	Decompose (thermal/catalytic)	Desulfurized gas, O_2, steam	Hydrogen, CO, CO_2
Steam cracking	Decompose (thermal)	Atmospheric tower heavy fuel/distillate	Cracked naphtha, coke, residual
Visbreaking	Decompose (thermal)	Atmospheric tower residual	Distillate, tar
Conversion processes-unification			
Alkylation	Combining (catalytic)	Tower isobutane/ cracker olefin	Isooctane (alkylate)
Polymerizing	Polymerize (catalytic)	Cracker olefins	High-octane naphtha, petrochemical stocks
Conversion processes-alteration or rearrangement			
Catalytic reforming	Alteration/dehydration (catalytic)	Coker/hydrocracker naphtha	High octane reformate/aromatic
Isomerization	Rearrange (catalytic)	Butane, pentane, hexane	Isobutane/pentane/hexane
Treatment processes			
Amine treating	Treatment (absorption)	Sour gas, hydrocarbons with CO_2 and H_2S	Acid free gases and liquid hydrocarbons
Desalting	Dehydration (absorption)	Crude oil	Desalted crude oil
Drying and sweetening	Treatment (absorption/ thermal)	Liquid hydrocarbons, LPG, alkyl feedstock	Sweet and dry hydrocarbons
Furfural extraction	Solvent extraction (absorption)	Cycle oils and lubricating feedstocks	High-quality diesel and lubricating oil
Hydrodesulfurization	Treatment (catalytic)	High-sulfur residual/gas oil	Desulfurized olefins
Hydrotreating	Hydrogenation (catalytic)	Residuals, cracked hydrocarbons	Cracker feed, distillate, lubricating
Phenol extraction	Solvent (extraction absorption/ thermal)	Lubricating oil base stocks	High-quality lubricating oils
Solvent deasphalting	Treatment (separation)	Vacuum tower residual	Propane heavy lubricating oil, asphalt
Solvent dewaxing	Treatment (cool/ filter)	Vacuum tower lubricating oils	Dewaxed lubricating basestock
Solvent extraction	Solvent (extraction absorption/ precipitation)	Gas oil, reformate, distillate	High-octane gasoline
Sweetening	Treatment (catalytic)	Untreated distillate/gasoline	High-quality distillate/gasoline

major secondary processing unit in the petroleum industry for converting gas oil streams into high-octane gasoline, cycle oils, LPG, and light olefins. After the carbon rejection route, it upgrades low-value streams (e.g., vacuum gas oil, atmospheric residue, deasphalted heavy oils, etc.) into distillates operating at low pressures and moderate temperatures. FCC is very attractive from a value addition perspective because it is a net volume generation process. It has gained a special place in the refinery because of its feed flexibility, ability to produce diverse products, and its quick response to the market demands through minor changes in process operating conditions. The economics of the FCC process are so attractive that it is almost impossible to imagine a modern refinery without this unit. Considering

TABLE 1.6—History of Petroleum Refining Processes

Year	Process Name	Purpose	Byproducts, etc.
1849	Canadian geologist Abraham Gesner distills kerosine from crude oil		
1859	An oil refinery is built in Baku (Azerbaijan)		
1860–1861	Oil refineries are built near Oil Creek, Pennsylvania; Petrolia, Ontario, Canada; and Union County, Arkansas		
1862	Atmospheric distillation	Produce kerosine	Naphtha, tar, etc.
1870	Vacuum distillation	Lubricants (original) cracking feedstocks (1930s)	Asphalt, residual coker feedstocks
1913	Thermal cracking	Increase gasoline	Residual, bunker fuel
1916	Sweetening	Reduce sulfur and odor	Sulfur
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulfur	Sulfur
1932	Coking	Produce gasoline basestocks	Coke
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Solvent dewaxing	Improve pour point	Waxes
1935	Catalyst polymerization	Improve gasoline yield and octane number	Petrochemical feedstocks
1937	Catalytic cracking	Higher octane gasoline	Petrochemical feedstocks
1939	Visbreaking	Reduce viscosity	Increased distillate, tar
1940	Alkylation	Increase gasoline octane and yield	High-octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield and octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
1954	Hydrodesulfurization	Remove sulfur	Sulfur
1956	Inhibitor sweetening	Remove mercaptan	Disulfides
1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality and reduce sulfur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking	Increase gasoline yield from residual	Heavy residuals
1975	Catalytic converter	The phaseout of tetraethyl lead begins	Cleaner air
1990s	SCANfining (Exxon), OCTGAIN (Mobil), Prime G (Axens), and S Zorb (Phillips)	Reformulated gasoline and low-sulfur diesel	Low sulfur fuel
2000	Deep or ultra-deep desulfurization (ULSD)	Decrease sulfur level in diesel (2 ppm)	Sulfur

the central role of FCC in refineries to produce better quality fuels in higher yields, a separate chapter, Chapter 6, is specifically devoted to a detailed discussion of the FCC process. In addition to high-octane gasoline as the principal product, FCC produces LPG as well as isobutane and olefin-rich light hydrocarbons (propene and butenes) that can be used in alkylation and polymerization processes to produce more high-octane gasoline in refineries. In addition to the alkylation and polymerization processes, the isomerization process has also gained importance upon the recent limitations placed on the aromatic content of gasoline. Chapter 7 reviews the processes and catalysts used for isomerization of light naphtha and lubricating oils for quality enhancement. Isomerization of light naphtha, particularly C_5 and C_6 paraffins, is practiced to achieve the desired research octane number (RON) for gasoline blend stock in view of the stringent fuel specifications implemented worldwide. Although the isomerization of C_5/C_6 paraffins has been known for a long while, only in recent years have commercial catalysts been developed for the isomerization of paraffins in the lubricating oil range. Over the years, catalyst and process have evolved and improved. Thus, the scope of

Chapter 7 is to understand the chemistry and development of hydroisomerization catalysts and the evolution of hydroisomerization processes based on these developments, and it brings out future challenges and opportunities.

With the prospects of declining conventional crude oil reserves and large reserves of heavy crudes scattered around the world, there is increasing interest in efficient processing of heavy oils defined with respect to API gravity, viscosity, and mobility at the field conditions. Because of these properties and the complexity of their chemical constitution, heavy oils present challenges for analysis and upgrading into light distillates that have large demands. Analysis and processing of heavy oils are discussed in full detail in Chapter 8. On the processing side, an integration of carbon rejection (solvent separation and thermal treatment), hydrogen addition (catalytic hydrogenation and hydrocracking), and heteroatom removal (hydrotreating) offers a viable means of upgrading for transportation over long distances and conversion into light distillates. Chapter 8 provides an overview of current analytical techniques and upgrading processes used to address the challenges of bringing the heavy oils into the refineries and to the market place.

As shown in Figure 1.3, even conventional oil may produce more than 50% residues from an atmospheric distillation column. A flow diagram for upgrading a typical heavy oil is shown in Figure 1.6. In general, refineries are moving in the direction of processing heavier oil, producing less coke and residues and producing more middle distillates with the current economic and environmental constraints. A configuration suggested for future refineries is shown in Figure 1.7. One major goal of future refineries is to produce ultralow sulfur diesel (ULSD) and other low-sulfur fuels. Further discussion on future refineries is given in Chapter 33.

Recent advances in the area of refining processes are presented in Chapter 9, whereas Chapter 10 is devoted to the advancements in catalysts used in the refining processes. Catalysts play a critically important role in refining and natural gas processing, and the selection of an appropriate catalyst can improve the selectivity and quality of product and help achieve higher conversion rates into desirable products. Catalysts are expensive and constitute one of the major operating cost items incurred for running a refinery.

1.4 NATURAL GAS PROCESSING AND HYDROGEN MANAGEMENT

The world production and consumption of natural gas is on the rise, and a rough estimate indicates that current world natural gas reserves could satisfy world energy demand until the end of this century and even beyond, which is what makes it be considered the world energy source for the 21st century. Natural gas is the cleanest fossil fuel and produces much less carbon dioxide (CO_2) than coal or oil. For example, for the production of 1 million Btu heat from natural gas, oil, and coal, the total amounts of CO_2 that are emitted into air are 117, 164, and 208 lb, respectively. However, the gas distribution chain is more complex than other fuels and has delayed the worldwide implementation compared with liquid fuels. It was not until the 1960s that the transport trials as liquefied natural gas (LNG) solved the existing limitations of natural gas as a local resource. Because transportation is a major issue in the natural gas

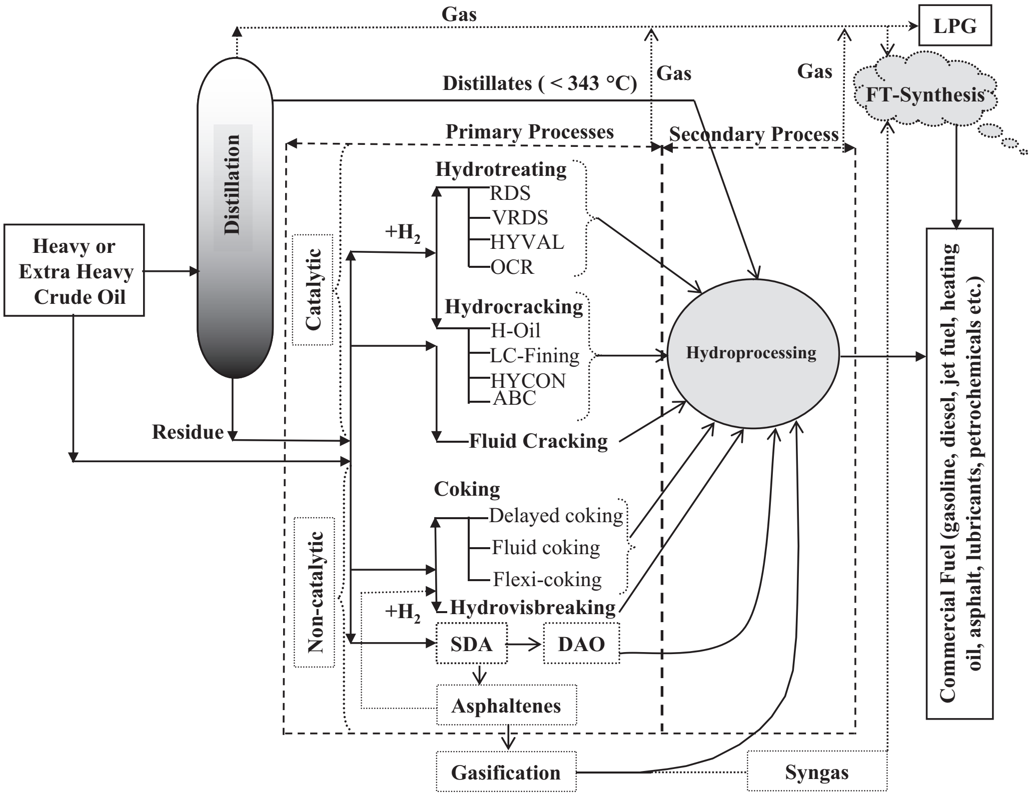


Figure 1.6—A flow diagram of typical oil refinery technologies for upgrading heavy crude oil and residue [10].

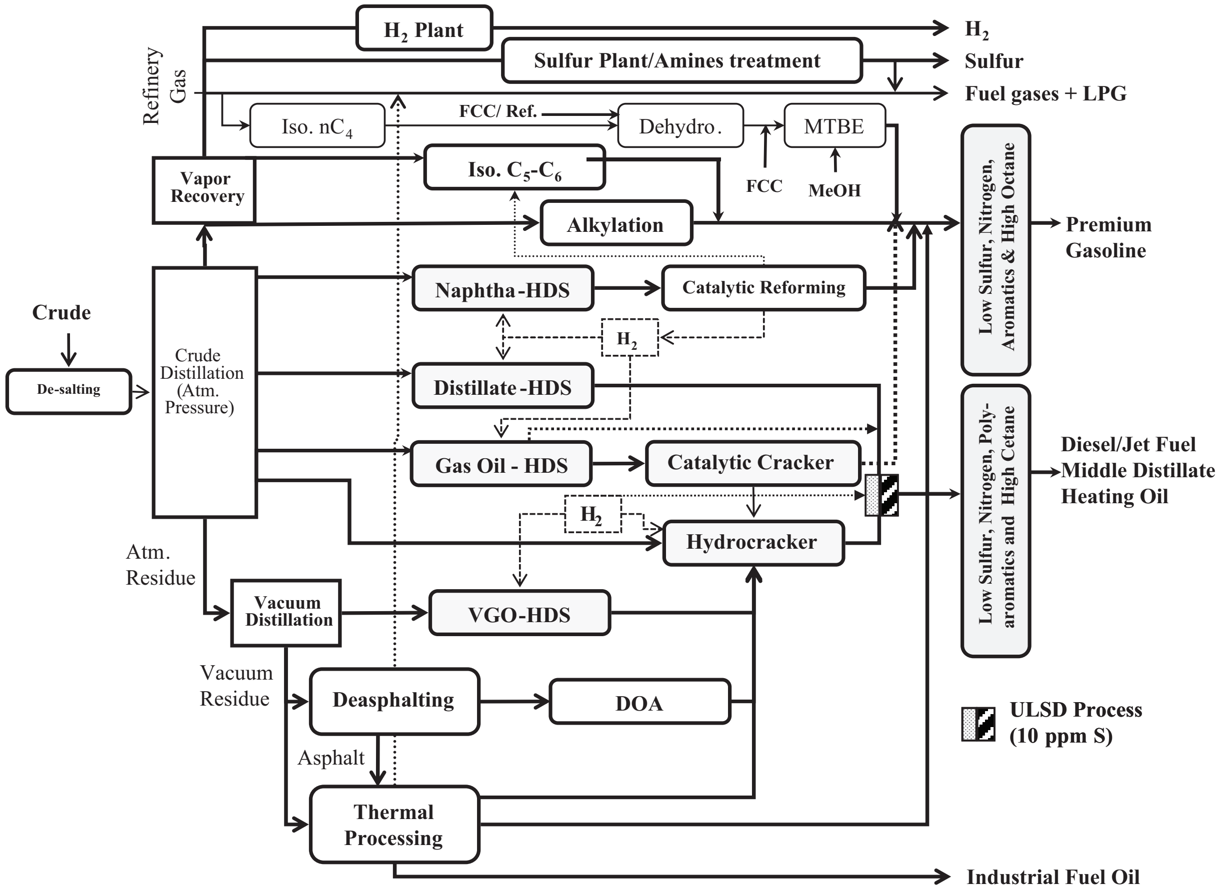


Figure 1.7—Possible petroleum refinery configuration of the future [5].

business, research on conversion of natural gas into liquid fuels has been very intensive during the last decades trying to overcome this limitation, and it is another reason to discuss natural gas processing in addition to petroleum refining in this book.

The associated or free gas produced from a reservoir goes through processes similar to crude oil at the field before it is sent to a gas processing plant. Commercial natural gas is primarily methane whereas raw natural gas at the wellhead contains other compounds such as ethane, propane, butane, and even heavier components as well as water, hydrogen sulfide (H_2S), CO_2, nitrogen, and some other compounds. Purification processes for natural gas—conditioning and fractionation—are hence critical to meet market specifications, and photographs of natural gas processing and sweetening plants are shown in Figure 1.8 [11]. In field conditioning, acid gases and water are removed by various separation methods. Acid gases (CO_2 and H_2S) are usually removed by chemical absorption with different amine technologies [monodiethanol amine (MDEA)-based solvents are the most common] or by alternative processes such as physical absorption (Benfield, Sulfinol, Selexol) for high-acid content gases. Membrane and molecular sieve adsorption processes [pressure sewing adsorption (PSA)] would be suitable for lower acid concentrations and might be used when it is required to reduce acid concentration to a very low level [12]. Water in natural gas is usually separated by absorption of water vapor through a solvent such as triethylene glycol (TEG). Heavier hydrocarbon components as related to natural gas liquids (NGL) must be removed from natural gas to meet specifications by using different technologies. Depending on local market needs, NGL may be sold as a mixed product or sent to fractionation processes to increase the market value of individual products as shown in Figure 1.9 [5]. Details on these processes as well as a review on natural gas liquefaction and regasification technologies are given in Chapter 11, which also covers alternative natural gas conversion technologies to liquid fuels [gas-to-liquid (GTL) technologies], which may become an economically viable option for large-scale gas monetization projects. Figure 1.10 shows a schematic of such processes [13].

Natural gas quality is mainly determined by its composition, particularly by its methane content. Natural gas with higher methane content has better quality because the ratio of hydrogen to carbon is higher in methane than any other hydrocarbon compound. One of the main uses of natural gas in petroleum and petrochemical plants is to use it for the production of hydrogen through a steam reforming process as shown in Figure 1.11 [14–16]. Figure 1.12 shows a hydrogen production plant in Europe with a capacity of 10,000 Nm³/h [17]. Hydrogen is used in petroleum refineries in conversion and finishing processes such as hydrocracking, hydrotreating, hydroconversion, and hydrofinishing for the upgrading of heavy ends. Chapter 12 is devoted to the production and management of hydrogen in the petroleum industries. This chapter first provides an overview of various technical aspects in refinery hydrogen

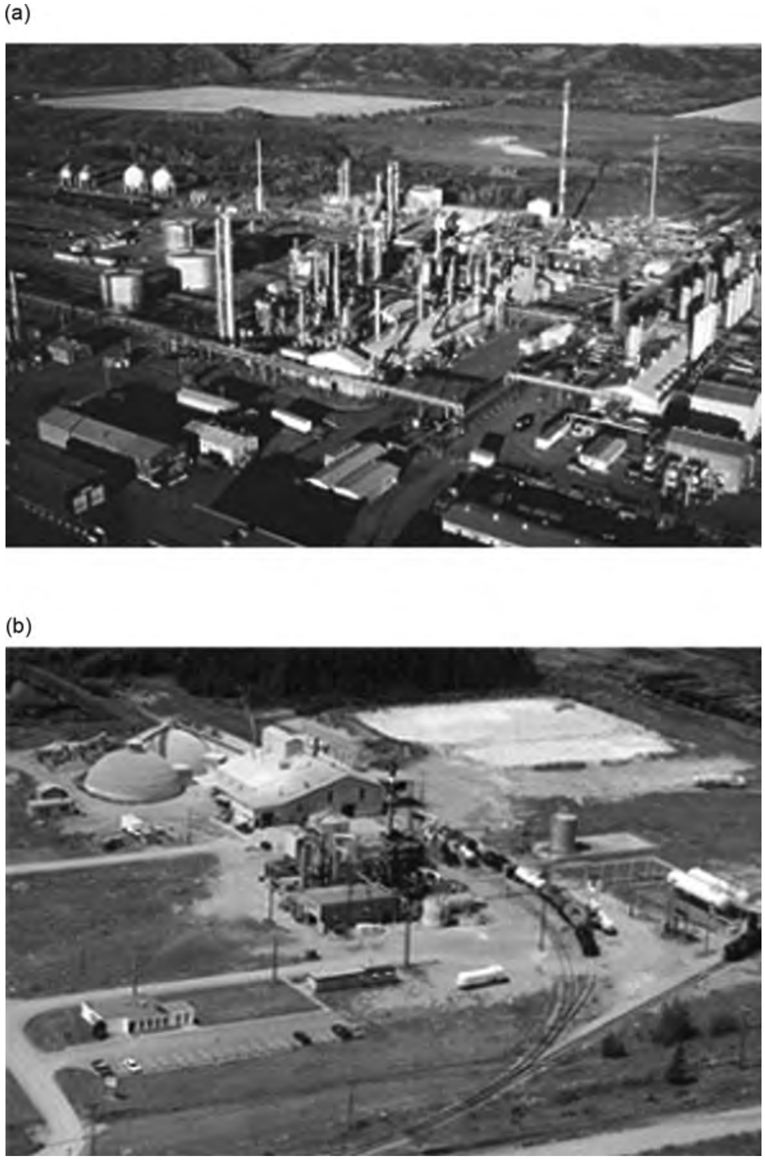


Figure 1.8—(a) Natural gas processing and (b) gas sweetening plants [11].

management, including basic information for hydrogen production, purification, transportation, and distribution. Because hydrogen supply becomes a bottleneck issue for many refineries to deal with stricter product specifications and a higher degree of heavy oil upgrading, a good hydrogen management practice becomes very important to maintain the competitiveness of a refinery. Therefore, a systematic approach, namely hydrogen pinch analysis, is introduced. It contains two steps—targeting and design—in which the targeting step quickly identifies the maximum hydrogen saving potential and the design step tries to exploit all possible design options to reach the target on the basis of mathematical programming. Details of the hydrogen pinch analysis technology are explained. Hydrogen undoubtedly is the best example of a perfect fuel. Having the highest heating value of any fuel on a mass basis as not releasing any carbon to the atmosphere upon combustion, it may play a role in energy future directions, as described in several chapters of this book.

1.5 DESIGN AND OPERATION OF REFINING AND NATURAL GAS PROCESSING UNITS

Refineries and gas processing plants are complex industries involving hundreds of units and pieces of equipment assembled together. The main process units include furnaces; heat exchangers; distillation, absorption, and stripping columns; separators; extraction units; and various types of reactors. Additionally, storage facilities, pipelines, pumps, compressors, and control units, among many other smaller components, are required. Optimal, economical, and safe operation of these units first requires careful design practices. A discussion of the detailed design of such units requires a dedicated handbook of process unit design. Chapter 13 gives a basic overview of design methods and calculations as well as specific methods for the major separation units and heat transfer equipment used by process engineers in the industry.

Reducing variability and enhancing process capability are the two distinctive imperatives in the competitive world

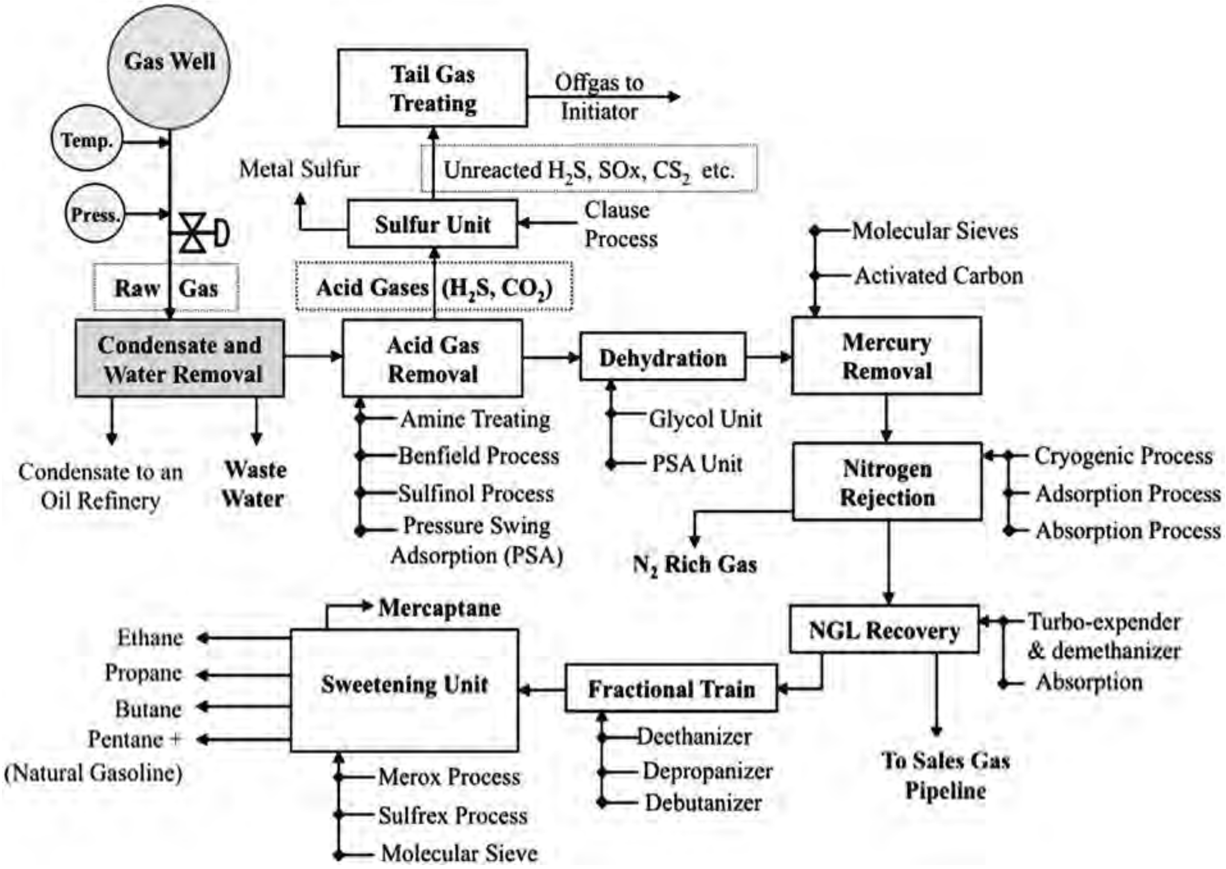


Figure 1.9—General scheme of natural gas processing [5].

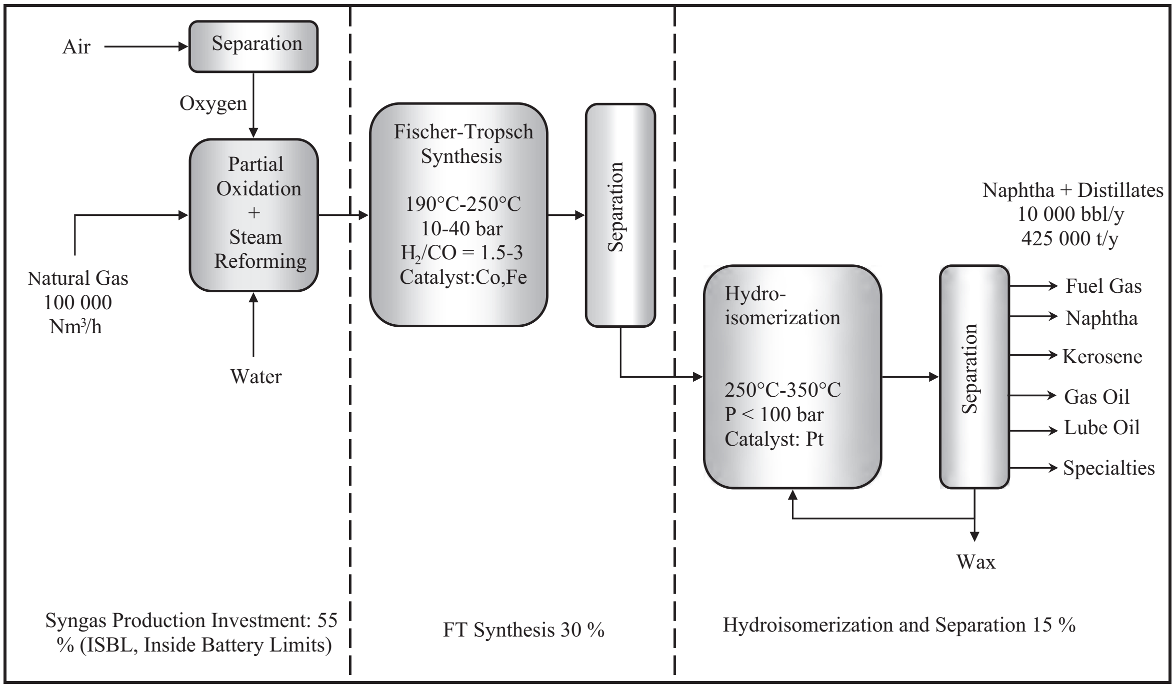
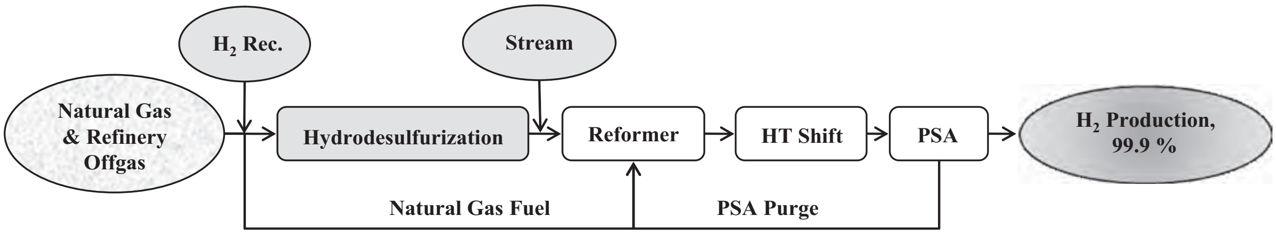


Figure 1.10—Natural gas upgrading: FT synthesis integrated GTL process [13].

of any manufacturing industry. Over the years, process control and instrumentation coupled with ever-increasing online computing power have brought about a paradigm shift in addressing these business objectives. Concepts such as global optimization, early event detection, geometric process control, etc., could be dovetailed on a real-time basis with relative ease to fulfill the performance set.

Chapter 14 helps readers obtain insight into basic process control approaches in manufacturing industries starting from simple feedback control to more advanced process



$$CH_4 + H_2O \rightleftharpoons CO + 3H_2O \qquad CO + H_2O \rightleftharpoons H_2 + CO_2$$

Figure 1.11—Natural gas to hydrogen production process schemes (PSA technology) [16].

control procedures, integrating the latest model-based quality measuring instruments such as near-infrared (NIR) analyzers for accurate and fast sample measurement for tighter control, enabling reduced "quality giveaway." Appropriate case studies are included for better understanding of the various controls as practiced in manufacturing industries. Reliability assurance of instrumentation and refinery of the future concepts are also discussed in Chapter 14 in order to trigger more concentrated efforts in the future on these topics.

Because of the importance of process control in modern refineries, Chapter 14 is followed by another chapter on unit control. Chapter 15 on modern computer process control provides a basis for understanding the various control technologies and their levels of integration, with the objective being to design and implement advanced process control (APC) applications that can help improve the operational profitability of the process units in a safe manner. The mix of technologies consisting of advanced regulatory control (ARC), conventional control, multivariable predictive control (MVPC)/model predictive control (MPC), inferential predictions, fuzzy logic control, advisory systems/abnormal situation management (ASM), and artificial neural networks (ANN) allows us to monitor, control, and optimize during the normal operating process conditions and during periods of fast ramping, feed changes, and unplanned events. Such APC applications have now become a norm for refining and petrochemical units, with several thousand implemented since the mid-1970s when the microprocessor and its associated distributed control systems (DCS) became available. The intention is not to provide an academic theory of control, but to provide sufficient base knowledge and practical configuration examples of what has actually worked in real-life applications for most of the major refining units. Briefly, Chapter 14 focuses on process control overview, from the basic elements to model predictive control, with case studies presented for some key units such as FCC or crude distillation units, whereas Chapter 15 provides the basis for understanding the key role of APC to meet refinery safety, operational, and economic objectives, with examples of application for most of the major refinery units.

Figure 1.12—A hydrogen plant in Belgium with a capacity of 10,000 m^3/h [17].

Although unit design and operations have been presented in Chapter 13, almost every chapter in which various processes are discussed includes a discussion on the design and operation of such units in further detail. For example, additional references to process design and operation have been included in Chapters 6 and 10 where FCC and other conversion-type processes are discussed, in Chapters 11 and 12 on natural gas processing and hydrogen production, as well as in chapters related to process simulation and control, corrosion, and alternative feedstocks such as heavy-oil processing and biorefineries.

Maintenance and inspection functions in a refinery are the backbone for safe and reliable plant operations and play a pivotal role in achieving the desired production target and profitability to the company efficiently; these are discussed in Chapter 16 in detail. Maintenance functions in the refinery constitute mechanical, electrical, instrumentation, and civil functions that are responsible for the monitoring, repair, and maintenance of equipment in its respective defined areas. Preventive maintenance, predictive maintenance, structured repair system, and full-fledged plant shutdown management are the necessities of reliability. Each type of maintenance activity that needs to be followed in an operating refinery or when the plant or units have been shut down as per plan has been covered here in detail. Efforts have been made to cover each type of maintenance such as preventive, predictive, and shutdown maintenance in this chapter and each one of them has been explained in detail. In the case of electrical and instrument equipment, emphasis has been placed on explaining the maintenance activities required to be performed on all major equipment along with general guidelines to be followed for making systems more reliable. Chapter 16 covers the various methods of inspection techniques that are followed in a refinery.

Corrosion inspection and control are discussed in Chapter 17. Metallic materials used to manufacture equipment for the petroleum refining industry are subjected to a wide variety of potential damage mechanisms, the most common being corrosion and environmental stress corrosion cracking. The safe operation of oil refineries depends on understanding these degradation mechanisms, making the proper material selection, devising corrosion control, inspection programs for earlier detection of problems, and monitoring material performance. Dry and wet corrosion are discussed in this chapter. Damage mechanisms other than corrosion are also described in their connection with particular refining processes.

1.6 REFINERY OFFSITE OPERATIONS AND TRANSPORTATION

A typical refinery or any liquid-based processing plant operations are categorized as onsite or offsite operations. The onsite activities are mainly concerned with safe, efficient, and optimized operations of process and ancillary units, whereas the offsite activities focus on crude blending, fuel blending, tank farm management, oil movement, terminal operations, etc. Typically, 80–85 % of refinery products for the end users are made in the offsite operations; hence, they can severely affect the refinery bottom line if these offsite activities are not designed, planned, and executed in an orderly and efficient manner. It is not uncommon that a refinery spends huge investments to optimize its process units and loses it all in outdated and inefficient offsite operations or both. Figure 1.13 shows a schematic diagram of refinery onsite and offsite operations [18].

It is of utmost importance for a refinery to produce and sell products with strict quality adherence following industry standards and governing ASTM test methods. Products are analyzed using laboratory analysis, online analyzers, and model predictive methods. Chapter 18 discusses all important aspects of product analysis and quality control, testing method standards, key specifications, etc. The cost of laboratory analysis is quite significant in a refinery, and Agrawal [19] has suggested a method to estimate laboratory analysis load and its cost and differentiate between the cost of laboratory analysis separately for onsite (process units) and offsite operations. In a case study of a 300-kbbl/day refinery, Agrawal [19] has demonstrated and it is shown in Figure 1.14 that many process streams require laboratory analyses for onsite operations but are less in frequency, whereas offsite operations require less laboratory analyses of tanks but are more in frequency.

Chapter 19 in this book discusses fuel blending technology, management of a blending project, and many important topics such as linear and nonlinear blend models, methods to handle blend nonlinearity, concepts of a recipe optimization and planning process in a refinery, etc. After the fundamental concepts are reviewed, the chapter discusses the design aspects of a blending project for the automation of field equipment and instrumentation, hardware, software, and blending tank quality measurement. The chapter concludes with methodologies to estimate various sources of errors and assess the current state of blending and the successful implementation of upgrade or revamp of a blending system. It is estimated that an integrated fuel blend control and optimization system can save on average 15–45 cents/bbl of gasoline production, amounting to $7–22 million/year in savings for a 300-kbbl/day refinery. Figure 1.15 shows the various functional modules

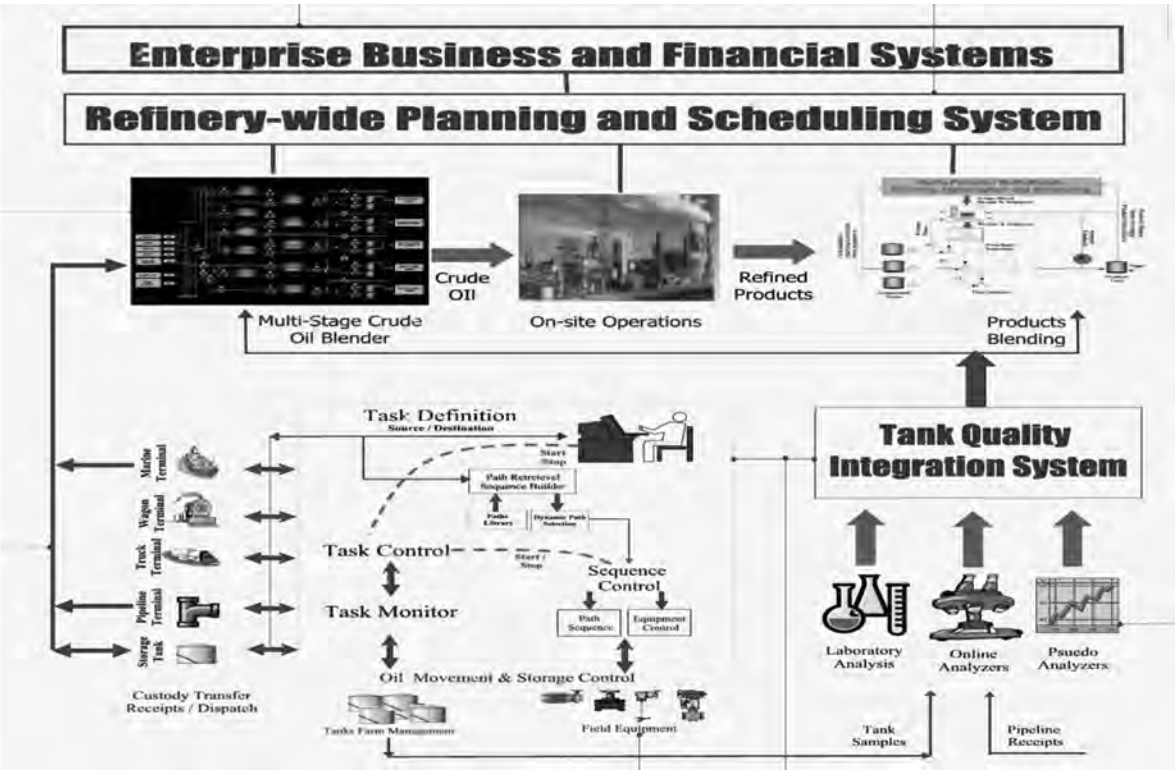


Figure 1.13—Integrated onsite and offsite operations [18].

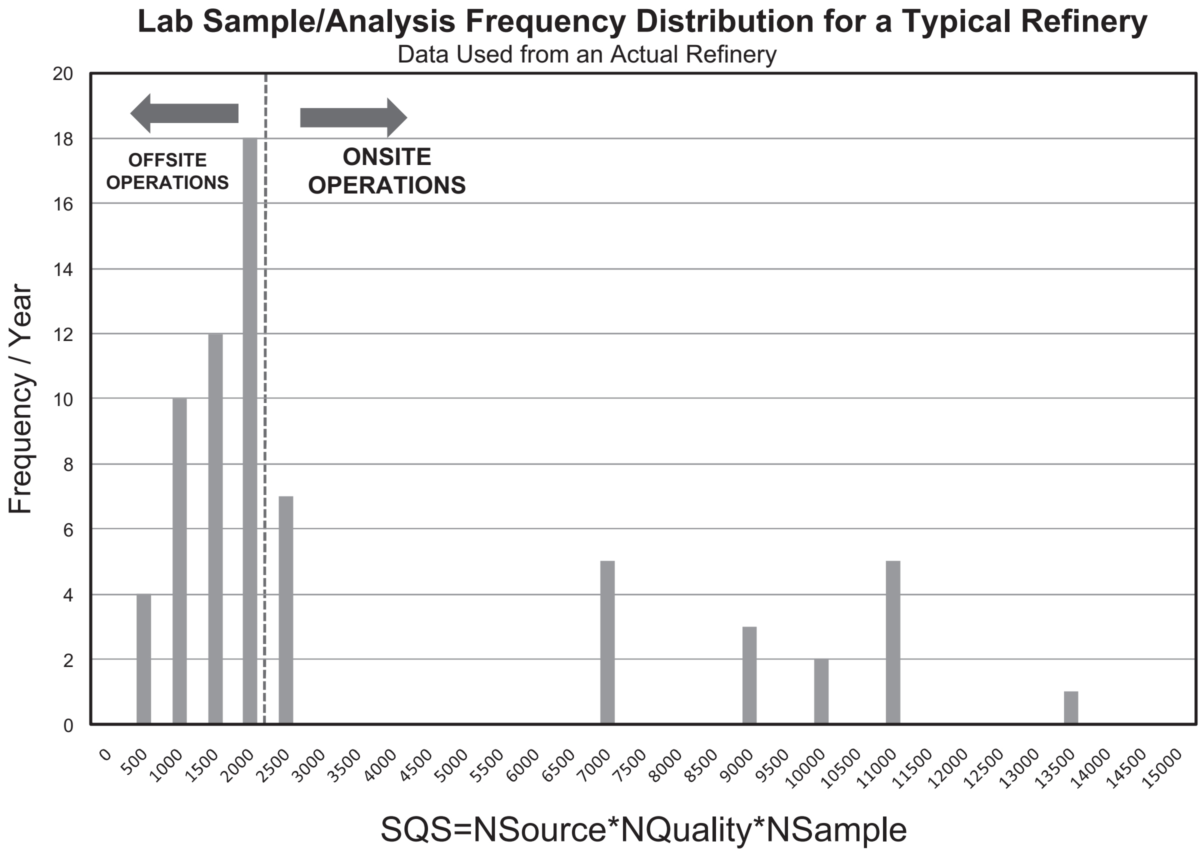


Figure 1.14—Typical distribution of laboratory analyses load for onsite and offsite operations [19].

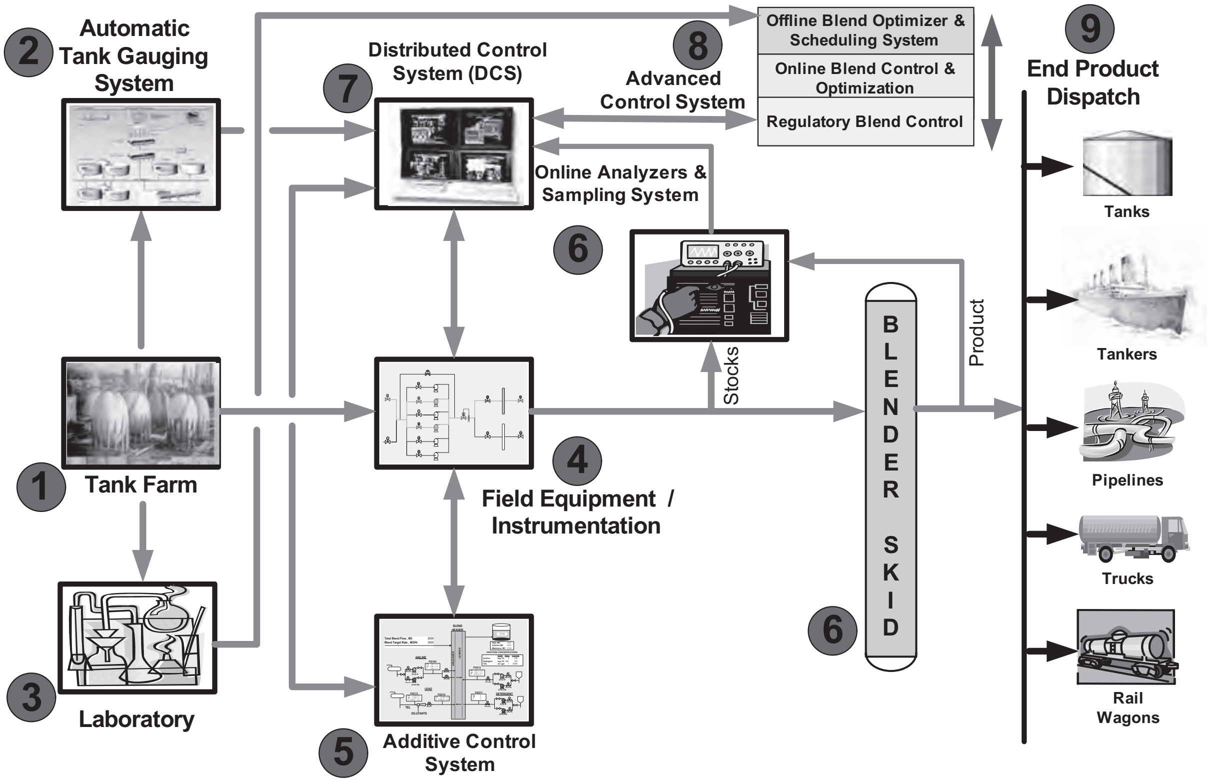


Figure 1.15—Integrated fuel blending control and optimization system modules.

of an integrated blend control and optimization system that are discussed in detail in Chapter 19 of this book.

Chapter 20 discusses all technical and management aspects of a tank farm in a typical refinery. It starts with the discussion of various types of tanks such as the cylindrical and spherical tanks used in a typical refinery. It then presents design methodologies to estimate the storage requirement on the basis of refinery complexity and mode of crude and product receipts and dispatch. The chapter also discusses process parameters, their methods to measure them by a tank gauging system, and how to calculate tank inventory using these measured parameters. Next, the methods and technology to measure/estimate tank qualities and fugitive emissions are discussed in the chapter. The chapter discusses the oil movement and storage system in a refinery and presents the design concept, control technology, and economic analysis to justify and implement an oil movement and storage (OM&S) project. Lastly, it covers refinery terminal operations and enumerates the problems and challenges of each of the terminals—marine, truck, railcar, and pipeline terminals.

Chapter 21 covers the transportation of crude oil, natural gas, and petroleum products. Almost the entire operation for the transportation of oil and gas takes place in one of two modes: pipeline transportation for inland and transcontinental trade and marine transportation (tankers) for international or intercontinental trade. Ocean tankers provide the most common method of internationally moving petroleum products. Marine transportation systems, or tank fleets, are the primary option available for the long-distance transportation of internationally traded energy commodities because they make use of a vast network of vessels and ports at a global scale. However, at some point the marine network relies on inland transportation systems for the final distribution of goods to the markets. For the case of inland fluid transportation, one of the most effective and efficient means of transportation is the use of pipelines.

1.7 REFINERY PLANNING AND SCHEDULING

Planning and scheduling are two distinct activities in refinery operation and management. Planning "plans the work" and scheduling "works the plan." Planning has a very wide time horizon from 1 to 3 months at the corporate and refinery levels whereas scheduling works on 1- to 2-day time periods. Planning cycles are further broken down into weeks and days by the refinery planner and blending- and oil-movement engineers. The information needed for planning cycles is the best estimate of parameters and process data and is tuned with the reconciliation and feedback strategy whereas scheduling is refined and readjusted to suit operation constraints and the dispatch schedule. Figure 1.16 shows the flow of information from planning to execution and feedbacks from actual execution data to planning for reconciliation of "plan versus actual."

The refinery planning process involves the building of a refinery model of all process units and solves and optimizes the process parameters on the basis of physical and process constraints. This is done using linear or nonlinear programming techniques or both. Chapter 22 gives an overview of these mathematical techniques to optimize the refinery planning process and illustrates it with an example of a simple refinery configuration.

The second part of Chapter 22 discusses the concept of, given a monthly plan of production and supply targets with

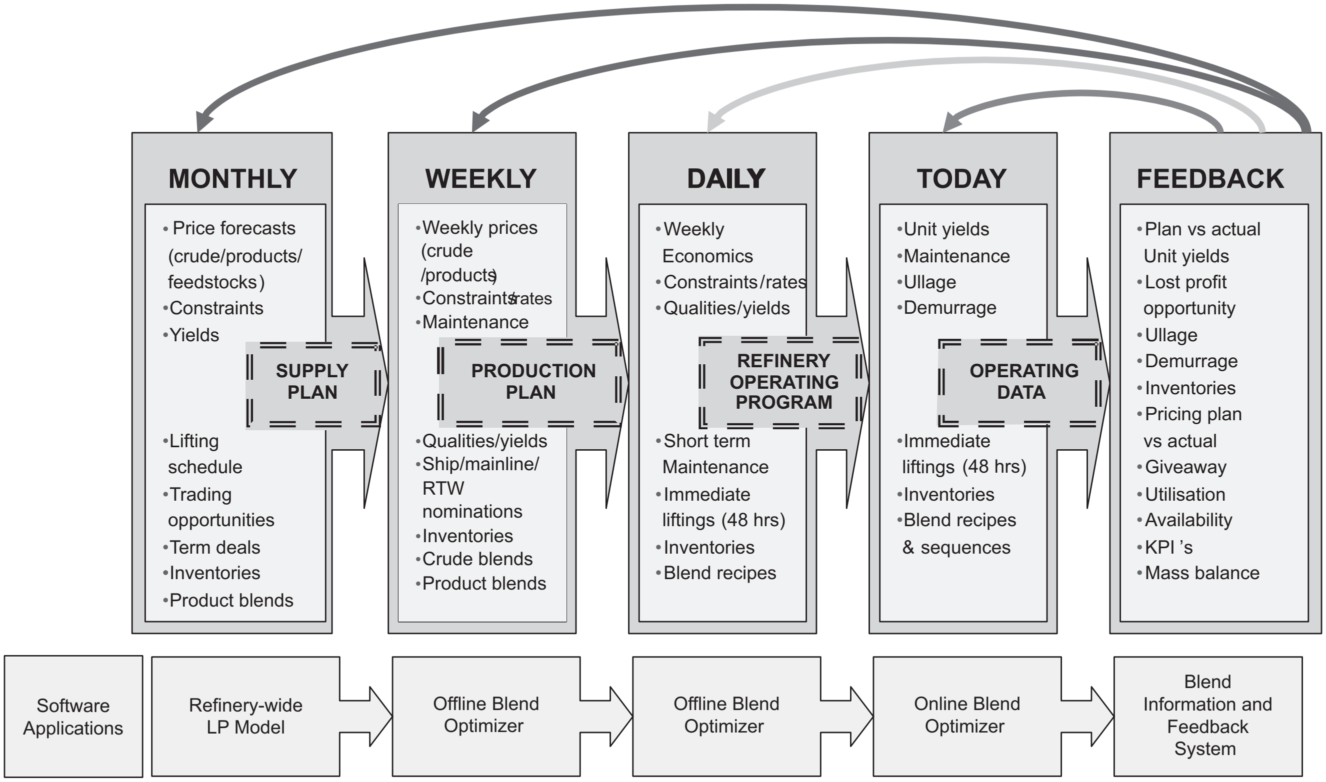


Figure 1.16—Stages of typical refinery planning cycles [18].

crude and product recipes, how to schedule activities such as tank swings, oil movement, and blending productions to minimize any severe effects on the refinery bottom line. The chapter also discusses tools and techniques to implement an efficient and effective scheduling system in the refinery and integrate it with the planning system.

1.8 REFINERY ECONOMICS AND FINANCIAL RISK MANAGEMENT

The refining industry is a global business, and its survival purely depends on its profitability and competitiveness. The most profitable refinery is the one that can convert the heaviest crude oils into the lightest petroleum products. Chapter 23 presents a primer on the concepts, systems, and mechanisms of the trading, costing, pricing, and valuation of crude oils and petroleum products. The roles of costs and profit margins for economic evaluations in the refining industry are discussed in this chapter. For a complete treatment, it is shown how oil markets have operated and evolved historically in terms of how the refining industry has developed from purely physical trading to a sophisticated financial market. Crude oil pricing mechanisms; product trading, pricing, and valuation; operating costs; raw material supply; capital costs; refinery profit margins and costs; and relations between refinery margins and product pricing are discussed in this chapter. Economical issues related to the refining industry are followed in Chapter 24, which discusses the complexity of modern refineries with respect to market restrictions. Refinery processes and operations are classified with respect to product demand and supply statistics in the United States and the world. Investment cost curves are presented and the methodological framework, data sources, and normalization procedures used in estimation are described, followed by a discussion of the limitations of analysis.

Chapter 25 introduces concepts of financial risk as applied to decision-making associated with refinery operations. Particular focus is given to the use of two-stage programming to make crude purchasing decisions as well as operational choices such as the throughput of different units. Most models consider the price as an external uncertain parameter. In addition, techniques to identify decisions that are less profitable, but also less risky, are presented. Finally, it is shown how commercial software can be utilized. It is therefore concluded that the techniques presented are mature and ready to be adopted in practice to run refinery businesses with lower financial risk.

1.9 CHARACTERISTICS OF MODERN REFINERIES

Modern refineries are characterized by their capability of converting heavier oils into more light- and middle-distillate products with little or no residues and production of higher quality fuels with ultralow sulfur contents. Economical, environmental, and safety factors are priority considerations in modern refinery management. All of these challenges are not only achieved by considering advanced, more efficient processes and more conversion units (FCC and hydrocracking) with improved new catalysts, but also with an intensive use of simulation and optimization tools in planning and operation as well as the implementation of more advanced control systems throughout this complex industry.

Whitel [20] has most recently published an interesting article on the role of automation in energy-saving in chemical plants. Petroleum refineries and petrochemical plants are large energy consumers—with energy second only to feedstocks as a variable operating cost. For example, a 5 % energy saving is worth over $4 million/year in increased operating margin for a typical North American naphtha-feedstock plant producing 500,000 t/year ethylene with an energy cost of $6 per million Btu (MMBtu). Feed type and quality, product composition, and configuration all affect the energy use of the plant. The difference between energy consumption of the most efficient and least efficient plants could be as high as 40 %. Surveys have also shown that the most important factor that affects energy use is the age of a plant, with the implications in inspection and maintenance. Advanced control and optimization also have a significant effect on potential energy savings. Basic and advanced process control systems in the refining industry are discussed in several chapters of this book.

Chapter 26 covers the current process simulation model building and application in refineries. Market competition in the refining industry is encouraging companies to optimize their processes to maximize margins and make better products while meeting more stringent constraints to comply with safety and environmental regulations. Simulation models may be consistently applied from planning the production to managing the operation, and even in process control, depending on the desired time horizon and providing the level of detail of the model to allow this flexibility, to support refining companies in this challenge.

The chapter focuses on some of the key aspects in building simulation models for refining processes. Applications of process simulation technologies in different areas of refinery operation (planning and scheduling, process engineering, and process control) are reviewed. Emphasis is placed on adequate technologies for fast and flexible updated stream characterization and rigorous thermodynamic calculations, which are critical to guarantee model reliability. These issues as well as model building techniques and future trends in modeling technologies are presented in Chapter 26.

Chapter 27 is devoted to maintenance simulation and optimization in refinery plants. A typical refinery experiences approximately 10 days of downtime per year because of equipment failures, resulting in an estimated economic loss of tens of thousands of dollars per hour. Therefore, appropriate maintenance actions are of paramount importance from a safety and economic point of view. Once safety levels have been achieved through appropriate maintenance, the question is how much preventive maintenance is economically advisable. Maintenance is defined as all actions appropriate for retaining an item/part/equipment in, or restoring it to, a given condition. The annual cost of maintenance (corrective and preventive) as a fraction of total operating budget can go up to 20–30 % for the chemical industry as discussed in Chapter 27. This chapter also outlines recent efforts to perform Monte Carlo simulation to obtain an assessment of the effect of existing corrective and preventive maintenance practices incorporating details of the available labor, task assignment rules, and parts inventory on plant economics. The performance of a genetic algorithm in conjunction with the Monte Carlo simulation is illustrated using the data from an FCC plant.

This critical role of computers and computerized systems, which has led to the implementation of APC in today's refineries, is emphasized from a slightly different focus in Chapter 28, which presents an integrated vision on the role of computers and automation in refinery operation. The application of computer-aided process operation systems in process design and control, operations planning, scheduling, and optimization has revolutionized modern refineries into integral entities with a degree of efficiency difficult to imagine without the implementation of these advanced information technology (IT) applications.

1.10 ENVIRONMENTAL AND SAFETY ISSUES

Like any other major industry, the refining industry must sustainably operate under economically competitive and environmentally responsible management. New regulations, particularly in developed countries, require stricter regulations and laws on fuels and pollutant emissions. The state of the world economy strongly affects energy markets. The availability of feedstocks and markets for the products affects the economics of the refining industry. Many industries tend to shift from one region to another because of new environmental regulations or varying market conditions. For example, global climate change has been cited as a reason for closing some refineries in the United States. However, although smaller refineries have been shut down, larger refineries expanded and overall refining capacity has risen by 13 % since the 1980s in the United States. The recent recession, use of alternative fuels (ethanol and biofuels), and the manufacture of more efficient cars caused a reduction in gasoline consumption in recent years in the United States and some other industrialized countries.

Environmental issues in refineries concerning water, air, and noise pollution and the associated pollution reduction and treatment methods are discussed in Chapter 29. Environmental considerations are increasingly affecting the bottom line of petroleum refineries (i.e., refining margins) and thus should be taken into account in the design and operation of refineries. Chapter 29 is divided into three main parts, each addressing the three major types of environmental pollution related to the operations of a refinery: water pollution, air pollution, and noise pollution. The chapter concludes with a general outlook of the shape of events to come, particularly in view of the anticipated impending massive effects of global climate change.

Chapter 30 reviews safety issues related to petroleum refineries. In petroleum refineries, safety concerns focus on two main areas: process safety and labor or personnel safety. Process safety involves the risk assessment and development and implementation of intervention plans concentrated on preventing or minimizing the risks from loss of containment of flammable, toxic, or reactive chemicals. Labor or personnel safety interventions focus on the operational procedures for the prevention or mitigation of hazards that can result in individual injuries or exposures. Both approaches to safety attempt to prevent or minimize the impact of accidents. Over the last 20–30 years, in petroleum refineries and similar processes, there have been several significant watershed incidents that have fueled the development of many of the regulations and prevention activities that apply today and that serve to minimize the impact of the hazards typically associated with petroleum refining. The driving forces behind much of what makes up a modern safety and health program in the petroleum refinery in the United States are the regulatory agencies—the Occupational Safety and Health Administration (OSHA) and the U.S. Environmental Protection Agency (EPA). This chapter will draw heavily from these regulations.

Chapter 31 discusses the management of the refining industry in conjunction with economic and environmental constraints. One of the main challenges in the refining industry is to maximize crude utilization at minimum cost while meeting regulations and customer requirements. The refinery's leadership must possess a range of leadership qualities, preferably personally in the refinery manager, but if not, then certainly amongst his small cadre of senior managers upon whom he can rely. The refinery's management is further faced with an increased variety of crude oils (heavier, more sulfur), an increased complexity of operations from an increased diversity of products, tighter rules on product specifications and lower sulfur content, uncertainty in future refinery margins (ups and downs), and positive average growth. Chapter 31 addresses these challenges and provides a suite of proven practices for successful refinery management.

1.11 BIOREFINING

Biofuel is a renewable form of energy that refers to fuels that can be produced from biological raw material (biomass). Forest and agricultural resources are the main biomass resources. At present, biomass provides 3 % of the total U.S. energy consumption, in comparison with 39 % (oil), 24 % (gas), 23 % (coal), 8 % (nuclear), and 3 % from other forms of renewable energy such as hydro, geothermal, wind, and solar energy. However, this proportion will change rapidly in coming decades, supported by new legislation, especially in developed countries. In 2007, the U.S. government announced a target of reaching in 2030 a 30 % substitution of transport fuel consumption by alternative fuels, mainly biofuels. In the European Union, the target of 5.75 % of total European transport fuel consumption coming from biofuels in 2010 was reviewed in 2007 and 2008, allowing for higher biodiesel content in commercial diesel and more challenging objectives for 2020. Similar legislations have been proposed in other countries around the world. The International Energy Agency (IEA) has forecasted an average 4–7 % of the total road transport world consumption in 2030 coming from biofuels.

On the basis of 2004 data from the U.S. Department of Energy, the annual rate of biomass consumption is 190 million dry tons, of which 35 million t is fuel woods and 18 million t is biofuels. In the United States, biomass consumption in the industrial sector will increase at an annual rate of 2 % through 2030. Additionally, biomass consumption in electric utilities will double every 10 years through 2030. Biopower will meet 5 % of the combined total industrial and electric generator energy demand in 2020. Transportation fuels from biomass will increase significantly from 0.5 % of the U.S. transportation fuel consumption in 2001 to 10 % in 2020 and 20 % in 2030. Production of chemicals and materials from bio-based products will increase substantially from approximately 12.5 billion lb or 5 % of the current production of target U.S. chemical commodities in 2001 to 12 % in 2010, 18 % in 2020, and 25 % in 2030 [21]. The European Union (EU) is the main consumer and producer of biodiesel, whereas the United States and Brazil are the main producers and consumers of bioethanol. Biomass is expected to become one of the major renewable resources for the production of feed, materials, chemicals, fuels, power, and heat. The global potential supply of biomass for energy use is very large.

Some of the key drivers to support this growth are consumer requirements for end products, nonrenewable fossil resource reduction, cleaner and safer chemical manufacturing, and economic improvements of food industry products by producing added-value products from wastes. Probably one of the main drivers supporting biofuels is related to climate change policies. The CO_2 generated in fuel combustion is fixed by plants to be converted again in biomass. Although not completely renewable (some energy is consumed in the process), in essence the carbon balance is very favorable compared with conventional fossil fuels. However, the generalized use of biofuels as an alternative energy has caused major concerns related to competition with food and pressure on land resources. Although some improvement has been made, the biofuel industry needs an internationally recognized and accepted certification scheme related to sustainability criteria.

According to IEA Bioenergy Task 42, biorefining is defined as the sustainable processing of biomass into a spectrum of marketable products and energy [22]. On the basis of this definition, seven types of biorefineries have been recognized: (1) conventional biorefineries, (2) green biorefineries, (3) crop biorefineries, (4) cellulosic feedstock biorefineries, (5) two platform concept biorefineries, (6) thermochemical biorefineries, and (7) marine-type biorefineries, as discussed in reference 23.

In a petroleum refinery, crude oil is converted into fuels (i.e., gas, gasoline, kerosine, etc.) and some non-fuel-type chemicals (i.e., waxes, solvents, etc.). In a biorefinery, biomass is converted into fuels such as bioethanol, biodiesel, biogas, and hydrogen as well as non-fuel materials such as basic and fine chemicals, biopolymers, and bioplastics. Many existing industries such as the sugar industry (from beet, cane) or vegetable oil from soy, pulp and paper from forest, biodiesel, and bioethanol industries fall into the category of conventional refineries. Biodiesel can be produced from vegetable oils and animal fats via chemical processing and transesterification using ethanol, catalyst, and separation of methanol and produced biodiesel. In this process, glycerin is also produced. A typical thermochemical route to biofuel involves gasification of biomass to syngas followed by catalytic Fischer-Tropsch conversion to biodiesel as demonstrated by Ladisch et al. [24].

According to the efficiency of the process to convert biomass, it is widely accepted today to refer to "first-generation" biofuels when only a fraction of the raw material is converted (leaving significant amounts of byproducts or residua not used for energy purposes), compared with future "second-generation" biofuels, which opens the range of vegetal species and focuses on maximization of raw material use. The focus in fast-growing plants, including marine crops, algae, and cyanobacteria, has made some refer to "third-generation" biofuels if or when the raw materials will be from plants genetically designed or from algae or cyanobacteria. However, the challenge to commercially develop second- and third-generation biofuels requires a significant effort in research and development.

TABLE 1.7—A Comparison between Key Parameters of Biodiesel Fuel and Conventional Fossil Fuel Diesel [24][a]

Fuel Property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM D6751
Kinetic viscosity at 40°C, mm^2/s	1.3–4.1	1.9–6.0
Specific gravity at 60°C, kg/L	0.85	0.88
Density, lb/gal	7.079	7.328
Water and sediment, % vol	0.05 max	0.05 max
Carbon, wt %	87	77
Hydrogen, wt %	13	12
Oxygen	0	11
Sulfur, wt %	0.0015	0.0–0.0024
Boiling point, °C	180–340	315–350
Flash point, °C	60–80	130–170
Cloud point, °C	–15 to 5	–3 to 12
Pour point, °C	–35 to –15	–15 to 10
Cetane number	40–55	47–65

[a] On average based on European standards from several studies.

The increasing role of biofuels in the energy market makes them appear in different chapters in this book. Statistical data on biofuels are covered in Chapter 3. Some specifications and properties of biofuels are given in Table 1.7 [24], but further details on biofuel properties are discussed in Chapter 4 whereas biofuels for transport and their biorefining processes are discussed in Chapter 32.

Finally, additional discussion on characteristics of future refineries is presented in Chapter 33. In this last chapter, after a brief review of refinery processes, several configurations proposed for future refineries and some new developments in the field are presented. Environmental and economical constraints, feedstock quality, product specifications, and process flexibility are considered in such future refinery scenarios.

1.12 IMPORTANCE OF THE BOOK

The downstream processing of petroleum and natural gas is a complex and huge industry that converts raw materials (mainly petroleum and natural gas) into a series of fuel and non-fuel products. The industry includes field processing, refining, and processing; fuel blending and quality control; and storage and transportation of feedstocks and products. Construction and sustainable operation of such industries involves detailed engineering and scientific tasks. The full coverage of these areas in a single book is a difficult task, if not impossible, as evident from the series of books published in the last 2 decades in this area for educational purposes or certain industrial sectors [26–38]. In fact, topics covered in each chapter of this handbook require a full book in themselves for detailed discussion.

However, this book attempts to discuss additional aspects of these industries with updated information by leading world experts in each field from industry and academia. Great emphasis is given to the processing of heavy oils, new processes, environmental and economical considerations, planning and scheduling, process control and automation of refining units, maintenance and safe operation of process units, quality control and product analysis, fuel and crude oil blending control and optimization, and tank farm management. In addition, alternative fuels such as hydrogen and biofuels in relation to petroleum fuel and the petrochemical industries have been given special attention and are covered in separate chapters. A vision of trends in petroleum processing toward future refineries is covered in the last chapter. The book should be useful to people from industry and academia as well as environmentalists and those from the transportation and automobile industries, governments, business people, investors, economists, managers, process engineers, operators, and policy- and decision-makers.

ACKNOWLEDGMENTS

The authors thank Mohan S. Rana of the Kuwait Institute for Scientific Research for providing some of the figures and tables related to fuel quality and refining processes as cited in the text.

REFERENCES

[1] Speight, J.G., *The Chemistry and Technology of Petroleum*, 3rd ed., Marcel Dekker, New York, 1998.

[2] Mansoori, G.A., "A Unified Perspective on the Phase Behavior of Petroleum Fluids," *Int. J. Oil Gas Coal Technol.*, Vol. 2, 2009, pp. 141–167.

[3] Arnold, K., and Stewart, M., *Surface Production Operations*, 2nd ed., Gulf Publishing, Houston, TX, 1998.

[4] Riazi, M.R., *Characterization and Properties of Petroleum Fractions*, MNL50, ASTM International, West Conshohocken, PA, 2005.

[5] Rana, M.S., Personal communications, Kuwait Institute for Scientific Research (KISR), Division of Petroleum Refining, Kuwait, March 2010.

[6] U.S. Energy Information Administration, U.S. Department of Energy, "Official Energy Statistics from U.S. Government," 2009, http://www.eia.doe.gov/emeu/international/reserves.html.

[7] Riazi, M.R., "Energy, Economy, Environment and Sustainable Development in the Middle East and North Africa," *Int. J. Oil Gas Coal Technol.*, Vol. 3, 2010, pp. 301–345.

[8] Peakoil, Australia, http://www.peakoil.org.au, accessed October 1, 2009.

[9] Occupational Safety and Health Administration, *Technical Manual Petroleum Refining Processes*, Chapter 2, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html, accessed February 20, 2011.

[10] Rana, M.S., Ancheyta, J., Maity, S.K., and Marroquin, G., "Comparison between Refinery Processes for Heavy Oil Upgrading: A Future Fuel Demand," *Int. J. Oil Gas Coal Technol.*, Vol. 1, 2008, pp. 250–282.

[11] Natural Gas website, http://www.naturalgas.org/naturalgas/processing_ng.asp, accessed March 1, 2011 (original source: Duke Energy Gas Transmission Canada).

[12] Universal Oil Products, http://www.uop.com.

[13] Courty, P., and Gruson, J.F., "Refining Clean Fuels for the Future," *Oil Gas Sci. Technol.*, Vol. 56, 2001, pp. 515–524.

[14] Patel, B., "Gas Monetisation: A Techno-Economic Comparison of Gas to Liquid and LNG," presented at the 7th World Congress of Chemical Engineering, Glasgow, Scotland, 2005.

[15] Davis, B.H., "Fischer-Tropsch Synthesis: Overview of Reactor Development and Future Potentialities," *Topics Catal.*, Vol. 32, 2005, pp. 143–168.

[16] Davis, R.A., and Patel, N.M., "Refinery Hydrogen Management," *Petrol. Technol. Quarter.*, Vol. 9, 2004, pp. 29–35.

[17] Rostrup-Nielsen, J.R., and Rostrup-Nielsen, T., "Large-Scale Hydrogen Production," *Cattech*, Vol. 6, 2002, pp. 150–159.

[18] Offsite Management Systems, LLC, *Strategic Fuels Blending Technology and Management-Training Manual*, Offsite Management Systems, LLC, Sugar Land, TX, 2009.

[19] Agrawal, S.S., "Advances in Tank Quality Measurements Can Help Cut Operational Costs," *Hydrocarbon Process.*, Vol. 86, 2007, p. 67.

[20] Whitel, D.C., "Save Energy through Automation," *Chem. Eng. Prog.*, Vol. 106, 2010, pp. 26–33.

[21] U.S. Department of Energy and U.S. Department of Agriculture, *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*, U.S. Department of Energy, Washington DC, 2005, http://www.biorefinery.nl/fileadmin/biorefinery/docs/Biomass_as_feedstock.pdf.

[22] "IEA Bioenergy Task 42 Biorefineries," http://www.IEA-Bioenergy.Task42-Biorefineries.com (accessed May 11, 2011).

[23] Van Ree, R., Annevelink, E., Tatus Report Biorefinery 2007, SenterNovem, René van Ree & Bert Annevelink, Report 847, ISBN-number 978-90-8585-139-4, November, 2007, http://www.biorefinery.nl/publications/.

[24] Ladisch, M.R., Mosier, N.S., Kim, Y., Ximenes, E., and Hogsett, D., "Converting Cellulose to Biofuels," *Chem. Eng. Prog.*, March, 2010, pp. 56–62.

[25] U.S. Department of Energy, *Biodiesel Handling and Use Guidelines*, 2nd ed., U.S. Department of Energy, Washington, DC, 2006 or Crimson Renewable Energy, LP, "Biodiesel Fuel Specifications and Comparison to Diesel Fuel," http://www.CrimsonRenewable.com.

[26] Fahim, M.A., Al-Sahhaf, T.A., and Elkilani, A., *Fundamentals of Petroleum Refining*, Elsevier, Amsterdam, The Netherlands, 2009, p. 516.

[27] Leffler, W.L., *Petroleum Refining in Nontechnical Language*, 4th ed., PennWell Corporation, Tulsa, OK, November, 2008, p. 270.

[28] Sarkar, G.N., *Advanced Petroleum Refining*, 1st ed., Khanna Publishers, New Delhi, India, 2008, p. 628.

[29] Gary, J.H., Handwerk, G.E., and Kaiser, M.J., *Petroleum Refining: Technology and Economics*, 5th ed., CRC, Boca Raton, FL, 2007, p. 488.

[30] Jones, D.S.J., and Pujadó, P.P. (Eds.), *Handbook of Petroleum Processing*, 1st ed., Springer, New York, 2006, p. 1353.

[31] Mokhatab, S., Poe, W.A., and Speight, J.G., *Handbook of Natural Gas Transmission and Processing*, Gulf Publishing Company, Houston, TX, 2006, p. 650.

[32] Hsu, C.S., and Robinson, P.R. (Eds.), *Practical Advances in Petroleum Processing*, 1st ed., Springer, New York, 2006, p. 866.

[33] Meyers, R., *Handbook of Petroleum Refining Processes*, 3rd ed., McGraw-Hill Professional, New York, 2003, p. 900.

[34] Parkash, S., *Refining Processes Handbook*, 1st ed., Gulf Professional Publishing, Houston, TX, 2003, p. 688.

[35] Speight, J.G., and Ozum, B., *Petroleum Refining Processes (Chemical Industries)*, 1st ed., CRC, Boca Raton, FL, 2001, p. 728.

[36] Maples, R.E., *Petroleum Refinery Process Economics*, 2nd ed., PennWell, Tulsa, Oklahoma, 2000, p. 474.

[37] McKetta, J.J., *Petroleum Processing Handbook*, 1st ed., CRC, Boca Raton, FL, 1992, p. 792.

[38] Nelson, W.L., *Petroleum Refinery Engineering*, 3rd ed., McGraw-Hill, New York, 1949, p. 830.

2

Feedstocks and Products of Crude Oil and Natural Gas Refineries

M.R. Riazi[1] and Semih Eser[2]

2.1 NATURE AND CONSTITUENTS OF PETROLEUM FLUIDS

As discussed in Chapter 1, petroleum fluids are mixtures of various hydrocarbons that may exist as gas or liquid in a petroleum reservoir. The principal elements of petroleum are carbon (C), hydrogen (H), and small quantities of heteroatoms of sulfur (S), nitrogen (N), and oxygen (O). It is generally believed that the petroleum hydrocarbons have been derived from the conversion of organic compounds in some aquatic plants and animals. The most important factors that affect conversion of organic compounds to petroleum hydrocarbons are (1) heat and pressure, (2) radioactivity such as gamma rays, and (3) catalytic reactions. Vanadium and nickel species are the most effective catalysts in the formation of petroleum and are needed for the conversion reactions. For this reason, these metals may be found in small quantities in petroleum fluids. Occasionally traces of radioactive isotopes such as uranium and potassium can also be found in petroleum. The conditions required for converting organic compounds into petroleum are (1) geological time frame in millions of years, (2) pressure up to 17 MPa (~2500 psi), and (3) temperature not exceeding 100–120 °C (~ 210–250 °F). In some cases, bacteria may have severely biodegraded the oil, destroying the light hydrocarbons. An example of such a case would be the large heavy oil accumulations found in Venezuela. Petroleum is a mixture of thousands of different identifiable hydrocarbons that are discussed in the next section. Once petroleum is accumulated in a reservoir or in various sediments, hydrocarbon compounds may be converted from one form to another with time and varying geological conditions. The main difference between various oils from different fields around the world is the difference in their composition of hydrocarbon compounds and impurities [1].

Compounds that only contain elements of carbon and hydrogen are called *hydrocarbons*, and they form the largest group of organic compounds found in petroleum. There might be as many as several thousand different hydrocarbon compounds in petroleum reservoir fluids. Hydrocarbon compounds have a general closed formula of C_xH_y, where x and y are integer numbers. The lightest hydrocarbon is methane (CH_4), which is the main component in natural gas. Methane is from a group of hydrocarbons called *paraffins*. Hydrocarbons are generally divided into four groups: (1) paraffins, (2) olefins, (3) naphthenes, and (4) aromatics. Paraffins, olefins, and naphthenes are sometimes called *aliphatic* versus aromatic compounds. The International Union of Pure and Applied Chemistry (IUPAC), a nongovernmental organization, provides standard names, nomenclature, and symbols for chemical compounds, including hydrocarbons [2].

Paraffins are also called alkanes and have the general formula of C_nH_{2n+2}, where n is the number of carbon atoms in a given molecule. Paraffins are divided into two groups of normal and isoparaffins. Normal paraffins or normal alkanes are simply written as n-paraffins or n-alkanes, and they are open, straight-chain saturated hydrocarbons. Paraffins are the largest series of hydrocarbons found in petroleum and begin with methane, which is also shown by C_1. Figure 2.1 shows several lighter paraffins found in petroleum fluids [3]. For example, the open formula for *n*-butane, *n*-C_4, can be shown as CH_3-CH_2-CH_2-CH_3, and for simplicity in drawing, only the carbon-carbon bonds are drawn and most C-H bonds are omitted.

The second group of paraffins is called *isoparaffins*, which are branched-type hydrocarbons and they begin with isobutane (also called methylpropane), which has the same closed formula as *n*-butane (C_4H_{10}). Compounds of different *structures* with the same closed formula are called *isomers*.

As shown in Figure 2.1, there are two isomers for butane, three for pentane, and five isomers for hexane (only four are shown in Figure 2.1.) Similarly, octane (C_8H_{18}) has 18 and dodecane ($C_{12}H_{26}$) has 355 isomers, whereas octadecane ($C_{18}H_{38}$) has 60,523 and C_{40} has 62×10^{12} isomers. The number of isomers rapidly increases with the number of carbon atoms in a molecule because of the rapidly rising number of their possible structural arrangements, as shown in Figure 2.2 [1]. It should be noted that many of these isomers may not be found in petroleum because they are not thermodynamically stable. For the paraffins in the range of C_5–C_{12} the number of isomers is more than 600, although only approximately 200–400 of them have been identified in petroleum mixtures. Isomers have different physical and chemical properties. The same increase in number of isomers with molecular weight applies to other hydrocarbon series. As an example, the total number of hydrocarbons (from different groups) having 20 carbon atoms is more than 300,000 [5].

Under standard conditions of temperature and pressure (STP), the first four members of the alkane series (methane, ethane, propane, and butane) are in gaseous form, from C_5H_{12} (pentane) to *n*-heptadecane ($C_{17}H_{36}$) are liquids, and *n*-octadecane ($C_{18}H_{38}$) or heavier compounds exist as wax-like solids at STP. Paraffins from C_1 to C_{40} usually appear in crude oil and represent up to 20 % of crude

---

[1] Kuwait University, Kuwait

[2] The Pennsylvania State University, University Park, PA, USA

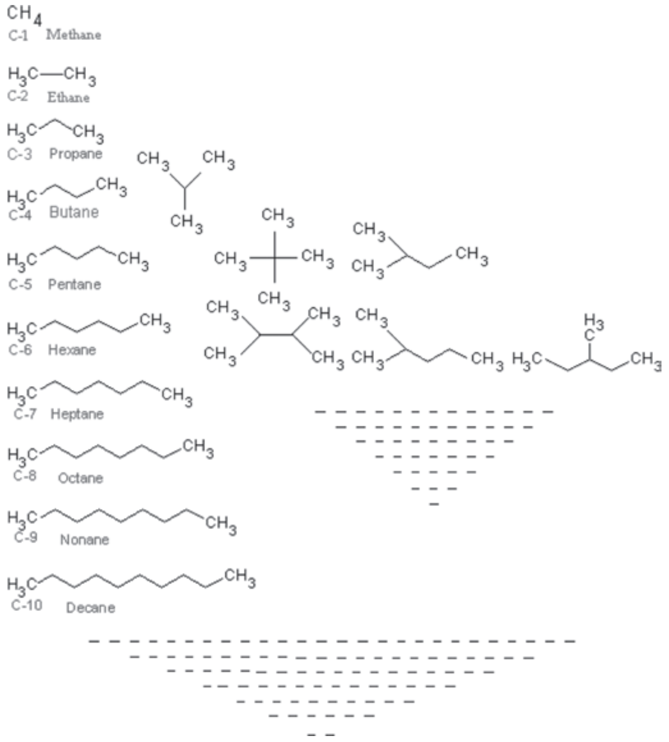


Figure 2.1—Lighter paraffin hydrocarbons present in petroleum and natural gas [3].

by volume. Because paraffins are fully saturated (no double bond) they are stable and remain unchanged over long periods of geological time.

Olefins are another series of noncyclic hydrocarbons, but they are unsaturated and have at least one double bond between carbon-carbon atoms. Compounds with one double bond are called mono-olefins or alkenes and include ethene (also named ethylene; $CH_2=CH_2$) and propene (or propylene; $CH_2=CH-CH_3$). In addition to the *structural isomerism* connected with the location of double bond, there is another type of isomerism called *geometric isomerism* that indicates the way atoms are oriented in space. The configurations are differentiated in their names by the prefixes *cis-* and *trans-*, such as *cis-* and *trans-*2-butene. Mono-olefins have the general formula of C_nH_{2n}. If there are two double bonds, the olefin is called a *diolefin* (or diene), such as butadiene ($CH_2=CH-CH=CH_2$). Unsaturated compounds are more reactive than saturated hydrocarbons (without double bond). Olefins are uncommon in crude oils because of their reactivity with hydrogen that saturates them; however, they can be produced in refineries through cracking reactions. Olefins are valuable products of refineries and are used as feedstocks for petrochemical plants to produce polymers such as polyethylene. Similarly compounds with triple bonds such as acetylene ($CH \equiv CH$) are not found in crude oils because of their tendency to become saturated [1].

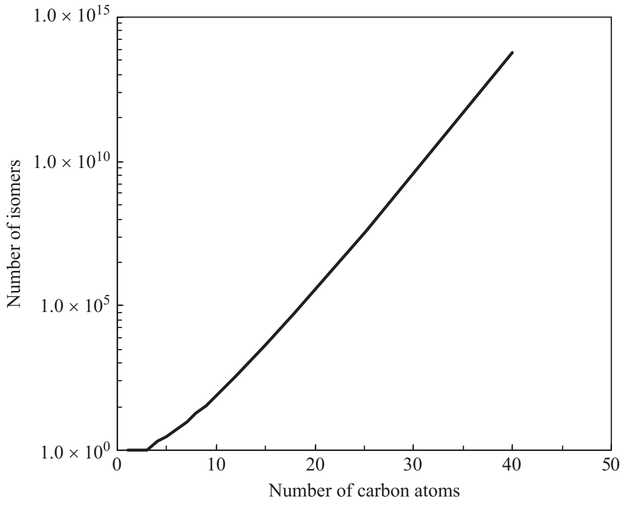
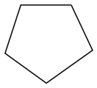
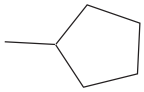


Figure 2.2—Number of possible alkane isomers [1].

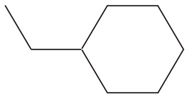
Naphthenes or cycloalkanes are ring or cyclic saturated hydrocarbons with general formula of C_nH_{2n}. Cyclopentane (C_5H_{10}), cyclohexane (C_6H_{12}), and their derivatives such as *n*-alkylcyclopentanes are normally found in crude oils. Three types of naphthenic compounds are shown below.



Cyclopentane
(C_5H_{10})



Methylcyclopentane
(C_6H_{12})



Ethylcyclohexane
(C_8H_{16})

If there is only one alkyl group from n-paraffins (i.e., methyl, ethyl, propyl, n-butyl, etc.) attached to a cyclopentane hydrocarbon, the series is called *n-alkylcyclopentanes*, such as the two hydrocarbons shown above where on each junction of the ring there is a CH_2 group, except on the alkyl group juncture, where there is only a CH group. Naphthenic hydrocarbons with only one ring are also called *monocycloparaffins* or *mononaphthenes*. In heavier oils, saturated multirings attached to each other called *polycycloparaffins* or *polynaphthenes* may also be available. Thermodynamic studies show that naphthene rings with five and six carbon atoms are the most stable naphthenic hydrocarbons. The content of cycloparaffins in petroleum may vary up to 60 %. Generally, any petroleum mixture that has hydrocarbon compounds with five carbon atoms also contains naphthenic compounds.

Aromatics are an important series of hydrocarbons found in almost every petroleum mixture from any part of the world. Aromatics are cyclic but unsaturated hydrocarbons with alternating double bonds that begin with a benzene molecule (C_6H_6). The name "aromatic" refers to the fact that such hydrocarbons commonly have fragrant odors. A group of lighter aromatic hydrocarbons is shown in Figure 2.3. Although benzene has three carbon-carbon double bonds, it has a unique arrangement of electrons with resonance structures of the double bonds (aromaticity) that allow benzene to be relatively stable. However, benzene is known to be a cancer-inducing compound. For this reason, the amount of benzene allowed in petroleum products such as gasoline or fuel oil is limited by government regulations in many countries. Under standard conditions, benzene, toluene, and xylene are in liquid form whereas naphthalene is in a solid state.

Some of the common aromatics found in petroleum and crude oils are benzene and its derivatives with attached methyl, ethyl, propyl, or higher alkyl groups. This series of aromatics is called *alkylbenzenes* and compounds in this homologous group of hydrocarbons have the general

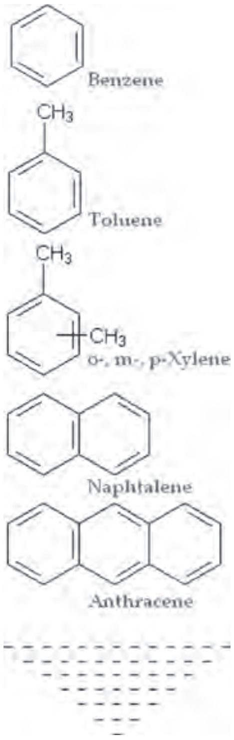
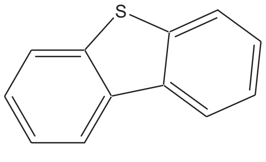


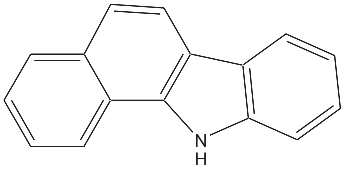
Figure 2.3—Lighter aromatic hydrocarbons present in petroleum and natural gas [3].

formula of C_nH_{2n-6} (where $n \geq 6$). Generally, an aromatic series with only one benzene ring is also called *monoaromatics* or mononuclear aromatics. Naphthalene and its derivatives that have only two unsaturated rings are sometime called diaromatics. Crude oils and reservoir fluids all contain aromatic compounds. However, heavy petroleum fractions and residues contain unsaturated multirings with many benzene and naphthene rings attached to each other. Such aromatics that are in solid form are also called *polyaromatic hydrocarbons* (PAHs) or polynuclear aromatics (PNAs). In this chapter, the terms of mono- and polyaromatics are used. Heavy crude oils usually contain more aromatics than light crudes. The amount of aromatics in coal liquids is usually high, and it could reach as high as 98 % by volume. It is common to have compounds with naphthenic and aromatic rings side by side, especially in heavy fractions. Monoaromatics with one naphthenic ring have the formula of C_nH_{2n-8}. There are many combinations of alkylnaphthenoaromatics [4,5].

Normally, high-molecular-weight polyaromatics contain several *heteroatoms* such as sulfur, nitrogen, or oxygen, but these compounds are still called aromatic compounds because their electronic configurations maintain the aromatic character. Two types of these compounds are shown below [1].



Dibenzothiophene



Benzocarbazole ($C_{16}H_{11}N$)

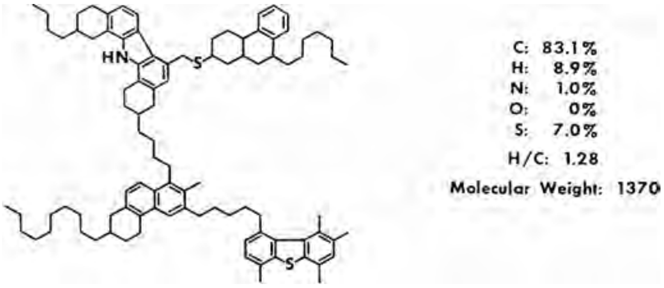


Figure 2.4—An example of asphaltene molecule [6].

Such heteroatoms in multiring aromatics are commonly found in asphaltene compounds, as shown in Figure 2.4, where, for simplicity, carbon and hydrogen atoms are not marked on the rings or on the paraffinic chains attached to the ring systems.

Sulfur is the most important heteroatom in petroleum and it can be found in cyclic (e.g., thiophenes) and noncyclic compounds such as mercaptans (R-S-H) and sulfides (R-S-R′), where R and R′ are alkyl groups. Sulfur in natural gas is usually found in the form of hydrogen sulfide (H_2S). Some natural gases contain H_2S as high as 30 % by volume. The amount of sulfur in a crude oil may vary from 0.05 to 6 % by weight. The presence of sulfur in finished petroleum products is harmful. For example, the presence of sulfur in gasoline can promote corrosion of engine parts. The amounts of nitrogen and oxygen in crude oils are usually less than the amount of sulfur by weight. In general, for petroleum oils the elemental composition varies within fairly narrow ranges, as shown below on a weight basis [5,6]:

Carbon (C), 83.0–87.0 %
Hydrogen (H), 10.0–14.0 %
Nitrogen (N), 0.1–2.0 %
Oxygen (O), 0.05–1.5 %
Sulfur (S), 0.05–6.0 %
Metals (nickel, vanadium, and copper), <1000 ppm (0.1 %)

Generally, in heavier oils (with lower API gravity) the proportions of carbon, sulfur, nitrogen, and oxygen elements increase, but the hydrogen content and the overall quality decrease. A further discussion on the chemistry of petroleum and the types of compounds found in petroleum fractions is provided by Speight [6]. Vanadium concentrations of greater than 2 ppm in fuels can lead to severe corrosion in turbine blades and deterioration of refractory in furnaces. Nickel, vanadium, and copper can also severely affect the activities of catalysts and result in lower quality products. The metal content may be reduced by solvent extraction with organic solvents. Organometallic compounds are concentrated in the asphaltenes and residues. Some major low-molecular-weight impurities in crude oil include carbon dioxide (CO_2), H_2S, metal oxides [aluminum oxide (Al_2O_3), iron(III) oxide (Fe_2O_3), silicon dioxide (SiO_2), etc.], nitrogen (N_2), oxygen (O_2), salts [sodium chloride (NaCl), calcium carbonate ($CaCO_3$), etc.], sulfur, and water (H_2O) [3].

2.2 RESERVOIR FLUIDS—CRUDE OIL AND NATURAL GAS

The word *fluid* refers to a pure substance or a mixture of compounds that are in the form of gas, liquid, or a mixture of liquid and gas (vapor). *Reservoir fluid* is a term used for the mixture of hydrocarbons found in a geological petroleum reservoir or the stream leaving a producing well. Three factors

TABLE 2.1—Types and Characteristics of Various Reservoir Fluids [1]

Reservoir Fluid Type	GOR (scf/stb)	CH_4 (mol %)	C_{6+} (mol %)	API Gravity of STO
Black oil	<1000	≤50	≥30	< 40
Volatile oil	1000–3000	50–70	10–30	40–45
Gas condensate	3000–50,000	70–85	3–10	≥45
Wet gas	≥50,000	≥75	<3	>50
Dry gas	≥100,000	≥90	<1	No liquid

API gravity of STO refers to the API gravity of sto produced at the surface facilities at standard conditions (289 K and 1 atm).

determine if a reservoir fluid is in the form of gas, liquid, or a mixture of gas and liquid. These factors are (1) composition of reservoir fluid, (2) temperature, and (3) pressure. The most important characteristic of a reservoir fluid in addition to specific gravity (or API gravity) is its gas-to-oil ratio (GOR), which represents the amount of gas produced at standard conditions in standard cubic feet (scf) to the amount of liquid oil produced at the standard condition in stock tank barrels (stb). Other units of GOR and its calculation methods are discussed in Chapters 1 and 10 of ASTM Manual 50 [1]. Reservoir fluids are generally categorized into four or five types, the characteristics of which are given in Table 2.1. These five fluids in the direction of increasing GOR are black oil, volatile oil, gas condensate, wet gas, and dry gas.

A natural gas is called *dry gas* if it does not produce any liquid hydrocarbons after the surface separator under standard conditions. A natural gas that produces liquid hydrocarbons after production at the surface facilities is called *wet gas*. The word “wet” refers to the presence of hydrocarbon liquids in a natural gas that condense at surface conditions. In dry gases no liquid hydrocarbon is formed at the surface conditions. Volatile oils have also been called *high-shrinkage crude oil* and *near-critical oils* because the reservoir temperature and pressure are very close to the critical point of such oils, but the critical temperature is always greater than the reservoir temperature [1]. Gases and gas condensate fluids have critical temperatures that are less than the reservoir temperature. Black oils contain heavier compounds; therefore, the API gravity of stock tank oil is generally lower than 40 and the GOR is less than 1000 scf/stb. The specifications given in Table 2.1 for various reservoir fluids, especially at the boundaries between different types, are somewhat arbitrary and may vary from one source to another. It is possible to have a reservoir fluid type with properties outside of the corresponding limits given above. Determination of a type of reservoir fluid by the above rule of thumb on the basis of the GOR, the API gravity of stock tank oil, or its color is not possible for all fluids. In general, oils produced from wet gas, gas condensate, volatile oil, and black oil increase in specific gravity (decrease in API gravity and quality) in the same order. Liquids from black oils are viscous and black in color, whereas the liquids from gas condensates or wet gases are clear and colorless. Volatile oils produce brown with some red/green color liquid. Wet gas contains less methane than a dry gas but a larger fraction of C_2–C_6 components. The main difference between these reservoir fluids is obviously found in their molecular composition. An example of the composition of different reservoir fluids is given in Table 2.2 [1].

In this table, C_{7+} refers to all hydrocarbons having seven or more carbon atoms; this group is called the heptane-plus fraction. C_6 refers to a group of all hydrocarbons with six carbon atoms (hexanes) that exist in the fluid. M_{7+} and SG_{7+} are the molecular weight and specific gravity, respectively, at 15.5 °C (60 °F) for the C_{7+} fraction of the mixture. It should be noted that molecular weight and specific gravity of the whole reservoir fluid are less than the corresponding values for the heptane-plus fraction. For example, for the crude oil sample in Table 2.2, the specific gravity of whole crude is 0.871, or an API gravity of 31. Details of such calculations are discussed in ASTM Manual 50 [1]. These compositions have been determined from a recombination of the compositions of the corresponding separator gas and stock tank liquid, which have been determined by various analytical tools (i.e., gas chromatography, mass spectrometry, etc.). Composition of reservoir fluids varies with the reservoir pressure and reservoir depth. In a producing oil field, the sulfur and amount of heavy compounds generally increase with production time. However, it is important to note that within an oil field, the concentration of light hydrocarbons and the API gravity of the reservoir fluid increase with the reservoir depth, whereas its sulfur and C_{7+} contents decrease with the depth [6]. The lumped C_{7+} fraction in fact is a mixture of many hydrocarbons up to C_{40} or higher. As an example, the number of pure hydrocarbons from C_5 to C_9 detected by chromatography tools in a crude oil from North Sea reservoir fluids was 70 compounds. Most recently, Mansoori has suggested that naturally found hydrocarbon petroleums can be categorized into seven groups, including two semi-solid forms of tar sands and oil shale [3]. The molecular weight distribution of these petroleum fluids is shown in Figure 2.5.

Reservoir fluids from a producing well are introduced to two- or three-stage separators that reduce the pressure and temperature of the stream to atmospheric pressure and temperature. The liquid leaving the last stage is called *stock tank oil* (sto) and the gas released in various stages is called *associated gas*. The liquid oil after necessary field processing is called *crude oil*. The main factor in operation and design of an oil-gas separator is to find the optimum operating conditions of temperature and pressure so that the amount of produced liquid (oil) is maximized. Such conditions can be determined through phase behavior calculations, which are discussed in detail in ASTM Manual 50 [1]. Reservoir fluids from producing wells are mixed with free water. The water is separated through gravitational separators on the basis of the difference between densities of water and oil. The remaining water from crude can be removed through dehydration processes. Another

TABLE 2.2—Composition (mol %) and Properties of Various Reservoir Fluids and a Crude Oil [1]

Component	Dry Gas (1)	Wet Gas (2)	Gas Condensate (3)	Volatile Oil (4)	Black Oil (5)	Crude Oil (6)
CO_2	3.70	0.00	0.18	1.19	0.09	0.00
N_2	0.30	0.00	0.13	0.51	2.09	0.00
H_2S	0.00	0.00	0.00	0.00	1.89	0.00
C_1	96.00	82.28	61.92	45.21	29.18	0.00
C_2	0.00	9.52	14.08	7.09	13.60	0.19
C_3	0.00	4.64	8.35	4.61	9.20	1.88
iC_4	0.00	0.64	0.97	1.69	0.95	0.62
nC_4	0.00	0.96	3.41	2.81	4.30	3.92
iC_5	0.00	0.35	0.84	1.55	1.38	2.11
nC_5	0.00	0.29	1.48	2.01	2.60	4.46
C_6	0.00	0.29	1.79	4.42	4.32	8.59
C_{7+}	0.00	1.01	6.35	28.91	30.40	78.23
	100.00	100.00	100.00	100.00	100.00	100.00
GOR (scf/stb)	…	69,917	4428	1011	855	…
M_{7+}	…	113	143	190	209.8	266
SG_{7+} (at 15.5 °C)	…	0.794	0.795	0.8142	0.844	0.895
API_{7+}		46.7	46.5	42.1	36.1	26.6

surface operation is the desalting process, which is necessary to remove salt from crude oils. Separation of oil, gas, and water from each other and removal of water and salt from oil and any other process that occurs at the surface are called *surface production operations* and are discussed in Chapter 11.

In addition to the impurities (hetoroatoms and metals) discussed earlier, some impurities may result from compounds that have been added to petroleum fluids for various reasons during their production, transportation, and storage. These include but are not limited to acids, alcohols, aromatic hydrocarbons, detergents, and polymers. Furthermore, petroleum fluids often contain compounds that result from the physical association with hydrocarbons; these may include colloids, crystalline solids, flocs, and slugs [3].

The crude oil produced from the atmospheric separator has a composition different from the reservoir fluid

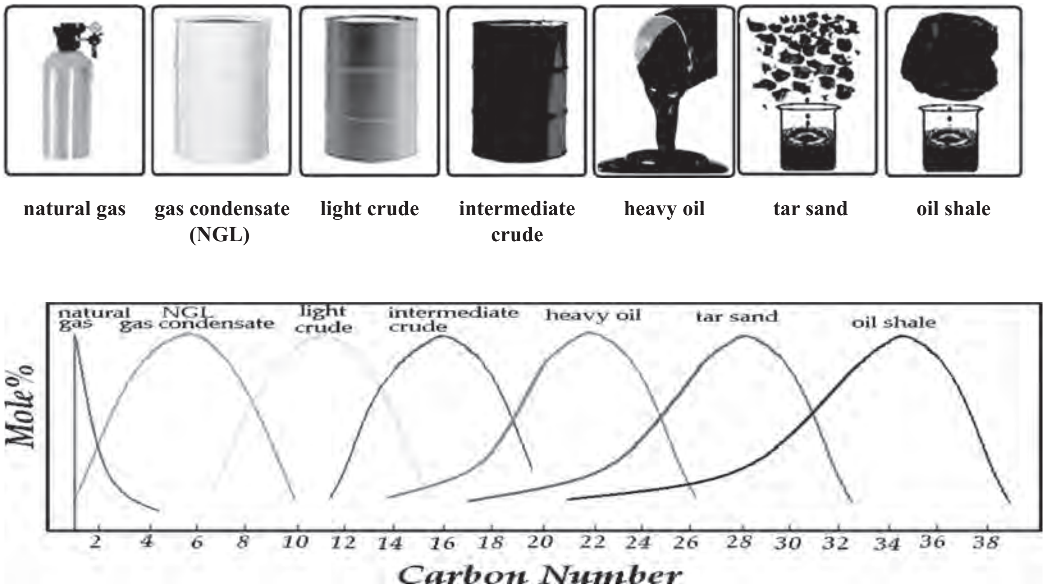


Figure 2.5—Various categories of natural gas and liquids naturally occurring in petroleum fluids and their approximate hydrocarbon molecular weight distributions according to their carbon numbers [3,4].

obtained from a producing well. The light gases are separated, and crude oils usually have almost no methane and a small C_2–C_3 content whereas its C_{7+} content is higher than the original reservoir fluid. As an example, the composition of a crude oil produced through a three-stage separator from a reservoir fluid is also given in Table 2.2 in the last column. Actually this crude is produced from a black oil reservoir fluid, the composition of which is also given in Table 2.2 (column 5).

Two important characteristics of a crude oil that determine its quality are the API gravity (specific gravity) and sulfur content. Generally, a crude with an API gravity of less than 20 (specific gravity > 0.934) is called a *heavy crude*, and a crude with an API gravity of greater than 40 (specific gravity < 0.825) is called a *light crude* [1,5]. Crudes with an API gravity of less than 10 are considered as extra heavy oil, such as bitumen. Similarly, if the sulfur content of a crude is less than 0.5 wt % it is called sweet oil. On the other hand, the term *sour oil* refers to crudes that have more than 0.5 wt % sulfur. It should be noted that these ranges for the gravity and sulfur content are relative and may vary from one source to another. Further classification of crude oils will be discussed in Chapter 4.

2.3 REFINING PROCESSES AND PRODUCTS FROM CRUDE OIL REFINERIES

A crude oil produced after necessary field processing and surface operations is transferred to a refinery for processing and conversion into various useful products. Petroleum refining (or *crude oil refining* in more precise terms) has evolved from simple batch distillation in the late 19th century to today's complex processing schemes in modern refineries. Refining processes can be generally divided into three major types: (1) separation, (2) conversion, and (3) finishing.

Separation is a physical process that is carried out by using different techniques to fractionate crude oil or its derivatives. The most important *separation* process is distillation, which occurs in a distillation column to separate the constituent compounds on the basis of differences in their boiling points. Other major physical separation processes include absorption, stripping, and solvent extraction. In the gas plant of a refinery, absorption by a liquid solvent retains C_{3+} hydrocarbons from a gas mixture and allows methane and ethane to be sent overhead as fuel gas. The solvent is then regenerated in a stripping unit. The *conversion* processes involve chemical changes that occur with hydrocarbons in reactors. The purpose of such reactions is to change the molecular weight and convert hydrocarbon compounds from one type to another. The most important reaction in modern refineries is cracking, which converts heavy hydrocarbons to lighter and more valuable hydrocarbons. Catalytic cracking and thermal cracking are commonly used for this purpose. Other types of reactions such as *reforming*, *isomerization,* and *alkylation* are used to produce high-octane-number gasoline. *Finishing processes* achieve the purification of various product streams by processes such as desulfurization or acid treatment to remove impurities and stabilize the fuels. Finishing processes that also include blending ensure that the refinery products meet the specifications dictated by performance characteristics and environmental regulations [6–8].

Crude oil in a refinery upon the desalting process enters the atmospheric distillation column where compounds are separated with respect to their boiling points. Hydrocarbons in a crude have boiling points ranging from –160 °C (boiling point of methane) to more than 600 °C (1100 °F), which is the boiling point of the heaviest distillable compounds in the crude oil. However, the carbon-carbon bond in paraffinic hydrocarbons breaks down at temperatures near 350 °C (660 °F). This process is called *cracking* and it is undesirable during the distillation process because it changes the chemical composition of the crude feed. For this reason, compounds having boiling points above 350 °C (660 °F), constituting the residuum fraction, are removed from the bottom of the atmospheric distillation column and sent to a vacuum distillation column. Because by distillation it is not possible to completely separate the constituent compounds of the crude oil, a distillation column does not produce pure hydrocarbon streams. Instead, distillate fractions are produced as defined according to the boiling point of the lightest and heaviest compounds in the mixtures of hydrocarbons. The lightest product of an atmospheric column is a mixture of methane and ethane (but mainly ethane), which has a boiling range of –180 to –80 °C (–260 to –40 °F) corresponding to the boiling points of methane and ethane, respectively. This mixture, referred to as "fuel gas" in a refinery, is the lightest *petroleum fraction*. Fractions with a wider range of boiling points contain a greater number of hydrocarbons. All fractions from a distillation column have a known boiling range, except the residuum, the upper boiling point of which is not usually known. The boiling points of the heaviest components in a crude oil are not really known because many of them would undergo cracking or other chemical reactions at temperatures lower than their boiling points. Identification of the structure and determining the properties of the heaviest compounds found in crude oils and petroleum residuum still present a difficult challenge to researchers. Theoretically, it can be assumed that the boiling point of the heaviest compound in a crude oil is infinity. Atmospheric residue contains compounds with carbon numbers greater than 25, whereas vacuum residue has compounds with a carbon number greater than 50 (M > 800). Table 2.3 lists some petroleum fractions produced from distillation columns along with their boiling point ranges and applications. In this table, the boiling points and equivalent carbon number ranges are approximate and they may vary according to the desirable properties of specific products. For example, the light gas fraction consists mainly of a mixture of ethane, propane, and butane; however, some heavier compounds (C_{5+}) may also exist in this fraction. The fraction is further fractionated to obtain ethane (a fuel gas), propane, and butane (petroleum gases). The petroleum gases are liquefied under pressure to produce liquefied petroleum gas (LPG) that can be used as fuel for heating and cooking in dwellings or as autogas [http://www.worldlpgas.com/]. In addition, butane may be separated from the gas mixture to be used for improving the vapor pressure characteristics (volatility) of gasoline in cold weather. Petroleum fractions separated by distillation may undergo further processing to produce the desired products. For example, gas oil may go through a cracking process to produce more gasoline. The principal refinery processes are discussed in Chapter 5 of this manual. Because distillation is not a perfect separation process, the initial and final boiling points for each fraction are not exact and especially the endpoints represent

TABLE 2.3—Some of the Petroleum Fractions Produced from Distillation Columns [1]

Petroleum Fraction	Approximate Hydrocarbon Range	Approximate Boiling Range	
		°C	°F
Light gases	C_2–C_4	–90 to –1	–130 to 30
Gasoline (light and heavy)	C_4–C_{10}	–1 to 200	30–390
Naphthas (light and heavy)	C_4–C_{11}	–1 to 205	30–400
Jet fuel	C_9–C_{14}	150–255	300–490
Kerosene	C_{11}–C_{14}	205–255	400–490
Diesel fuel	C_{11}–C_{16}	205–290	400–550
Light gas oil	C_{14}–C_{18}	255–315	490–600
Heavy gas oil	C_{18}–C_{28}	315–425	600–800
Wax	C_{18}–C_{36}	315–500	600–930
Lubricating oil	$>C_{25}$	>400	>750
Vacuum gas oil	C_{28}–C_{55}	425–600	800–1100
Residuum	$>C_{55}$	>600	>1100

approximate values. Fractions may be classified as narrow or wide depending on their boiling point range. As an example, the fractionation of an Alaskan crude oil into various products by distillation is graphically shown in Figure 2.6. The weight and volume percentages for the products are close to each other. It can be seen in Figure 2.6 that more than 50 % of the crude is processed in the vacuum distillation unit. The vacuum residuum consists mainly of resin- and asphaltene-type compounds containing high-molecular-weight multiring aromatics. The vacuum residuum may be further processed for upgrading or mixed with lighter petroleum fractions to obtain saleable products.

Distillation of a crude oil can also be performed in the laboratory to divide the mixture into many narrow boiling point range fractions with a boiling range of approximately 10 °C. Such narrow range fractions are sometimes referred to as *petroleum cuts*. When boiling points of all of the cuts in a crude are known, then the boiling point distribution (distillation curve) of the whole crude can be obtained. In a petroleum cut, hydrocarbons of various types are lumped together in four groups of paraffins (P), olefins (O), naphthenes (N), and aromatics (A). For olefin-free petroleum cuts, the composition is represented by the PNA content. Crude oils are generally free of olefins.

As mentioned earlier, the petroleum fractions presented in Table 2.3 are not the final products of a refinery. They go through further separation (physical), conversion (chemical), and finishing processes to achieve the product specifications set by the market and government regulations. Through refining processes (discussed in Chapter 5), the petroleum fractions shown in Table 2.3 are converted to *petroleum products*. The terms "petroleum fraction," "petroleum cut," and "petroleum product" are usually used interchangeably, but this is not appropriate because each term has a specific meaning that is different from the other two. In general, the petroleum products that are obtained in a refinery can be divided into two groups— fuel products and nonfuel products—as discussed in the following sections.

2.3.1 Petroleum Fuel Products

The major *petroleum fuel products* of a refinery are LPG, gasoline, jet fuel, diesel and heating oil, residual fuel oil, and petroleum coke as described below [1,7–10]. The specifications of these fuels are discussed in Chapter 4 of this manual.

1. LPGs are mainly used for domestic heating and cooking (50 %), industrial fuel (clean fuel requirement) (15 %), feedstock for steam cracking (25 %), and as a motor fuel (autogas) for spark ignition engines (10 %). LPG is produced by crude oil refining or natural gas fractionation. The estimated world production in 2005 was 250 million tons per year (≅8 million bbl/day) [10]. LPG consists mainly of a mixture of propane (C_3H_8) and *n*-butane (C_4H_{10}), but it may also include ethane (C_2H_6), ethylene (C_2H_4), propylene (C_3H_6), butylene (C_4H_8), isobutane, and isobutylene in small concentrations. Propane, butane, or propane/butane mixtures can be liquefied at ambient temperature under moderate pressure. LPGs are considered ideal fuels because they can be transported and stored in liquid form and used as a gas or a liquid. Propane can be safely used at ambient temperatures from approximately –40°C (–104°F) to 45°C (113°F), whereas butane can be used at temperatures from 0°C (32°F) to approximately 110°C (230°F) [8]. They have high energy density, low sulfur content, and they burn cleanly.

   LPGs have been used increasingly as auto fuel under the generic name "autogas." The composition of autogas varies depending on the prevailing ambient temperatures in the countries it is used. At moderate ambient temperatures, it consists of 60–70 % propane and 30–40 % butane [9]. The advantages of using LPG compared with gasoline and diesel include lower fuel and maintenance cost and lower engine emissions. See Chapter 4 for specifications on autogas and variations in specifications in different countries.
2. *Gasoline* is perhaps one of the most important products of a refinery. In the United Kingdom it is referred to as *petrol*. Gasoline is obtained by blending various

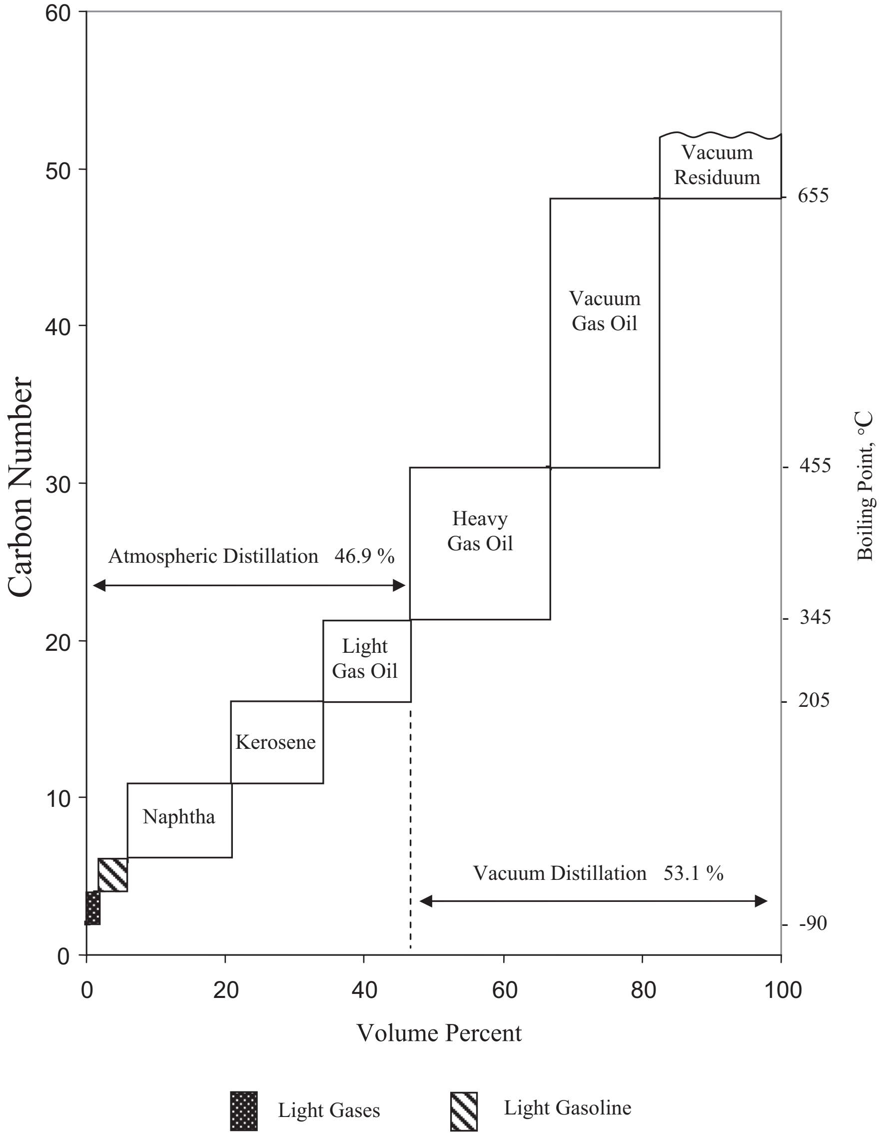


Figure 2.6—Products and composition of Alaska crude oil [1].

streams obtained from different refinery operations, including crude oil distillation, catalytic cracking, and catalytic reforming. It contains hydrocarbons from C_4 to C_{11} (molecular weight of ~100–110). It is used as a fuel for cars with spark-ignition engines. Its main characteristics include anti-nock (octane number), volatility (distillation data and vapor pressure), stability, and density. The main evolution in gasoline production has been the introduction of nonleaded gasoline (referred to as "unleaded gasoline," which excludes using tetraethyl lead as an additive to increase the octane number) in many parts of the world and the use of *reformulated gasoline* (RFG) in the United States. The RFG has less butane, less aromatics, and more oxygenates. Sulfur content of gasoline should not exceed 0.03 % by weight. Further properties and characteristics of gasoline will be discussed in Chapter 4. The U.S. gasoline demand in 1964 was 4.4 million bbl/day and increased from 7.2 to 8.0 million bbl/day in a period of 7 years from 1991 to 1998 [1]. In the 1990s, gasoline was approximately one-third of the refinery products in the United States, whereas in July 2007 gasoline production was approximately 9.33 million bbl/day, or 37.5 % of total products according to the API report.

3. *Kerosene* is a distillate fraction of crude oil that boils between 150°C and 250°C and is primarily used for producing *jet fuel* to power gas turbine or jet engines. To a much smaller extent, kerosene is used as fuel for lighting and cooking, particularly in rural areas where access to natural gas, LPG, and electricity is limited. Jet fuel, which is also called "aviation turbine fuel," is a premium fuel that has shown a faster increase in demand than any petroleum fuel because of expanding civil and military aviation. In 2007, an estimated consumption for jet fuel was 205 million t [10]. The main characteristics of jet fuel include sulfur content, cold resistance (more stringent performance for military jet fuel), density, aromatics content, and ignition quality. ASTM and the International Air Transport Association (IATA) have issued specifications for commercial (e.g.,

Jet A, Jet A-1, the Russian TS-1) and military jet fuel (JP-8) that differ only in freezing point [9].

4. *Diesel* and *heating oil* are used for motor fuel and domestic purposes. Diesel is obtained from fractional distillation of crude oil between 200°C and 350°C. The main characteristics are ignition (for diesel oil), volatility, viscosity, cold resistance, density, sulfur content (corrosion effects), and flash point (safety factor). There are basically three kinds of diesel fuel: No. 1, No. 2, and No. 4. Diesel No. 1 is for use in farm and city buses, whereas diesel No. 2 is for use in automobile, truck, and railroad vehicles. Diesel No. 4 is for use in railroad, marine, and stationary engines [9]. Diesel fuels used in city buses have a lower endpoint, lower sulfur content, and higher cetane number.
5. Residual *fuel oil* is used for industrial fuel, thermal production of electricity, and motor fuel (low speed diesel engines). Its main characteristics are viscosity (good atomization for burners), sulfur content (corrosion), stability (no decantation separation), cold resistance, and flash point (for safety). Basically there are five types of fuel oils in commercial use: No. 1, No. 2, No. 4, No. 5, and No. 6. Fuel oil No. 1 is used for stoves and farms, fuel oil No. 2 is for home heating uses, No. 4 is used for light industrial uses, No. 5 is used for medium industrial applications, and No. 6 is used for heavy industrial and marine applications [9]. Fuel oil No. 1 has the lowest density, boiling point, flash point, pour point, viscosity, and sulfur content, whereas fuel oil No. 6 is the heaviest fuel oil, with high sulfur content and high viscosity.
6. Petroleum coke, which is a solid byproduct obtained from delayed coking or fluid coking of vacuum distillation residue, may be used as industrial fuel depending on its sulfur and metal contents [11]. It contains less than 1 %wt ash, but it needs to be burned in industrial furnaces with strict controls on emissions. Important properties of fuel coke include grindability, volatile matter content, sulfur content, and nickel and vanadium contents. Nonfuel uses of petroleum coke are described in the next section.

2.3.2 Nonfuel Petroleum Products

The major *nonfuel petroleum products* include solvents, naphthas, petrochemical feedstocks, lubricating oils, waxes, asphalts, and petroleum cokes [1,7–9,11]. Brief descriptions of the nonfuel products and their uses are given below.

1. *Solvents* are light petroleum cuts in the C_4–C_{14} range that have numerous applications in industry and agriculture. For example, white spirits that have boiling point ranges between 135 and 205 °C are used as paint thinners. The main characteristics of solvents are volatility, purity, odor, and toxicity. Benzene, toluene, and xylenes (BTX) are used as solvents for glues and adhesives. *Naphthas* constitute a special category of petroleum solvents with boiling ranges corresponding to those of white spirits. Similar to BTX, naphthas may be used as raw materials for producing petrochemical feedstocks, as described below. Therefore, naphthas are considered to be industrial intermediates that are subject to commercial specifications
2. *Petrochemical feedstocks* that are produced in the refinery include C_6 to C_8 aromatics (BTX and ethyl benzene) and C_2 to C_4 olefins. In petrochemical plants, these feedstocks are used to produce plastics and resins, pharmaceuticals, antifreeze agents, detergents, solvents, dyes, and agricultural chemicals such as fertilizers, pesticides, and herbicides. BTX and ethyl benzene are produced in refineries [in fluid catalytic cracking (FCC) and catalytic reforming units] and in petrochemical plants through reforming of naphtha. The C_3 to C_4 olefins are produced in FCC units, and C_2 and C_3 olefins are produced by coking processes in a refinery and steam cracking of naphtha or gas oils in petrochemical plants.
3. *Lubricants* are composed of a main base stock obtained from dearomatized and dewaxed vacuum gas oils for controlling the viscosity and freezing point and are combined with additives to obtain the desired performance characteristics. Among the most important characteristics of lubricants are thermal stability, viscosity, and the viscosity index, which reflects the change of viscosity with temperature. Aromatics are usually eliminated from lubricants to improve their viscosity index. Lubricants consist mostly of isoparaffinic compounds. Additives used for lubricants include viscosity index additives such as polyacrylates and olefin polymers, antiwear additives (i.e., fatty esters), antioxidants (i.e., alkylated aromatic amines), corrosion inhibitors (i.e., fatty acids), and antifoaming agents (i.e., polydimethylsiloxanes). Lubricating greases constitute another class of lubricants that are semisolid. The specifications for lubricants include viscosity index, freezing points, aniline point (indication of aromatic content), volatility, and carbon residue (indication of thermal stability).
4. *Petroleum waxes* are of two types: the paraffin waxes in petroleum distillates and the microcrystalline waxes in petroleum residua. In some countries such as France, paraffin waxes are simply called paraffins. Paraffin waxes have high melting points; they are removed by dewaxing of vacuum distillates to control the pour points of lubricating oil base stocks. Paraffin waxes are mainly straight-chain alkanes (C_{18} to C_{36}) with a very small proportion of isoalkanes and cycloalkanes. Their freezing point is between 30 and 70 °C, and the average molecular weight is approximately 350. When present, aromatics appear only in trace quantities. Waxes from petroleum residua (microcrystalline form) are less defined aliphatic mixtures of *n*-alkanes isoalkanes, and cycloalkanes in various proportions. Their average molecular weights are between 600 and 800, their carbon number range is C_{30} to C_{60}, and the freezing point range is 60–90 °C. Paraffin waxes (when completely dearomatized) have applications in food industry and food packaging. They are also used in the production of candles, polishes, cosmetics, and coatings [6,8]. Waxes at an ordinary temperature of 25 °C are in solid states, although they contain some hydrocarbons in liquid form. When melted, they have relatively low viscosity.
5. *Asphalt* is produced from vacuum distillation residues by solvent deasphalting. Asphalts contain nonvolatile high-molecular-weight polar aromatic compounds such as asphaltenes and cannot be distilled even under very high vacuum conditions. In some countries asphalt is called bitumen, although this is not a strictly correct use of the term bitumen. Asphaltic materials (containing

asphaltenes and resins) are used as binders for paving the roads. The major properties of asphalt that determine its quality include flash point (for safety), composition (wax content), viscosity, softening point, weathering properties (resistance to oxidation or degradation), specific gravity, and stability or chemical resistance.

6. There are some other products such as white oils (used in pharmaceuticals or in the food industry), aromatic extracts (used in the paint industry or the manufacture of plastics), and coke (as a fuel or to produce carbon electrodes for aluminum refining). Aromatic extracts are black materials composed essentially of condensed PNAs and heterocyclic nitrogen or sulfur compounds, or both. Because of this highly aromatic structure, the extracts have a good solvent power. *Petroleum cokes* produced by delayed coking of vacuum distillation residue can be specified as sponge, or shot cokes, depending on their microstructure [11]. Sponge cokes that have low ash, low sulfur, and low metal contents can be used for making carbon anodes that are used in electrolysis of alumina to manufacture aluminum. Shot cokes that are much harder than sponge cokes have a niche application for producing titanium dioxide [11]. Delayed coking of FCC decant oils produces a special coke called "needle coke" that is used to produce graphite electrodes for electric-arc furnaces for recycling scrap iron and steel. Important properties of calcined needle cokes include density, ash content, and the coefficient of thermal expansion [11].

In general, more than 2000 petroleum products within some 20 categories are produced in refineries in the United States [6,8]. Some of these products obtained from a

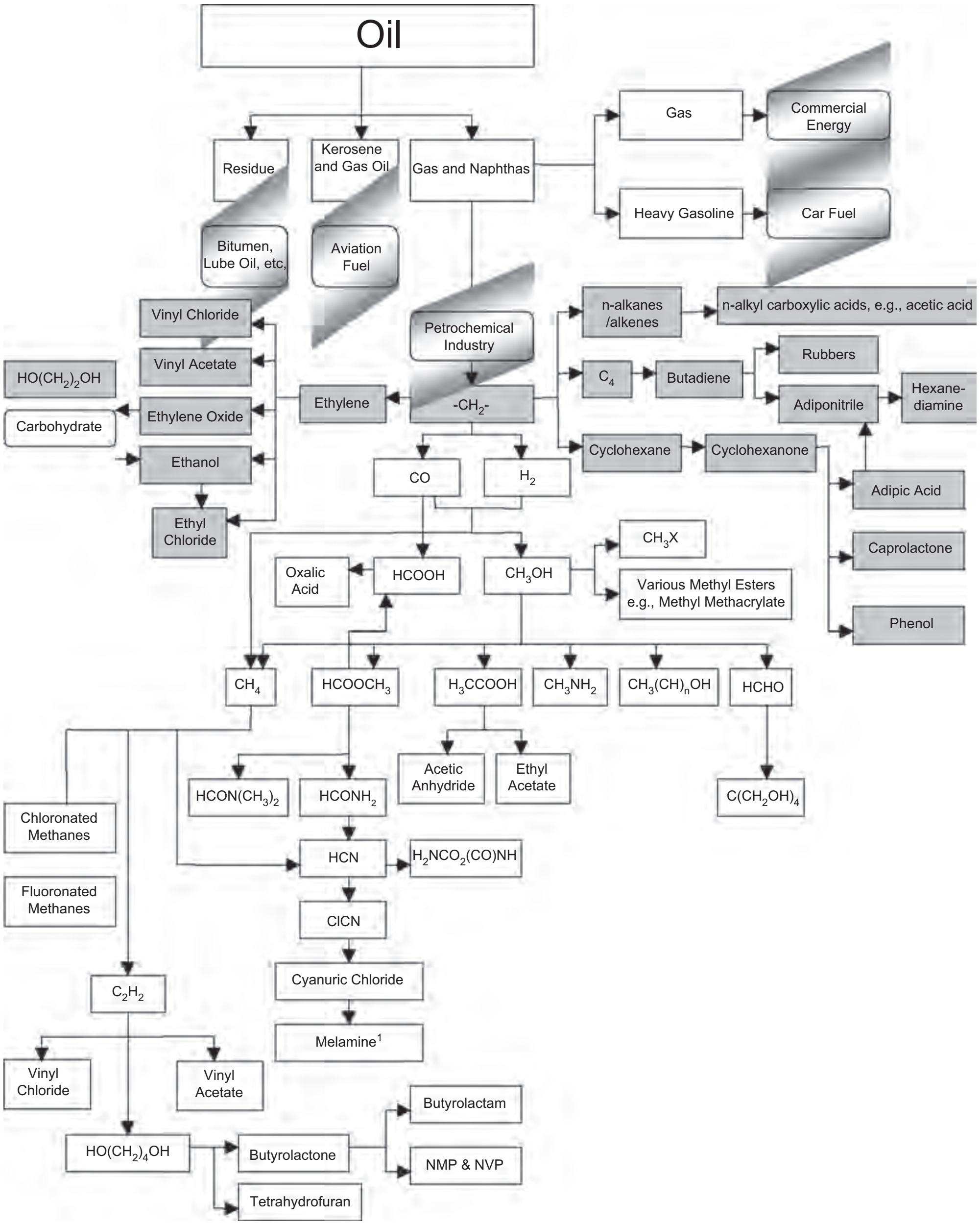


Figure 2.7—Some products produced from crude oil processing [12].

typical crude oil are shown in Figure 2.7 as presented by de Jong et al. [12]. In this figure, fuel products directly produced in refineries are marked in color, whereas many chemicals may be produced in the follow-up processes in a petrochemical plant. Blending techniques are used to make multiple products according to the desired properties or to improve product quality. The product specifications must satisfy customers' requirements for good performance and government regulations for safety and environmental protection. Therefore, to be able to plan refinery operations, the availability of a set of product quality prediction methods is very important [1].

2.4 NATURAL GAS AND ITS PRODUCTS

The typical composition of natural gas is given in Table 2.2. Usually natural gases contain CO_2 and H_2S known as acid gases, but the main components are methane, ethane, and propane, although hydrocarbons as heavy as C_{11} may be present. Natural gases may also contain inert gases such as nitrogen and helium. Pipeline gases containing mainly nitrogen, helium, C_1, C_2, and C_3 in liquefied form are called LNG. The liquefied form of gases C_2, C_3, and C_4 is called LPG. Pentanes and heavier including isobutane can be separated from natural gas as natural gasoline. Natural gas liquids (NGLs) and light and heavy naphthas may also be separated naturally from natural gas. At normal pressure conditions, only C_5 and heavier components are in liquid form. Methane needs to be refrigerated to –259°F to have it as liquid. For storage of natural gas at normal temperatures (above boiling point), it is necessary to compress it, which is known as compressed natural gas (CNG). Liquid mixtures of C_3 and C_4 are ideal fuel for many applications. They are stable, high-energy content, relatively low sulfur, and clean burning fuels that can be transported as liquid and used as liquid or gas. LPG can be produced from natural gas and crude oil. LPG is also a preferred feedstock for petrochemicals, gas cracking, and plastics. The first commercial use of LPG from crude oil or natural gas was in 1912. Propane used in LPG is not suitable for gasoline (it is very volatile) or for use in natural gas (heavy component in natural gas pipeline), so its best application is in LPG. The ratio of C_3–C_4 in LPG mainly depends on the temperature because at high temperatures (summer) more C_4 and at low temperatures (winter) more C_3 is used in the mixture. Tanks containing LPG should never be filled with liquids to allow space for vapors and volume expansion for safety reasons [8].

Natural gas and NGLs are also the main feedstocks for petrochemical plants. Through absorption processes, H_2S can be separated from natural gas, and upon oxidation of H_2S sulfur can be produced. Through distillation/extraction processes, components such as C_2, C_3, C_4, and heavier compounds are separated. Methane as the main component of natural gas can be used through processes such as reforming and oxidation to produce a group of chemicals such as CO_2, hydrogen, ammonia,, methyl chloride, acetylene, methanol, nitric acid, urea, acrylonitrile, vinyl chloride, ethanol, propanol, butanol, formaldehyde, pharmaceuticals and feeds to pharmaceutical industries, carbon tetrachloride, acetaldehyde, vinyl resins, etc.

The next main components of natural gas are ethane and propane. These components can be converted to ethylene and propylene through cracking processes. Ethylene can be used to produce many products such as polyethylene, ethylene oxide, ethyl chloride, ethanolamine, ethylene glycol, acetaldehyde, styrene, ethyl benzene, detergents, etc. Propylene is used to produce a group of compounds through processes such as oxidation, hydration, polymerization, and alkylation. These products include cumene, polymers, isopropyl alcohol, allyl chloride, acetone, glycerin, epoxy resins, isobutanol, acetic acid, nitroglycerin, etc.

Butanes in natural gas may be in the form of isobutene or *n*-butane, which can be separated through a distillation process. These components can be converted to products such as isobutylene, *tert*-butyl alcohol, butadiene, polybutadiene, nylon, methyl ethyl ketone, synthetic resins, lube oil additives, *tert*-butyl phenol, etc., through dehydrogenation, polymerization, and copolymerization processes.

2.5 BIOFUELS

Biofuels represent a group of fuels derived from biomaterials such as vegetable oil or biomass. A good example of a biofuel is biodiesel, which is a cleaner fuel than petrodiesel and can be produced from renewable sources such as vegetable oil, palm oil, cooking oil, or animal fat. These oils undergo a process called transesterification, in which they react with an alcohol such as methanol or ethanol with sodium hydroxide or potassium hydroxide as catalyst [13–16]. Transesterification converts fats and oils (triglycerides) into alkylesters of fatty acids that have similar properties to those of petroleum diesel. The process produces large quantities of glycerol as a byproduct. Biodiesel does not contain any sulfur or aromatics. Therefore, in comparison to petroleum diesel, the combustion of biodiesel results in a reduction in unburned hydrocarbons, carbon monoxide, and particulate matter emissions. Because it has a higher flash point it is safer to store and to handle [15–17]. Biodiesel can be used in its pure form (B100) or in blends with petroleum diesel in a wide range of concentrations (e.g., B2, B5, B20) in diesel engines.

Another group of biofuels comprises bioalcohols, which are biologically produced alcohols. The most commonly used bioalcohols are ethanol, propanol, and butanol. Butanol can be used directly in spark-ignition (gasoline) engines without any alteration. Butanol can produce more energy than ethanol and is less corrosive because it is less soluble in water. However, ethanol is the most commonly used biofuel in the world and in particular in Brazil. Ethanol can also be mixed with gasoline at any ratio, but use of 15 % bioethanol in gasoline (marked by E15) is common. Mixtures of gasoline and ethanol produce less pollution than gasoline upon combustion, especially in cold winters and high altitudes. However, ethanol has a lower heating value than gasoline [13].

Other types of biofuels include biogas and solid biofuels. Biogas is produced when organic material is anaerobically digested by anaerobes. Biogas consists of methane, and landfill gas is created in landfills because of natural anaerobic digestion. Charcoal and wood are examples of solid biofuels. The combined processes of gasification, combustion, and pyrolyis can produce syngas, which is a biofuel. This syngas can be directly burned in internal combustion engines. Syngas can be used to create hydrogen and methanol. Syngas can be transformed to a synthetic petroleum substitute using the Fischer–Tropsch process. Finally, a third-generation biofuel is produced from algae, which is called "oilage" [13].

REFERENCES

[1] Riazi, M.R., “Characterization and Properties of Petroleum Fractions, MNL50,” ASTM International, West Conshohocken, PA, 2005.

[2] “IUPAC: International Union of Pure and Applied Chemistry (IUPAC),” http://www.iupac.org (accessed July 7, 2009).

[3] Mansoori, G.A., “A Unified Perspective on the Phase Behavior of Petroleum Fluids,” *Int. J. Oil, Gas Coal Technol.*, Vol. 2, 2009, pp. 141–167.

[4] Riazi, M.R., “Energy, Economy, Environment and Sustainable Development in the Middle East and North Africa,” *Int. J. Oil, Gas, Coal Technol.*, Vol. 3, 2010, pp. 301–345.

[5] Altagelt, K.H., and Boduszynski, M.M., *Composition and Analysis of Heavy Petroleum Fractions*, Marcel Dekker, New York, 1994.

[6] Speight, J.G., *The Chemistry and Technology of Petroleum*, 3rd ed., Marcel Dekker, New York, 1998.

[7] Wauquier, J.-P., *Petroleum Refining. Vol. 1 Crude Oil. Petroleum Products. Process Flowsheets*, Editions Technip, Paris, 1995.

[8] Gary, J.H., Handwerk, G.E., and Kaiser, M.J., *Petroleum Refining, Technology and Economics*, 5th ed., Marcel Dekker, New York, 2007.

[9] Totten, G.E., Westbrook, S.R., and Shah, R.J., *Fuels and Lubricants Handbook: Technology, Properties and Testing*, MNL37, ASTM International, West Conshohocken, PA, 2003.

[10] Parkash, S., *Petroleum Fuels Manufacturing Handbook*, McGraw-Hill, New York, 2010.

[11] Eser, S., and Andresen, J., “Properties of Fuels, Petroleum Pitch, Petroleum Coke, and Carbon Materials,” in *Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing*, MNL37, G.E. Totten, R.J. Shah, and S.R. Westbrook, Eds., ASTM International, West Conshohocken, PA, 2003, pp. 757–786.

[12] de Jong, E., van Ree R., van Tuil, R., and Elbersen, W., *Biorefineries for the Chemical Industry—A Dutch Point of View, A Joint Research Report from Agrotechnology and Food Innovations, Wageningen, The Netherlands and the Energy Research Centre of the Netherlands (ECN)—Biomass Department*, Petten, The Netherlands, http://www.biorefinery.nl/fileadmin/biorefinery/docs/biorefineries_for_the_chemical_industry_a_dutch_point_of_view.pdf (accessed July 2009).

[13] “Biofuels: The Fuel of the Future,” http://biofuel.org.uk/types-of-biofuel.html (accessed July 7, 2009).

[14] Srivastava, A., and Prasad, R., “Triglycerides-Based Diesel Fuels,” *Renew. Sustain. Energy Rev.*, Vol. 4, 2000, pp. 111–133.

[15] “Natural Resources Canada: Biodiesel,” http://oee.nrcan.gc.ca/transportation/alternative-fuels/index.cfm?attr=8 (accessed July 7, 2009).

[16] Meher, L.C., Vidya Sagar, D., and Naik, S.N., ”Technical Aspects of Biodiesel Production by Transesterification—A Review,” *Renew. Sustain. Energy Rev.*, Vol. 10, 2006, pp. 248–268.

[17] Morf, O, “BIODIESEL: A Guide for Policy Makers and Enthusiasts,” National Agricultural and Environmental Forum, Siddharthanagar, Bhairahawa, Nepal, http://www.naef-nepal.org (accessed July 7, 2009).

3

Worldwide Statistical Data on Proven Reserves, Production, and Refining Capacities of Crude Oil and Natural Gas

M.R. Riazi[1], Mohan S. Rana[2], and José Luis Peña Díez[3]

3.1 INTRODUCTION

The world's energy is produced from various sources, including oil, gas, coal, and nuclear and renewable sources such as solar, wind, water, biomass, and geothermal sources. Oil, gas, and coal are fossil-type hydrocarbons that are not renewable and currently make up more than 80 % of the world's energy consumption. Oil and gas may be produced as different naturally occurring hydrocarbon fluids from natural gas to bitumen and shale oil as shown in Figure 3.1 for seven classifications [1]. Heavier fluids contain compounds with higher carbon number and higher carbon-to-hydrogen ratios, which means lower quality for the oil and less desirable feedstock in terms of production and processing costs.

Major oil and gas fields are located largely in the Middle East, as shown in Figure 3.2 [2,3]. Approximately 60 % of the world's oil reserves are located in the Middle East, as shown in Table 3.1. In fact, Saudi Arabia, Iran, Kuwait, and Iraq from the Middle East along with Venezuela from South America formed the Organization of Petroleum Exporting Countries, known as OPEC, in 1960. Later, nine other oil-producing countries joined OPEC, and these countries are now major world oil producers. This trend will continue, according to the recent International Energy Agency (IEA) reference scenario, in which OPEC will account for 54 % of the total world's oil supply by 2030, compared with 45 % today [4]. Middle Eastern producers will supply 50 % of U.S. oil imports, 50 % of Europe's, 80 % of China's, and 90 % of Japan's oil imports. Reservoir lifetime (ratio of proven reserves to production rate) of non-OPEC producers is much lower than OPEC's: approximately 15 years for non-OPEC and more than 70 years for OPEC-producing countries, as shown in Table 3.1 [4,5].

World natural gas reserves have traditionally trended upward, and the beginning of 2009 showed that total world natural gas reserves stood at 6254 trillion ft^3, of which Middle East shares are 2549 trillion ft^3 [6,7]. In 2001, an organization of natural-gas-exporting countries informally known as the Gas OPEC was formed by Russia, Qatar, and Iran. The members now also include Algeria, Bolivia, Egypt, Equatorial Guinea, Iran, Libya, Qatar, Nigeria, Russia, Trinidad and Tobago, and Venezuela as well as Kazakhstan and Norway as observers. This organization recently elected a Russian as its director [8]. The lifetime of gas reserves at present rates is much higher than oil reserves, as shown in Table 3.2; however, as production and consumption of natural gas increases, the lifetime of such reserves is expected to decrease in present scenarios. The rate of consumption of natural gas in non–Organization for Economic Cooperation and Development (OECD) countries (mainly from Asia) in the next few decades is expected to be higher than OECD countries according to the Energy Information Administration (EIA).

Hydrocarbon production has been traditionally based on the most accessible fluids (conventional oil and gas), whereas resources difficult to develop by technical or economical reasons have been usually referenced as "unconventional resources." Heavy oils (having an API gravity < 20) or extra-heavy oil (with API gravity < 10) together with sand oils and shale oil form the group of unconventional oils. Venezuela, Canada, and Russia are known to have the largest worldwide heavy-oil resources. Current production of unconventional oil is much lower than conventional types; however, as the price of oil increases, the production and processing of unconventional oils become more economical and feasible. On the other hand, tight gas, shale gas, and coal-bed methane stand as the main short-term unconventional gas resources. The geographical distribution is dispersed, with large resources in North America and China. The case of shale gas is particularly relevant because the development of U.S. resources is playing a significant role in changing the global gas markets.

Crude-oil availability has been a topic of discussion during the last decades, producing much literature supporting conflicting positions. Although the discussion is still alive, with added uncertainty provided by the recent economic downturn, it seems there is a major confidence in hydrocarbon availability, with the challenge being to increase the production from brown fields through enhanced recovery processes and make economically feasible the exploitation of more difficult reservoirs (especially unconventional). As becoming generally agreed, it is "the end of easy oil" [9,10].

The oil refining industry is presently at a critical juncture because of the variations in the crude-oil scenario and emission regulations. Between 2000 and 2009, the industry witnessed capacity variation and product quality challenges

---

[1] Kuwait University, Kuwait
[2] Kuwait Institute for Scientific Research, Kuwait
[3] Repsol, Madrid, Spain

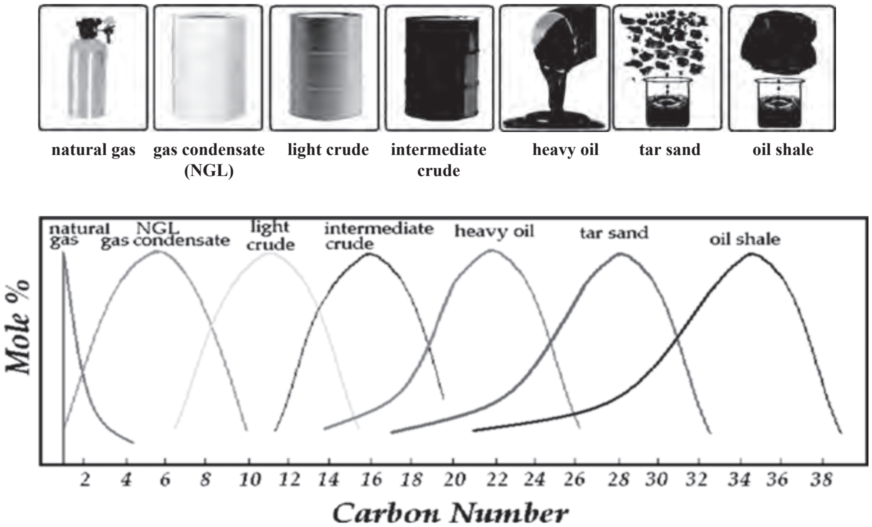


Figure 3.1—Normal condition of the seven naturally occurring petroleum fluids [1].

Figure 3.2—Major oil and gas giant fields in the Middle East [2,3].

with disparities in demand. The focus of the oil industry has been on crude-oil production, but the inadequacy of refining capacity has become the main industry concern. The global trend indicated that the world oil refining industry has to face several challenges for demand and supply. On the demand side, the growing activity of the transport sector will involve increasing quantities of cleaner liquid fuels as motor gasoline and diesel fuels. In this regard, North American and European demand will tend to reduce for gasoline whereas diesel will remain unchanged or slightly increased. Contrary to North American and European regions, Asia, Central and South America, and the Middle East will be known as an explosion region, which will lead the movement of oil products market. On the supply side, the crude-oil shares in the total primary energy supply will remain high, at least during the next decade. The conventional crude-oil supply will decrease, but heavy- and extra-heavy crude oil and tar sands supply will be increased. In any case and independently from the crude-oil quality, demand and supply in all petroleum streams will have to meet environmental constraints to limit the emissions specifications.

TABLE 3.1—Proven Conventional Oil Reserves by Regions at the End of 2008 in Billion Barrels of Oil [4]

Region	10^9 Barrels	Percent	R/P[a]
Middle East	754.1	59.9	78.6
Europe and Eurasia	142.2	11.3	22.1
Africa	125.6	10.0	33.4
South and Central America	123.2	9.8	50.3
North America	70.9	5.6	14.8
Asia-Pacific	42.0	3.3	14.5
World (total)	**1258.0**	**100.0**	**42.0**
OPEC	955.8	76.0	71.1
Non-OPEC	174.4	13.9	14.8
Former Soviet Union	127.8	10.1	27.2
World (total)	**1258.0**	**100.0**	**42.0**

[a] R/P, reserves-to-production ratio.

TABLE 3.2—Proven Conventional Gas Reserves by Regions at the End of 2008 in Trillion Cubic Feet [4]

Region	TCF[a]	Percent	R/P[b]
Middle East	2680.9	41.0	–
Europe and Eurasia	2220.8	34.0	57.8
Africa	517.5	7.9	68.2
South and Central America	258.2	4.0	46.0
North America	313.1	4.8	10.9
Asia-Pacific	543.5	8.3	37.4
World (total)	**6534.0**	**100.0**	**60.4**

[a] TCF, trillion cubic feet; [b] R/P, reserves-to-production ratio.

3.2 SHARE OF PETROLEUM AND NATURAL GAS IN WORLD'S ENERGY CONSUMPTION

This section summarizes the share of oil and gas in providing energy in the past and future for different regions and applications. Factors affecting increase in energy consumption and share of other sources of energy such as renewable, coal, and nuclear factors are also reviewed. Some common unit conversions for various forms of energy used in this chapter are given in Table 3.3 [11].

3.2.1 Energy Consumption

The analysis of current world energy needs is critical to the understanding of future energy scenarios and the relationship with fossil fuel reserves. World energy needs have increased exponentially during the last century, approximately 4 times the population growth in the same period. On the basis of the fossil fuel availability, the world population almost quadrupled from 1.6 billion in 1900 to 6.1 billion in 2000 [12], whereas energy consumption grew from approximately 21 quads to over 400 quads in the same time [13]. In 2002, total energy consumption in the United States was 97.4 quads [14], almost 24 % of the world demand. According to the EIA [6], the international energy outlook for global energy demand in 2006 was 472 quadrillion Btu. From an energy point of view, 1 quadrillion (10^{15}) Btu energy can be produced by approximately 45 million tons of coal, or 1 trillion ft^3 of natural gas, or 170 million bbl of crude oil. The evolution of world energy consumption during the last 50 years is shown in Figure 3.3.

There is a strong correlation between economic development and energy consumption, as shown in Figure 3.4. When this relationship is analyzed individually for each country, major differences in specific energy consumption become visible (Figure 3.5), although the general trend continues to be valid [15]. These differences are the consequence of many factors, from energy efficiency to domestic demand, with strong climate dependence. Energy consumption per capita has significantly increased during the last decades in developing countries, as opposed to OECD countries, in which stabilization has taken place [16], as presented in Figure 3.6. Although there is a possibility for these values being modified in the future by the progressive implementation of laws and carbon policies with a focus on energy efficiency, they provide a basis for understanding the present energy consumption distribution and the differences appearing in the structure of the energy portfolio share for different regions.

The use of diverse energy fuels has changed over time. Coal surpassed wood's usage, the main energy source over most of human history, in the late 19th century and was, in turn, overtaken by oil, another fossil fuel. In the first half of the 20th century, oil began to replace coal, and by the 1970s oil had become the leader in world energy supply contribution. Figure 3.7 shows the evolution of the contribution of different sources to energy production in recent decades.

Fossil fuels are the most attractive energy sources in terms of efficiency: they are highly concentrated, which enables large amounts of energy to be stored in relatively small volumes, and they are relatively easy to handle and distribute. Oil still provides more than one third of the world energy consumption, but projections indicate that this proportion will decrease in the coming decades. According to EIA, production of oil in this decade was nearly constant and less than 80,000 bbl/day, in which OPEC produced approximately one third of this amount. Natural gas started to make a significant contribution in the second half of the 20th century and it is gaining a key role in energy global markets in the beginning of this century. The contributions from other energies (mainly nuclear and hydro) continue to be minor.

The structure of energy mix in energy consumption shows significant changes when comparing different areas. Table 3.4 summarizes the share of total energy consumption by fuels in 2007 as published by several institutions. Primary energy consumption in various regions and the world based on data from BP is also shown in Figure 3.8 [11]. These data are represented in Figure 3.9, organized as energy charts to emphasize the geographical differences in their main source of energy. From this information, several conclusions can be outlined:

- Fossil fuels (oil, gas, and coal) represent approximately 90 % of the world's energy consumption, with oil being the main energy source, and gas and coal with similar contributions.

TABLE 3.3—Approximate Values of Energy Equivalency for Various Fuels

1 ft^3 (standard cubic foot, SCF) of gas is equivalent to 1000 Btu or 1000 SCF ≈ 1 MMBtu
1 bbl of oil is equivalent to 5500 SCF of gas
1 bbl of oil is equivalent to 0.158987 (~0.159) m^3, or approximately 159 L
1 MMBtu is equivalent to 0.17 bbl (or ~23 kg) of crude oil[a]
1 Quadrillion (10^{15}) Btu energy is approximately equivalent to 45 million t of coal
1 Quadrillion (10^{15}) Btu energy is approximately equivalent to 1 trillion ft^3 of natural gas or 170 million bbl of crude oil
1 t (1000 kg) of coal gives approximately 28 MMBtu of heat
1 Mtoe is equivalent to 1 million t of oil equivalent = 41.87×10^{15} J = 3.97×10^{13} Btu[a]
1 toe is 1 ton of oil equivalent, which is 7.14 bbl of oil equivalent[a]
1 MMBtu is equivalent to 36 kg of coal
1 bbl of crude oil is approximately 5500 ft^3 (0.0055 MMcf) gas ≈ 0.21 t of coal
1 t oil is equivalent to 1.5–1.8t of coal (equivalent heating value)
1 gal of gasoline gives approximately 0.11 MMBtu
Heating value of ethanol (a biofuel) is approximately two thirds the heating value of gasoline

[a] The value depends on the type and gravity of crude oil and varies from one source to another and could be 1 MMBtu = 23–25 kg oil equivalent.

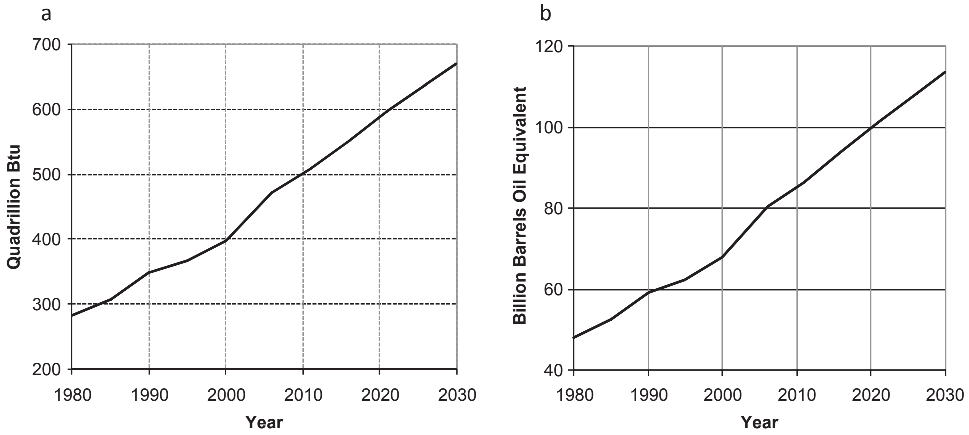


Figure 3.3—World energy consumption and projections to 2030: (a) in quadrillion Btu energy and (b) in billion barrels of oil equivalent based on data from EIA [13]. Data from 1980 to 2006 are history and 2007 to 2030 are projections.

Figure 3.4—World specific energy consumption per capita in 2008 (ton of oil equivalent) [4].

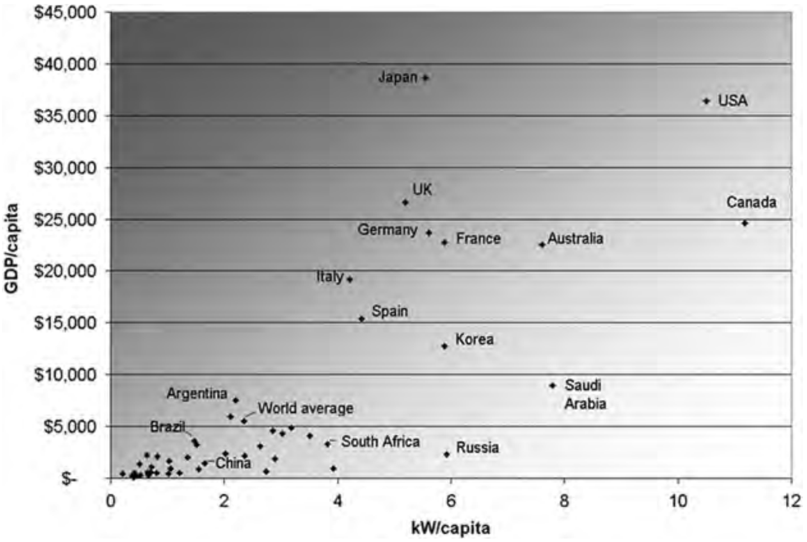


Figure 3.5—Relation between development and energy consumption for selected countries. *Source*: [15] with figure from Frank van Mierlo and data from 2006 (IEA).

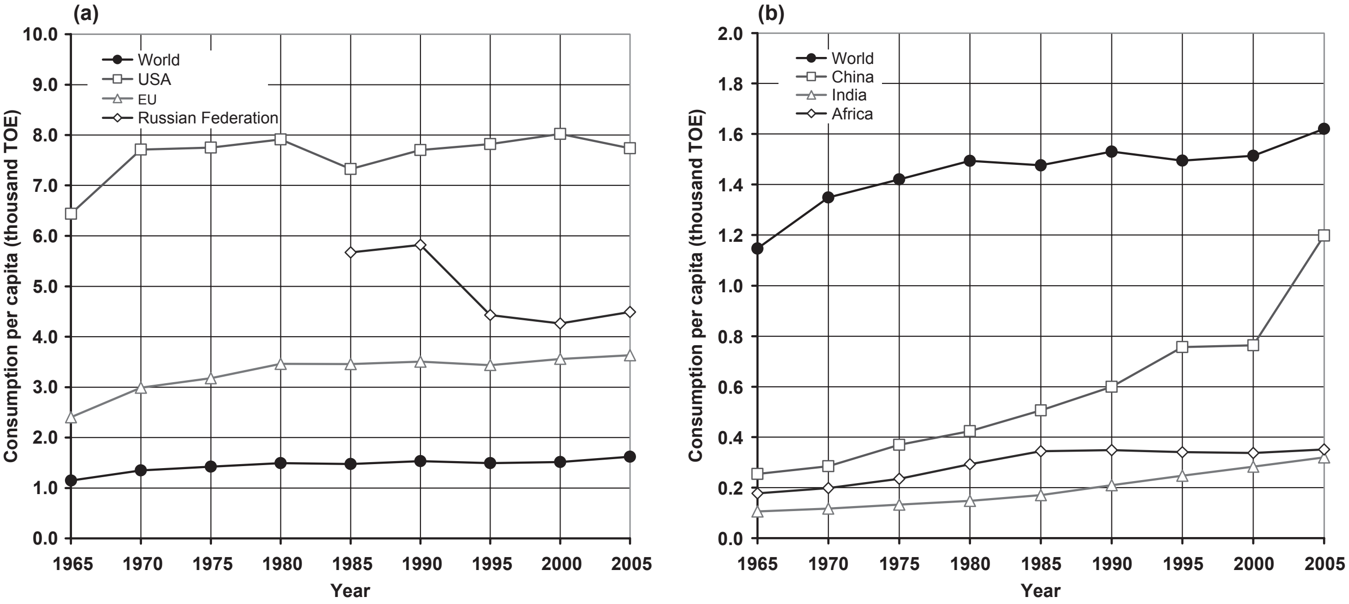


Figure 3.6—Primary energy consumption per capita, 1965–2005 [4]. Population data from the United Nations [12].

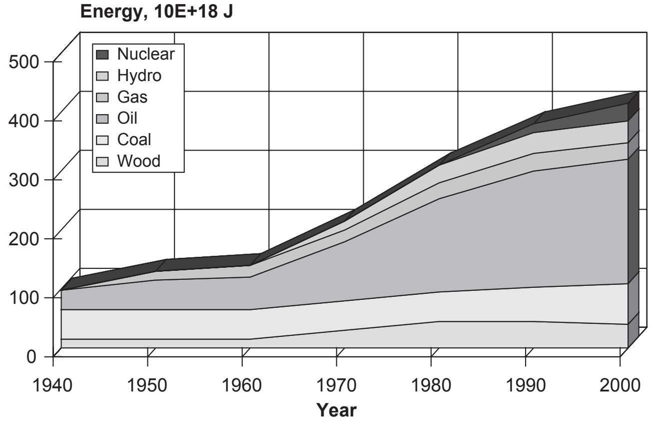


Figure 3.7—Contribution of different sources to energy production in past years [17].

- In the United States and the European Union (EU), consumption distribution is similar to the average world data, with oil and gas as two of the major shares. In the United States, coal has more participation in the energy map (23 % vs. 18 % in the EU), whereas in the EU, nuclear and renewable shares have more presence than in the United States.
- The energy mix in the Middle East is mainly based on oil and gas, with minor contributions from the rest.
- Russian dependence on gas is significant (>50 %) compared with the other areas.
- In the Asia-Pacific area (China and India), approximately 50 % of the total energy consumption is from coal, whereas natural gas and nuclear sources have minor contributions.
- Africa presents a totally different distribution, with a major dependence on coal and biomass.

TABLE 3.4—Share of Total Energy Consumption by Fuel in 2007

	Source	Oil (%)	Gas (%)	Coal (%)	Nuclear (%)	Renewables[a] (%)	Energy Consumption (10^6 toe)
World	[18]	34.1	20.9	26.5	5.9	12.6	12,013
United States	[19]	40.7	23.7	22.7	8.4	4.5	2343
EU	[20]	36.2	23.9	18.4	12.6	8.8	1967
Russia	[20]	19.7	54.4	15.2	6.3	4.4	672
China	[20]	18.2	3.1	65.6	0.8	12.3	1969
India	[20]	23.7	5.6	40.8	0.7	29.3	595
Middle East	[20]	52.2	45.3	1.8	0.0	0.7	552
Africa	[20]	21.1	13.1	16.9	0.5	48.4	629

[a]Including hydro, biomass, and other renewables.

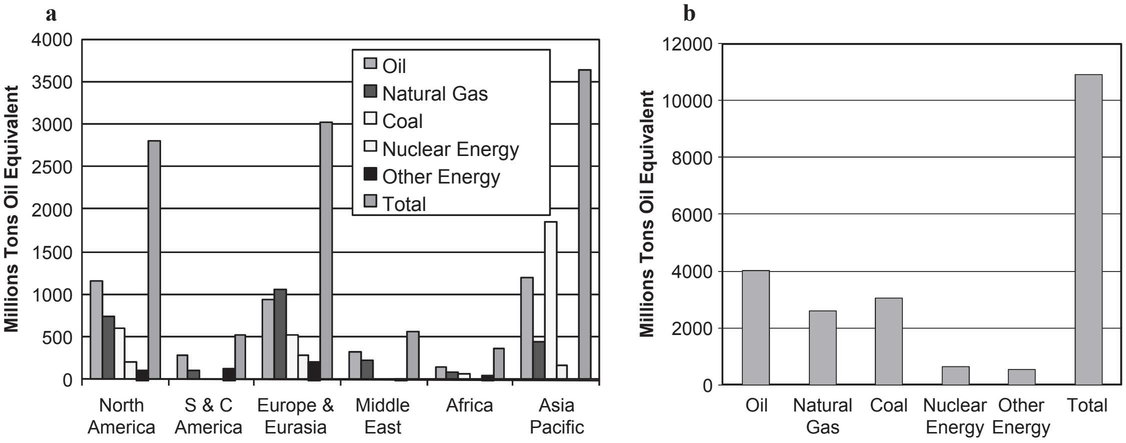


Figure 3.8—Primary energy consumption: (a) per region and (b) per fuel [11].

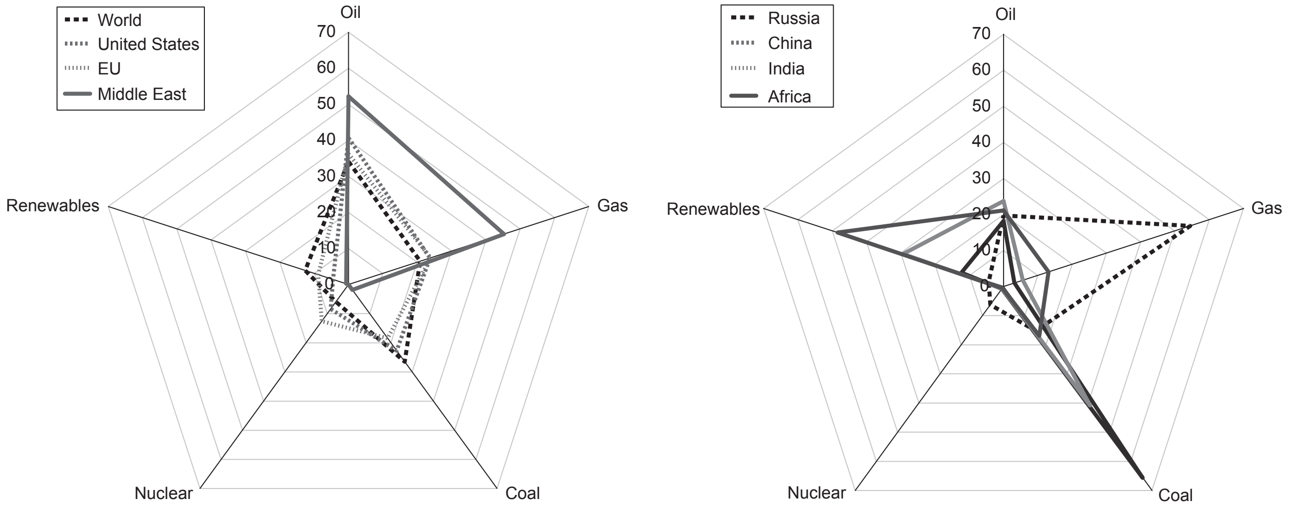


Figure 3.9—Energy dependence charts for different areas [13–15].

- Nuclear contribution, although minor, is only significant in OECD countries, but it does not reach representative contributions in South and Central America, Africa, and the Middle East.

A strong relationship also exists between the source of energy and its application. The approximate primary energy consumption by source and sector is represented in Figure 3.10, according to EIA, for recent available data [21]. Oil contributions in 2008 were 37 % of total energy, and oil is mainly used in the transportation sector (94 %). Natural gas contributes 24 % of total energy and is used mainly in residential and commercial applications. Coal and nuclear energy are exclusively used for electric power generation. This distribution does not change significantly when compared with most developed countries.

The present consumption scenario is the result of a period of cheap and easily available fossil fuels with a strong interrelationship among development, population growth, and energy resources [22]. The validity of this scenario in the future will depend on the expected country and individual consumption trends as well as energy availability under similar conditions.

3.2.2 Future Consumption Trends

According to EIA [13], the international energy outlook for global energy demand in 2006 was 472 quadrillion Btu and will increase to 552 quadrillion Btu in 2015 and then to 678 quadrillion Btu in 2030, with an increase of 44 % in 25 years (average annual growth 1.5 %) as shown in Figure 3.3. The scenarios proposed by alternative sources provide similar annual growths. The IEA reference scenario [18] projects a world primary energy demand yearly increase by 1.5 % between 2007 and 2030, from 12,000 million tons of oil equivalent (Mtoe) to 16,800 Mtoe, with an overall increase of 40 %.

The first decrease in energy consumption in decades came in 2009 because of the world economic downturn. The economic slowdown is creating a real decline in energy demand that may persist for the short term, although all of the scenarios provide similar quick resumption and long-term upward trends [23]. Increase in the energy consumption will very much depend on how these scenarios about world economy recovery become a reality. For three economy cases, energy consumption through 2030 is shown in Figure 3.11. Most of the energy consumption increase is due to energy consumption in non-OECD countries. For the United States and OECD countries, the increase in energy consumption by 2030 is moderate as given by the EIA International Energy Outlook [13]. The rapid growth in energy demand for this period is expected to be for non-OECD nations, while the energy demand increase for the same period would be 73 % (Figure 3.12). This is mainly related to faster economic growth rate for nations outside of the OECD, which is expected to have a gross domestic product (GDP) of approximately 5 % in comparison with 2 % GDP growth per year for the OECD countries [11]. Under the reference EIA scenario (1.5 % average annual consumption growth rate), OECD countries would have a 0.6 % annual increase, whereas for non-OECD countries the annual growth rate would be 2.3 %, 4 times higher.

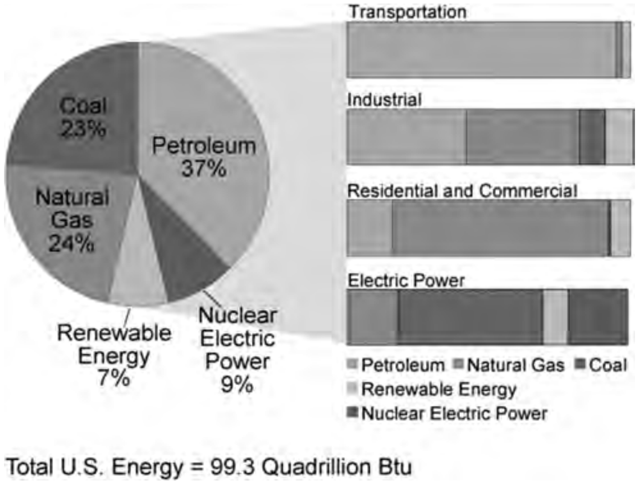


Figure 3.10—U.S. primary energy consumption by source and sector [21].

Energy efficiency is another important factor to consider when analyzing future energy consumption scenarios. Although economic growth in developed countries has reduced the required energy consumption, this improvement has not been sufficient to prevent total final energy needs from rising, as presented in Figure 3.6a. Most of the sectors have succeeded in reducing energy consumption per capita except in private household consumption, mostly because of greater ownership of electrical equipment. Figure 3.13 shows the trend during the last decade in the EU [24], with significant decreases in energy intensity in all sectors except household, where stabilization has occurred during the last few years. This trend is expected to continue, and energy conservation will probably start to play a role in household consumption on the basis of higher environmental pressures and the implementation of directives for minimum energy performance standards. Significant progress in energy savings could be achieved with minor personal lifestyle changes.

World economy and rate of energy consumption also depend on the oil and energy prices in general. Every oil price hike is usually followed by a decrease in demand, which in turn causes oil prices to decline. Oil price

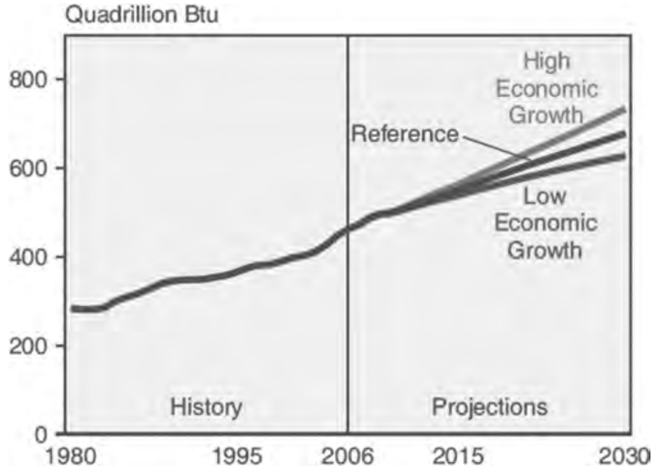


Figure 3.11—World marketed energy consumption in three economic growth cases and projections to 2030 [13].

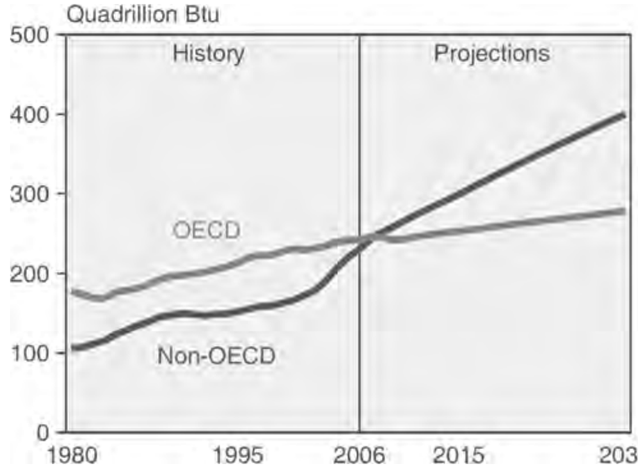


Figure 3.12—World marketed energy consumption: OECD vs. non-OECD countries 1980–2030 [13].

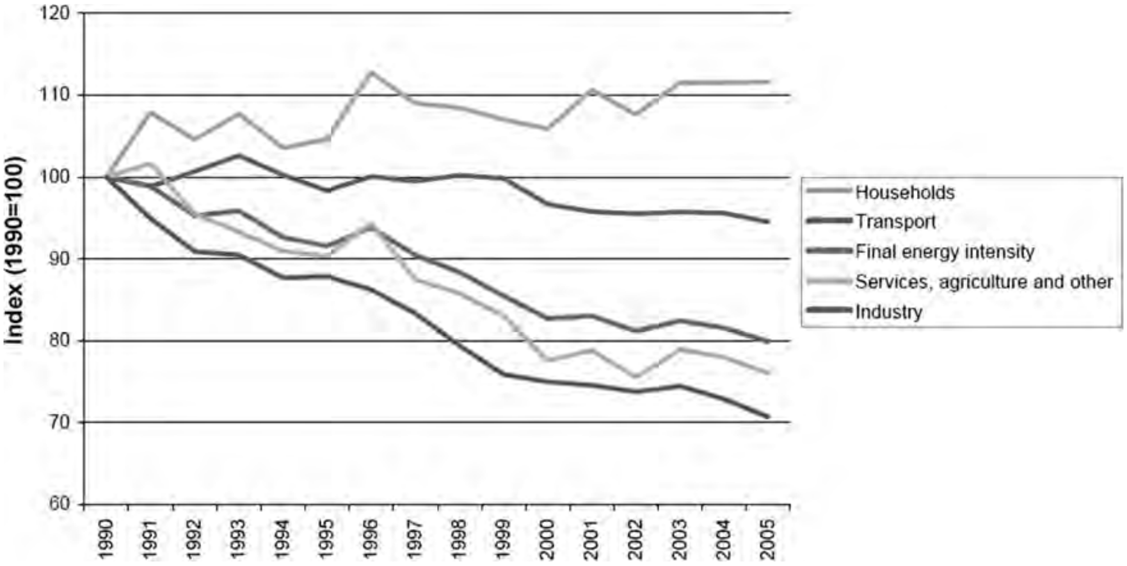


Figure 3.13—Index of final energy intensity and energy intensity by sector, EU-27 [24].

reached a peak value of $148/bbl in July 2008, which was related to the world economic crisis. However, during the following 2 years, the oil market did not respond to the price variations, and the price collapse in 2009 did not stimulate demand. The oil market is not a traditional supply/demand market; it is partly driven by external factors and has limited flexibility [15]. Economic downturn, war and political tension in the oil-producing countries, and world population growth also contribute to tensions in oil prices. Figure 3.14 shows projections of oil prices until 2030 for three economic growth cases. The impact of the current economic crisis on energy consumption seems to be limited in time according to recent data [23], although some supply challenges are expected, as seen later in this chapter. This situation, together with the higher pressure imposed by new greenhouse gas (GHG) legislations, will probably increase the need for alternative energies to cover this increasing gap.

The previous factors will have an impact in the structure of energy mix, especially in the long term. The base scenario does not identify major changes in the distribution of world energy consumption by different fuels or projections to 2030, as shown in Figure 3.15 [13]. The contribution of various sources of energy for electricity production from 2006 to 2030 according to the EIA is shown in Figure 3.16 [13]. The share of oil for electricity generation almost remains constant, whereas shares of renewable sources, natural gas, and coal will increase.

However, as projections vary from one source to another, other sources expect major changes in the world energy distribution during the rest of the century, with oil demand beginning to decrease by 2020; for natural gas, the peak in demand is reached around 2050 and decreases after that date, as shown in Figure 3.17 [17]. On the basis of these sources, by the end of the century contribution of renewable sources of energy such as solar, wind, or biomass may be higher than that of oil and gas. According to other sources [e.g., the German Advisory Council on Global Change (GACGC), Berlin], nuclear energy contributes only slightly to total energy production and consumption whereas solar energy is the biggest source for energy production by 2050–2100, as shown in Figure 3.18 [25].

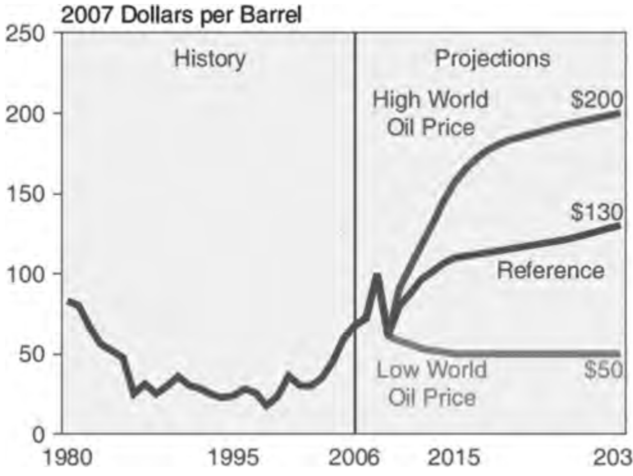


Figure 3.14—World oil prices in three economic growth cases [13].

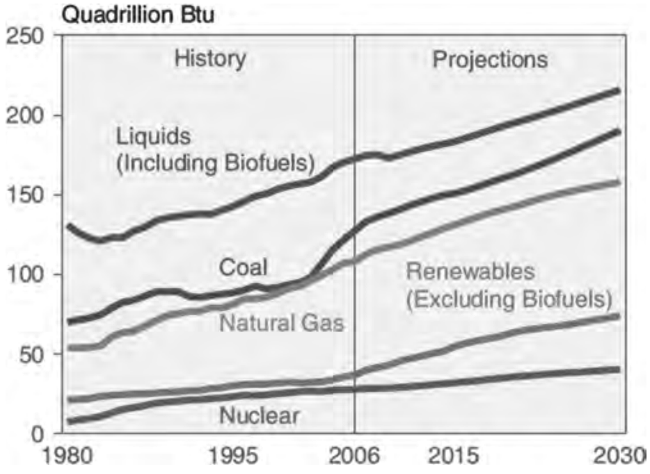


Figure 3.15—World marketed energy use by fuel type and projections to 2030 [13].

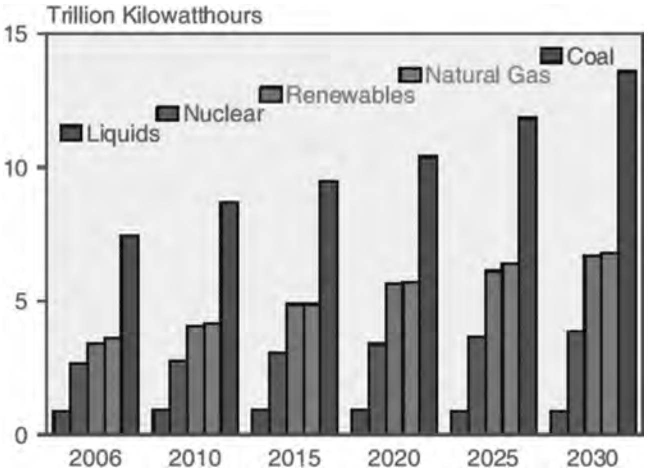


Figure 3.16—World electricity generation by fuel, 2006–2030 [13].

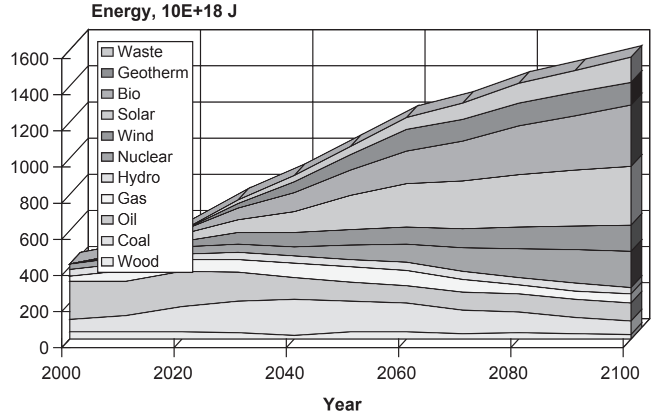


Figure 3.17—Anticipated contribution of different sources to energy production in the 21st century [17].

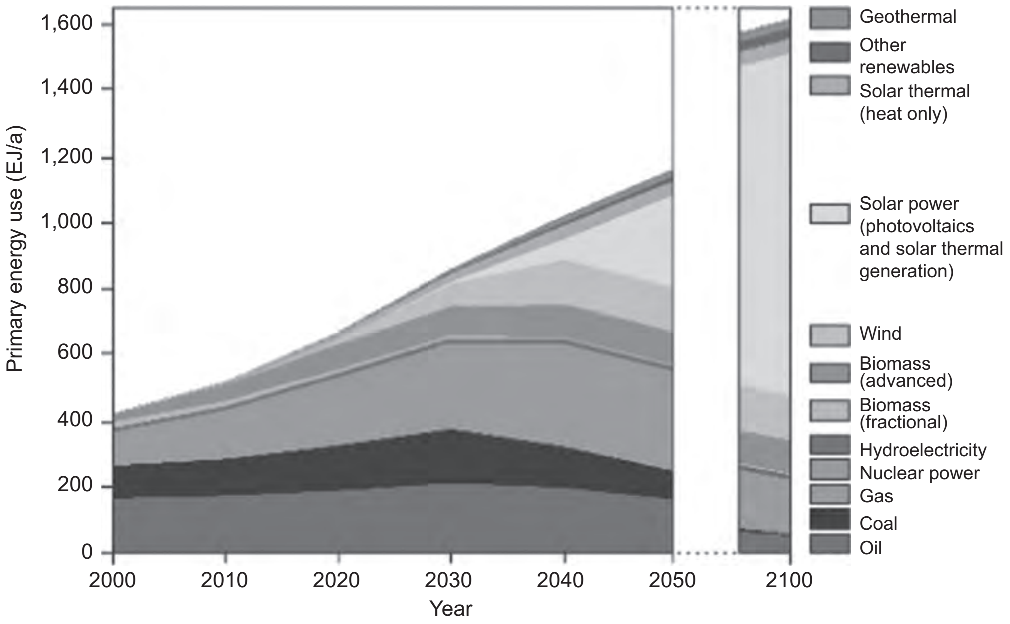


Figure 3.18—Projected energy use by 2050 and 2100 [17].

3.3 PETROLEUM AND NATURAL GAS RESERVES

3.3.1 Hydrocarbon Resource Classification

Within this chapter, an updated vision about the amount of fossil hydrocarbons remaining under the surface will be presented. How these resources are measured and classified is a challenge in itself. Although based on similar basic principles taking into account the certainty about the existence of the resources and the considerations about the extraction feasibility, there are many different definitions at technical and legal levels. These differences make analyzing data provided by different sources challenging, and this has been one of the possible causes of past confusions when comparing scenarios on the basis of published data.

The classification can typically be categorized into three main groups [26]:

- *Security disclosures [U.S. Securities and Exchange Commission (SEC), Canadian Securities Administrators (CSA), UK Sorp]:* These agencies provide financial accounting rules to provide reserves information to investors to compare the performance of publicly traded oil and gas companies. The main focus is recoverable (and hence valuable) fluids.
- *Government and industry reporting (Norway, Former Soviet Union, China):* In this case, the focus of the agencies is the future energy availability for each country. Apart from recoverable fluids, the probability of geological-based success is also considered, in some cases for large geographical areas not limited to countries [U.S. Geological Survey (USGS)].
- *Technical standards [Society of Petroleum Engineers (SPE), United Nations Framework Classification (UNFC)]:* These are independent standards presented to promote international consistency in total resource assessment processes and terminology. Although SPE classification applies to oil and gas, UNFC extends to other energy minerals.

There have been many efforts to achieve a harmonized classification, pointing out the benefits of providing a single definition for the different stakeholders [27]. Some of the most important technical associations related to oil and gas, the SPE, the World Petroleum Council (WPC), the American Association of Petroleum Geologists (AAPG) and the Society of Petroleum Evaluation Engineers (SPEE), proposed in 2007 a unified guideline on resource definition and classification called the Petroleum Resources Management System (PRMS) [28].

This system classifies resources and reserves according to the level of uncertainty about the volume of recoverable fluids and the probability to exploit them economically (Figure 3.19). The first classification attends to the reservoir discovery, defining resources as "prospective" if undiscovered but with different degrees of geological probability of existence. Discovered resources are classified as "contingent" (noncommercial) or "reserves" if the economic and technical evaluation declares the resources commercial with current technologies. Contingent resources and reserves present different degrees of probability. In the latter, the common definition of "proven," "probable," and "possible" stands for discovered hydrocarbons for which there are 90 %, 50 %, and 10 % probability, respectively, that they can be extracted profitably with the field development assumptions. The common notation of reserves as 1P, 2P, and 3P is related to the degree of probability used in the definition. Proven reserves information will be used through the statistics in this chapter except when indicated.

These classifications allow for homogeneity in the definition and classification, but they do not affect the measurement, which, in practice, will depend on each country's legislation. It must be noted that there are two key issues significantly affecting the estimation of reserves in each category: technology and price. Over the time, continuous developments have made possible the transformation of prospective resources into contingent resources through the improvement in exploration technologies, whereas production technologies allow for converting resources into reserves. At the same time, the oil price fluctuations may move resources to reserves with price increases, or the opposite when there is a price drop, like the situation created during the recent world economic crisis.

The differences in the basis used of the definition and the factors affecting the classification have created confusion over how much oil will be available for commercial production in the long term, and they probably represent one of the reasons that over the previous decades oil reserves have been repeatedly quoted as being sufficient to satisfy future energy demand.

Another classification commonly used, following a different approach, divides resources into conventional and unconventional. These terms are in wide usage, but they lack a standard definition, adding additional deterministic criteria to the proved reserves. SPE established the limits between the two categories according to parameters such as localized or continuous-type deposits, hydrodynamic influences, specialized extraction technologies, or surface processing before sale, as shown in Figure 3.20. Tight and shale gas, coal-bed methane (CBM), and natural gas hydrates (NGH) are commonly referred to as unconventional gases, whereas heavy and extra-heavy oil, bitumen, and oil shale are the corresponding unconventional oils.

3.3.2 Crude-Oil Reserves

3.3.2.1 CONVENTIONAL CRUDE OIL

According to EIA [13] total proven world oil reserves as of January 1, 2009 were 1342 billion bbl, with a geographical distribution in various parts of the world as shown in Figure 3.21. This is somewhat greater than the 1258 billion bbl in 2008 that were given in Table 3.1, maintaining the trend observed during the last decades. During the period of 1980–2008, shown in Figure 3.22, global proven oil reserves have presented a continuous yearly increase as a result of successful prospection activities and production technology developments [4,11]. Although in most regions proven reserves increased, in some areas the growth has not been relevant (Asia-Pacific) or reserves have even

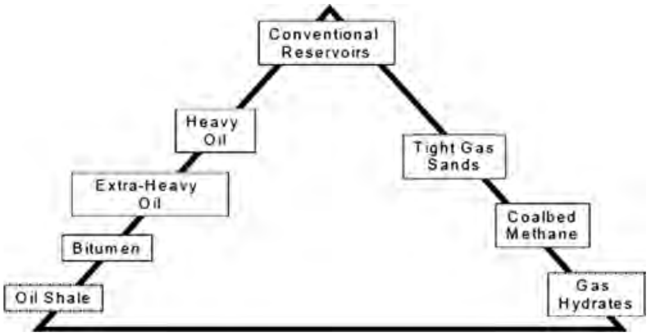


Figure 3.20—Conventional vs. unconventional hydrocarbons according to Society of Petroleum Engineers [26].

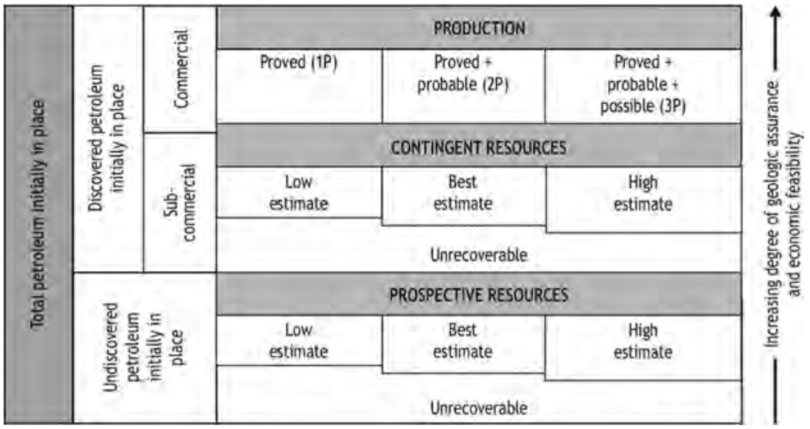


Figure 3.19—Hydrocarbon resource classification [26,28].

decreased (North America). Six countries (Saudi Arabia, Iraq, Kuwait, United Arab Emirates, Iran, and Venezuela) control most world crude oil, accounting for two thirds of proven reserves. Changes in oil reserves from 1980 to 2008 in different geographical areas are shown in Figure 3.23, A and B, detailing the distribution and most relevant variations in countries covering most reserves.

- *Middle East:* The region had the greatest increase of proven reserves in the analyzed period and accounted for 60 % of world reserves in 2008. Although new oil reserves continue to be discovered all over the world, most forecasts indicate that dependence on Middle Eastern oil will increase in the coming years with the decline of other basins. All of the countries have increased their reserves in the last decades, with Saudi Arabia accounting for more than one third of the region reserves.
- *North America:* North America is the second area in proven reserves, and the only area with a net reserves reduction in the last decades. The contribution to world reserves fell from approximately 15 % in 1980 to approximately 6 % in 2008. Most of this reduction is related to Mexican challenges in reserves replacement because of the decline the country is facing in several giant fields despite increased exploration efforts. Inclusion of unconventional oil may significantly increase oil reserves in regions such as Canada.

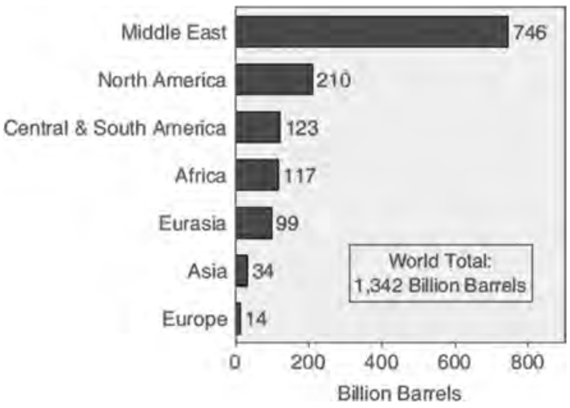


Figure 3.21—World proven oil reserves geographical distribution (January 1, 2009) [13].

- *South and Central America:* These areas have largely increased their reserves from 1980, most of them coming from Venezuela, which increased their proven reserves 5 times in that period. In 2008 the region accounted for approximately 10 % of world reserves, with increasing impact of the new deepwater reservoirs in Brazil.
- *Europe and Eurasia:* The change in reserves from the former Soviet Union to the new political distribution makes it difficult to compare data from the period before 1998. However, as a summary, most of the reserves growth in the area is from the Russian Federation and Kazakhstan, whereas most European fields, especially in the North Sea, are facing a significant decline. In 2008, the area accounted for approximately 11 % of world reserves, without significant change during the last years.
- *Africa:* The development of North and West Africa in the late 1990s and during this decade has produced a continuous increase in proven reserves that allow Africa to maintain its average 10 % contribution to world reserves. Libya, Nigeria, and Angola accounted for the main increase in reserves during this period.
- *Asia-Pacific:* The contribution of this area to the world reserves is minor (~3 % in 2008) and has not changed significantly in the last decades. The decline of Indonesian fields has been replaced by new reserves in different countries without discoveries with a major impact in the area reserves.

The data used to build previous charts and analysis correspond to proven reserves [4]. There are significant differences in estimates from existing resources that could be moved to reserves through adequate oil price and technology availability. As a reference, Lakatos [17] estimated with data from USGS world proven reserves to be approximately 170 Gt, with another 155 Gt in predicted resources, for a total crude-oil reserves estimation of 325 Gt.

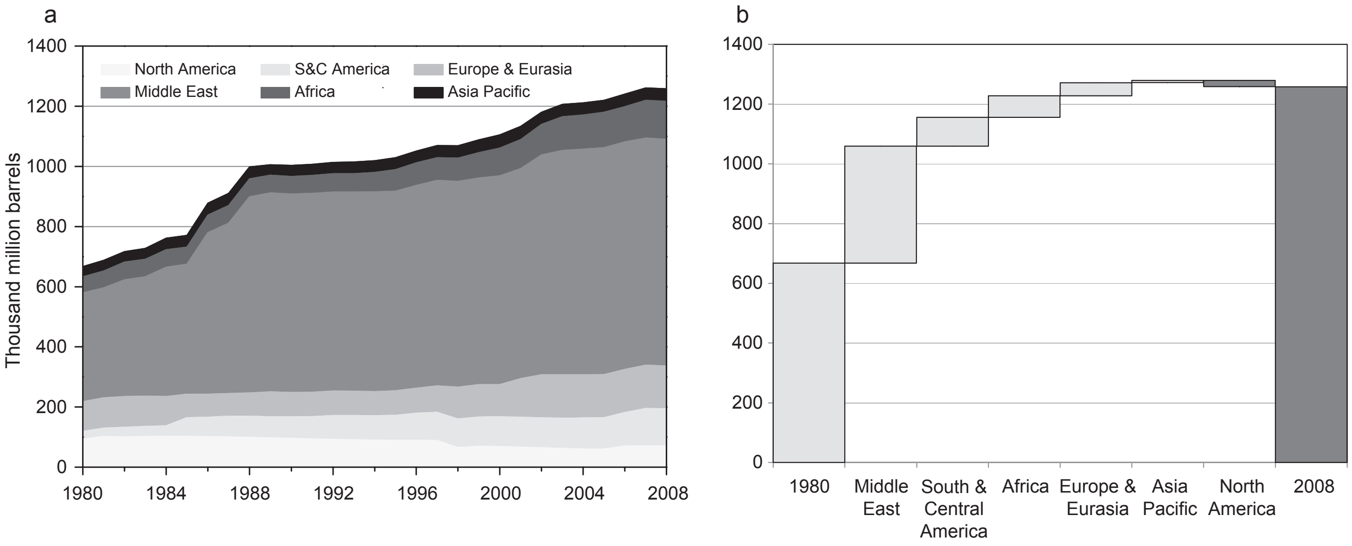
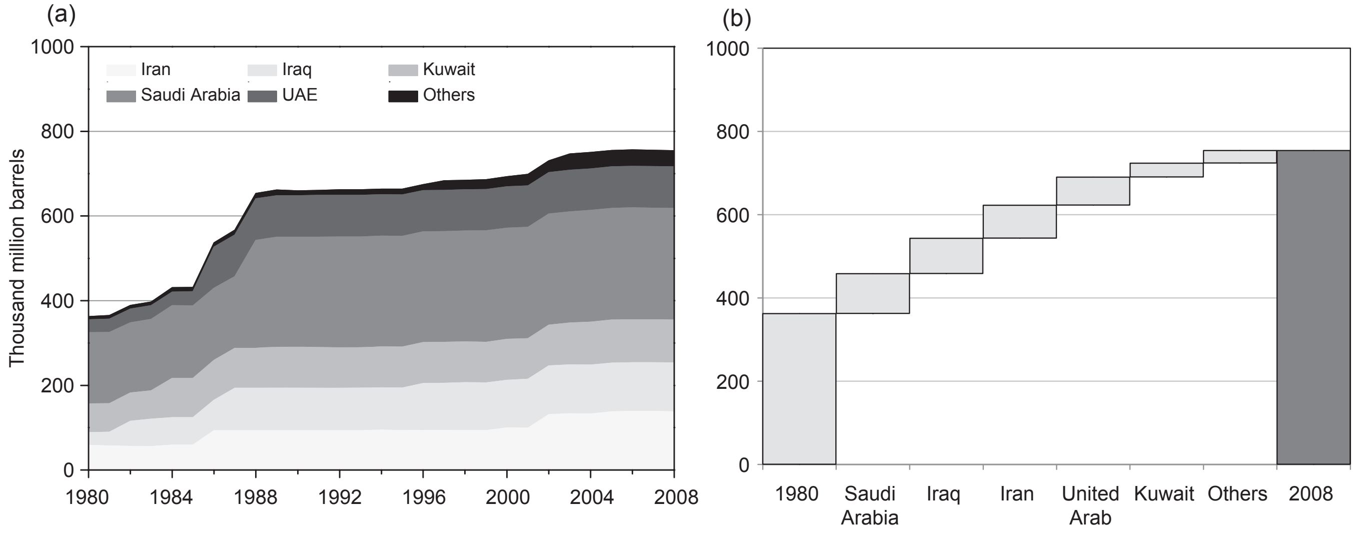
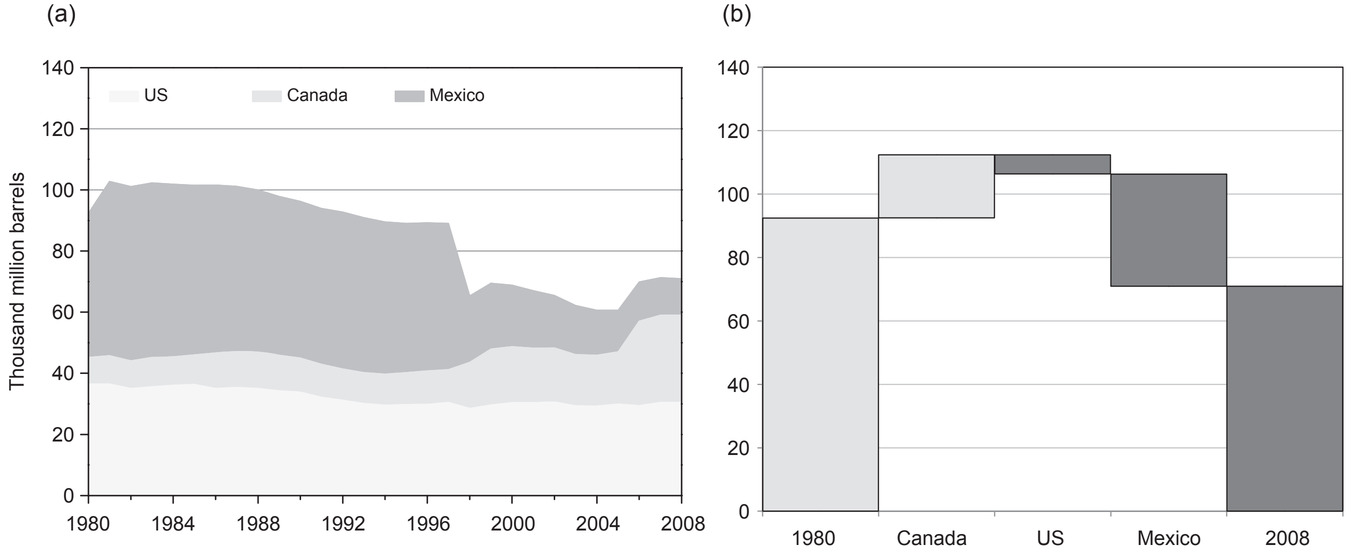


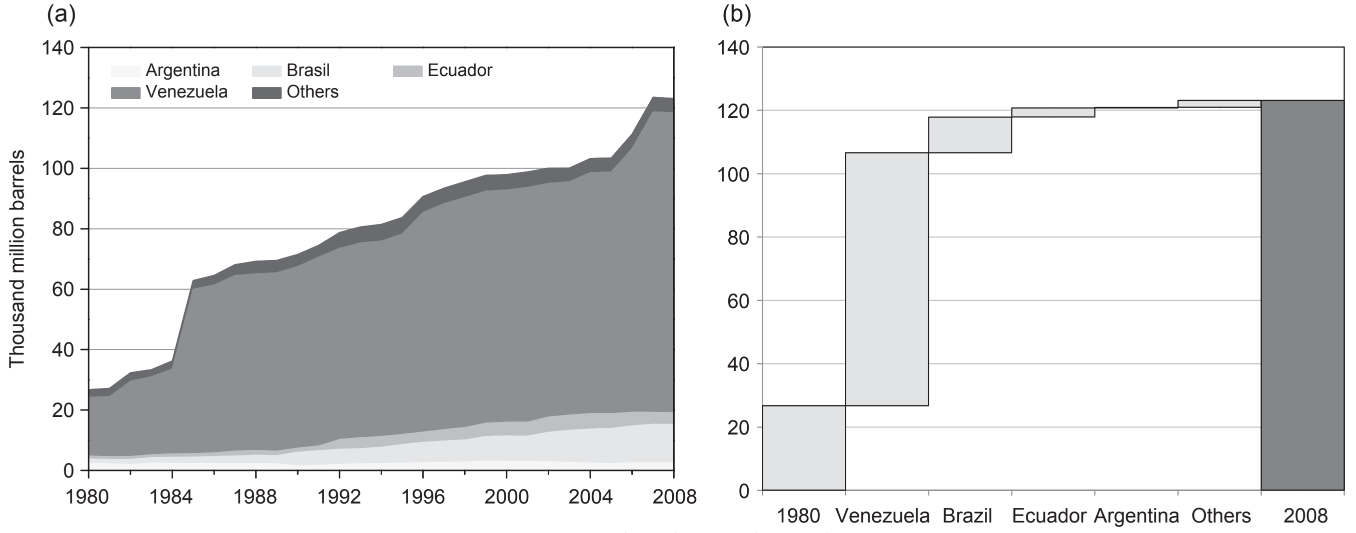
Figure 3.22—World conventional oil reserves (a) evolution and (b) changes 1980–2008 [4].



Middle East

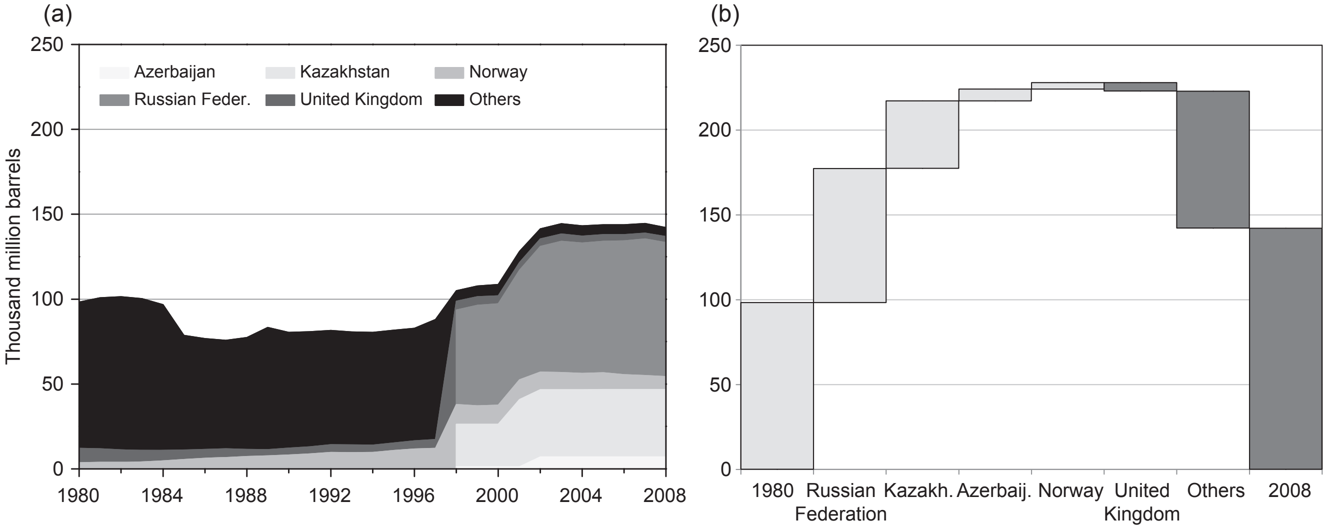


North America

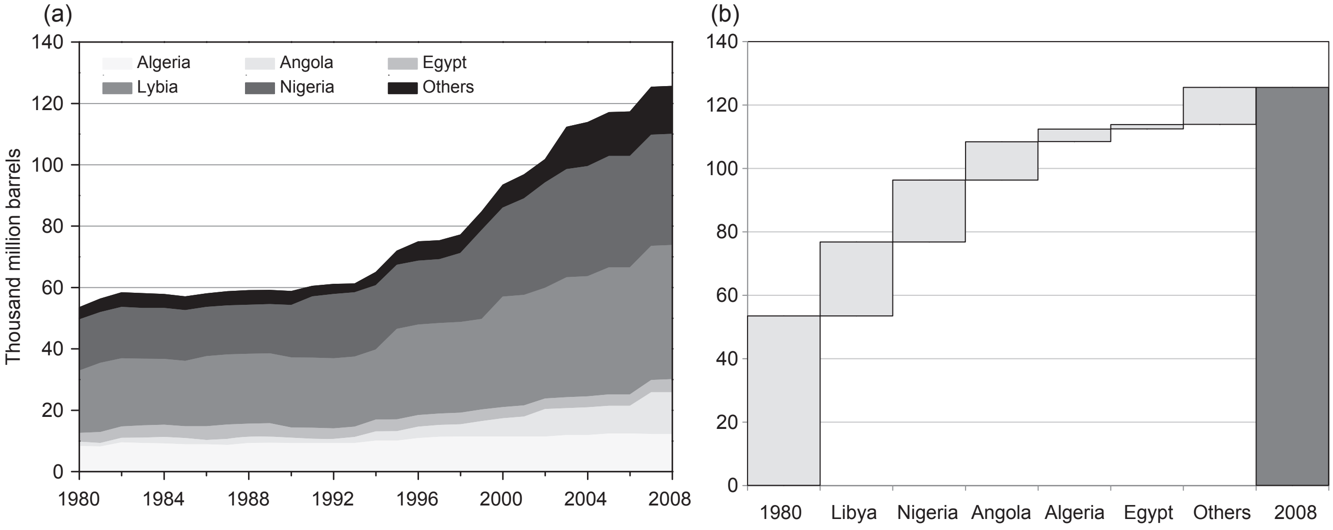


South and Central America

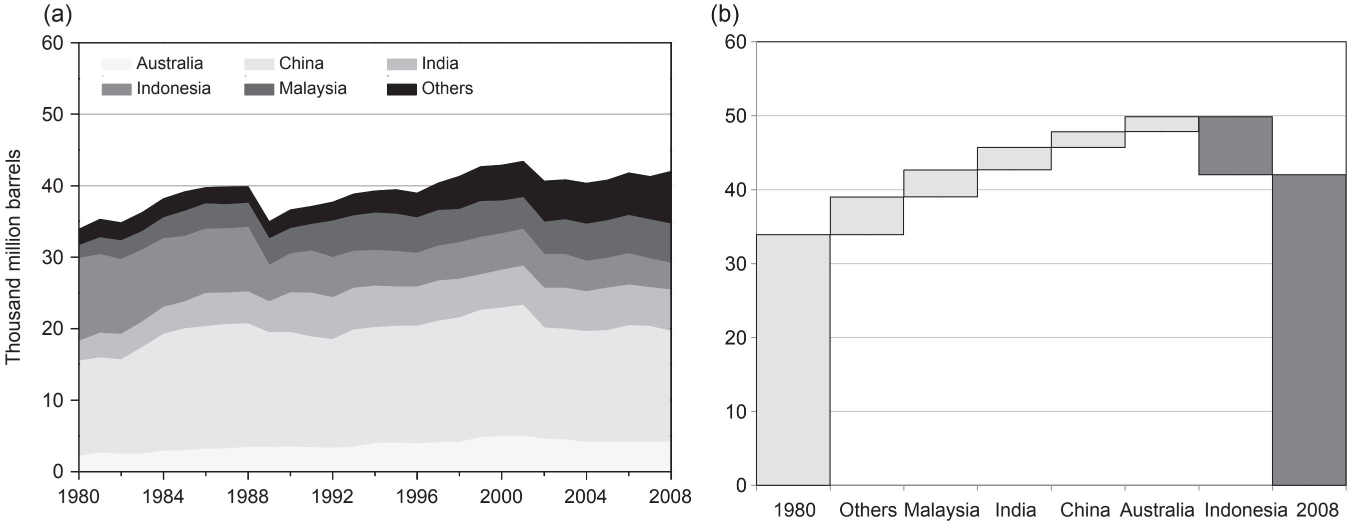
Figure 3.23A—Regional conventional oil reserves (a) evolution and (b) changes 1980–2008 [4].



Europe and Eurasia



Africa



Asia-Pacific

Figure 3.23B—Regional conventional oil reserves (a) evolution and (b) changes 1980–2008 [4].

3.3.2.2 UNCONVENTIONAL CRUDE OIL

Fast depletion of conventional oil and the increase in oil price provides an opportunity for other available sources of energy such as heavy oils, bitumen, and tar sands, usually known as unconventional oils. As shown in Figure 3.1, heavy oil is very viscous, with viscosity ranges from 10 to 10,000 cP. This makes it difficult to flow, avoiding conventional oil production in some places through conventional methods, and with recovery factors for heavy-oil reserves less than 10 %. Heavy oils have an API gravity less than 20 and are deficient in hydrogen, having higher aromatic hydrocarbon, sulfur, and heavy metal content, which increases the processing cost as compared with conventional and lighter oils.

Distribution of heavy oil throughout the world is shown in Figure 3.24. IEA estimates that there are approximately 6 trillion bbl in place worldwide, from which 2.5 billion bbl are in Canada, 1.5 billion bbl in Venezuela, 1.0 billion bbl in the Russian Federation, and 0.1–0.2 billion bbl in the United States [29,30]. Other sources propose alternative data: If extra-heavy oil and bitumen are also considered in this estimate, then the total oil reserves are more than 10 trillions bbl. Total amount of proven conventional oil reserves is more than 1.3 trillion bbl. Distribution of conventional versus unconventional oil around the world is shown in Figure 3.25 [31]. More detailed distribution of heavy oil and bitumen in different regions and the world is shown in Figure 3.26**.** Although in the Middle East most proven oil reserves are conventional oil, which can be produced with conventional methods, in Canada most oil reserves are unconventional and bitumen type, which may be produced with techniques yet to be developed with higher oil price.

Canada's oil reserves are located in the province of Alberta, and the oil production in Alberta is currently approximately 1 million bbl/day, but this production will increase in the future. In addition, Alberta has large oil sand reserves that can hold billions of barrels of oil. Alberta's internationally recognized oil reserves now stand at 175 billions bbl of oil. This is the world's second-largest crude reserve after Saudi Arabia's oil reserves. However, the cost of oil production from oil sand is high because the process of separating oil from the sand is energy- and labor-intensive and as such it has been cost-effective when global oil prices have been high. Analyses estimate world oil prices need to be more than \$80/bbl for the Canadian oil sands to be economically viable [32]. Canada's reserves are mainly bitumen (~400 billion m^3), whereas Venezuela' reserves are mainly heavy oil (~230 billion m^3). Iraq and Kuwait each have heavy-oil reserves of approximately 30 billion m^3 each. The United States and Nigeria also have bitumen reserves of approximately 20 billion m^3 each according to Schlumberger [33]. In addition to these heavy oils, more discoveries are being made for conventional oils from countries that have not been known for their oil reserves. The best example of this group of countries is Angola in Africa, with reserves now standing at 20 billion bbl of oil. Most recently, some new giant oil fields have been discovered in Saudi Arabia, Iraq, and Iran. Proven Middle Eastern oil reserves in 1980 were approximately 360 billion bbl and in 2007 reached approximately 730 billion bbl, an increase of more than 100 % in 27 years.

Figure 3.24—Distribution of heavy oil in the world [29].

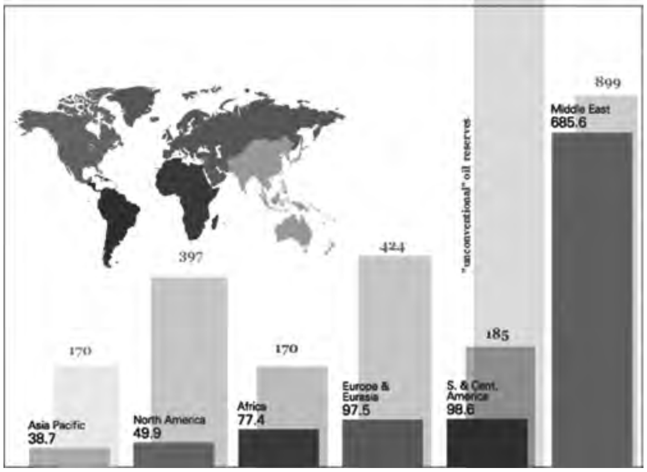


Figure 3.25—Conventional and unconventional oil reserves: Numbers are in billions of barrels [31].

Figure 3.27 represents unconventional oil resources and production cost compared with other energy sources [34]. Despite technology efforts, unconventional oil production needs significantly higher crude-oil prices to make this energy source more economic [35]. Carbon emissions and water requirements present additional challenges compared with conventional oil production, which can make required oil prices even higher for heavy-oil exploitation to become feasible.

3.3.3 *Natural Gas Reserves*

3.3.3.1 CONVENTIONAL GAS

Distribution of natural gas reserves in different regions and the world according to EIA [13] is shown in Figure 3.28. From these data, the estimated world total conventional gas reserves is 6254 trillion ft^3, compared with the data published by BP [4] of 6534 trillion ft^3 referenced in Table 3.1. Natural gas reserves are widely distributed around the world in association with petroleum or as dry gas. During the period of 1980–2008, shown in Figure 3.29, global proven natural gas reserves have doubled, with trends similar to those observed in crude-oil reserve evolution. By far most proven reserves of natural gas are located in three countries—Iran, Qatar, and the Russian Federation—accounting for more than half of the world's reserves. Changes in gas reserves from 1980 to 2008 in different geographical areas are shown in Figure 3.30, A and B, which

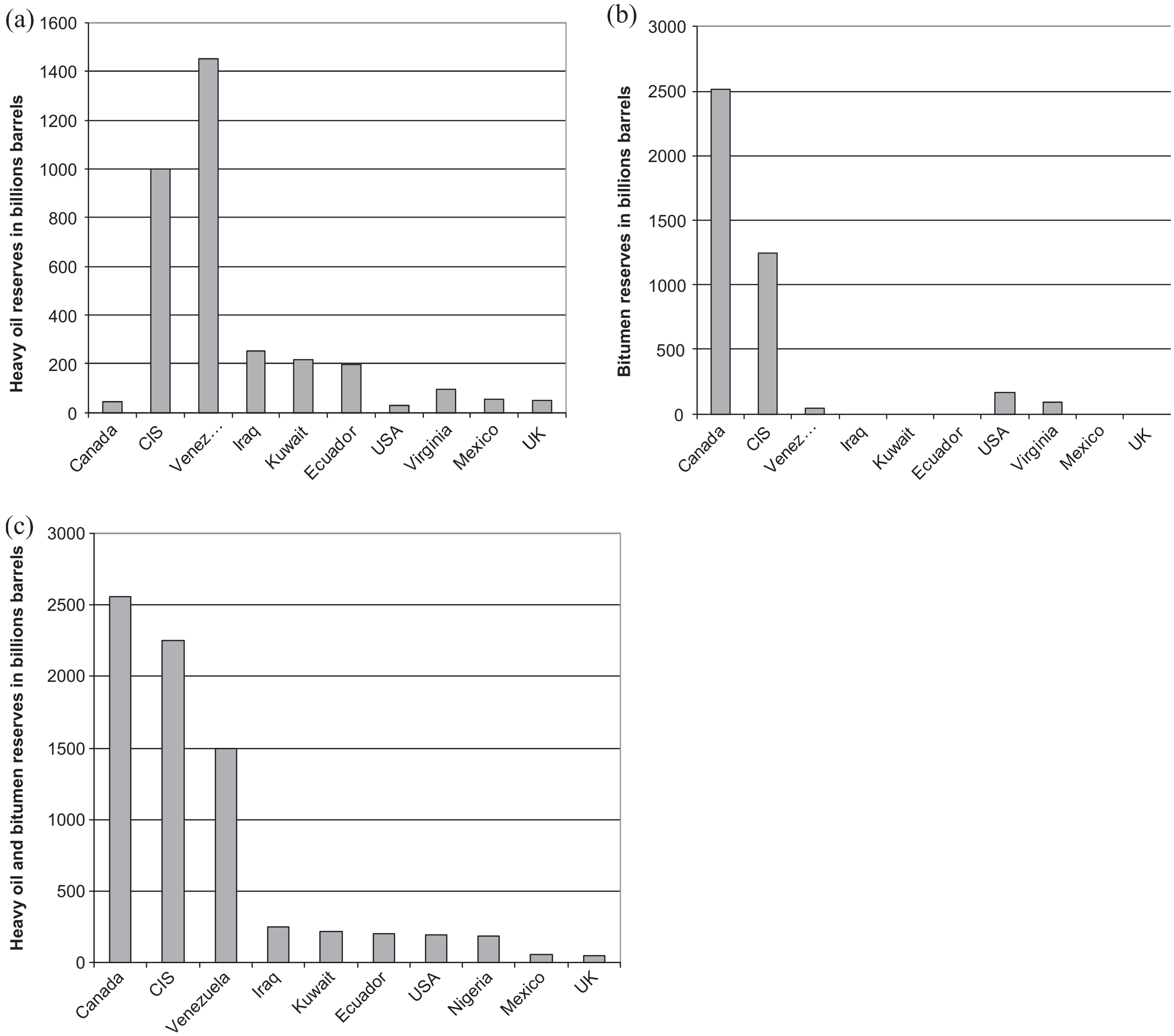


Figure 3.26—Global distribution of heavy oil and bitumen: (a) heavy oil, (b) bitumen, (c) heavy oil and bitumen total. CIS (Commonwealth of Independent States) refers to all countries of Former Soviet Union (USSR) except Baltic states and its headquarter is in Minsk.

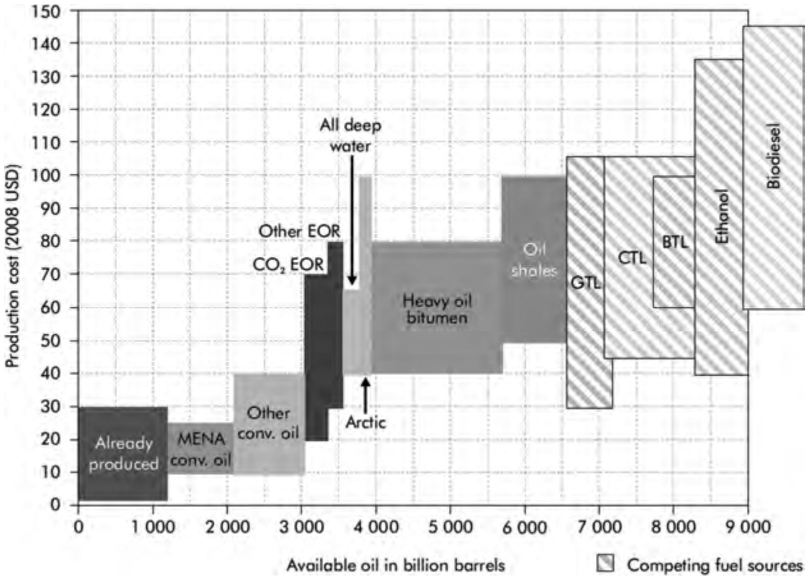


Figure 3.27—Resources/production curve of heavy oils compared with other energy sources [34].

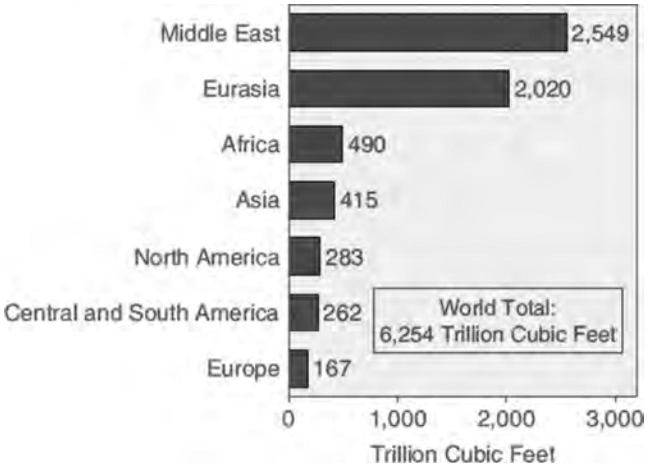


Figure 3.28—World natural gas reserves by geographic region (January 1, 2009) according to EIA [13].

details the distribution and most relevant variations in the main producing countries.

- *Middle East:* The Middle East also holds the largest world natural gas reserves, having increased proven reserves approximately 4 times and accounting in 2008 for approximately 40 % of world reserves. All Middle Eastern countries have increased their reserves in the last decades, especially Qatar and Iran.
- *North America:* North America is one of the areas with less proven natural gas reserves (<5 %) and is the only area with a net reserves reduction in the period. Canada and Mexico are responsible for this decline, with a minor increase in U.S. proven reserves. However, the contribution of the United States to unconventional gas reserves, especially shale gas, is significant.
- *South and Central America:* South and Central America have largely increased their reserves from 1980, with most coming from Venezuela, which increased its proven reserves approximately 4 times in that period, as well as the new Bolivian reserves. The global contribution to gas reserves is minor in the rest of the countries of this area, with a decline in Argentinean reserves.
- *Europe and Eurasia:* As was mentioned with crude-oil data, the period before 1998 is difficult to compare in the former Soviet Union. Most of the reserves are located in the Russian Federation, which accounts for approximately 25 % of world natural gas proven reserves.
- *Africa:* North Africa (Algeria and Libya) possesses most gas reserves in the continent of Africa, although significant increases took place in the last decades in West Africa (Nigeria) and Egypt, maintaining the contribution to world gas reserves at approximately 7 %.
- *Asia-Pacific:* The contribution of this area to the world reserves has increased in the period, with additional reserves in most countries. Indonesia, Australia, China, and Malaysia account for most of the reserves, which correspond to approximately 8 % of world reserves.

The challenge to move resources to reserves in natural gas is likely to come from unconventionals, especially shale gas. However, to transport gas from production to demand centers is a major issue because many of the largest reserves are in remote areas. Russian gas is exported mainly to northern European countries, whereas southern Europe is supplied with Algerian gas. As in the case of oil reserves, the Middle East holds the largest gas reserves in the world, but in this case they are more difficult to move to market.

3.3.3.2 UNCONVENTIONAL GAS

Although natural gas increased its contribution to the energy mix during the last decades, the same did not happen with unconventional gas (shale gas, tight gas, and CBM). Until the last years, the attention in most of the world was still focused on conventional natural gas reserves, with very few cases of unconventional gas development. According to Figure 3.27, to make unconventional gas development economically feasible requires equivalent oil prices to be even higher than unconventional crude oil. However, the recent boost in production levels from shale gas in the United States and the huge potential resources available in different areas are starting to make unconventional gas field development attractive.

Although there is not an agreement among different sources regarding the estimated gas volumes in place, most

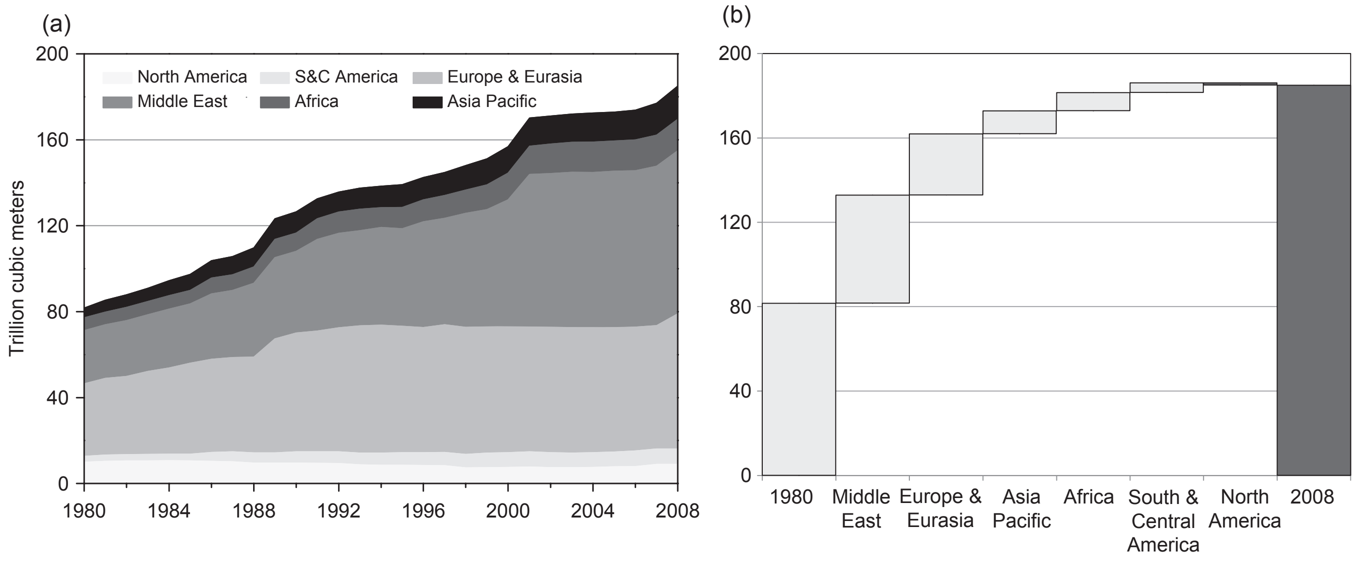
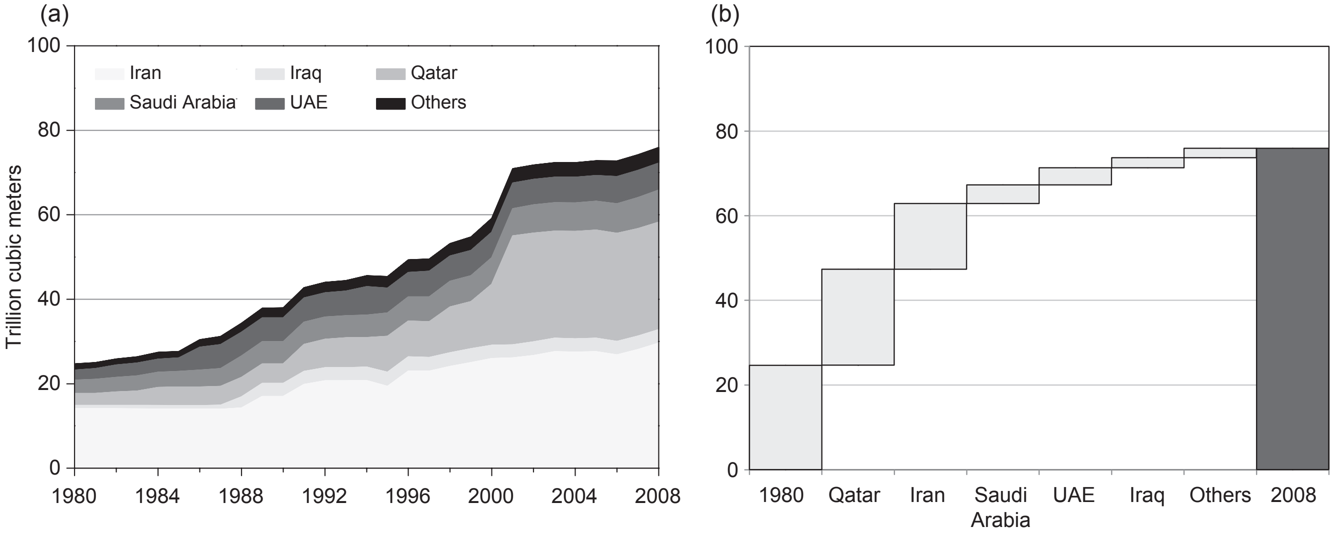
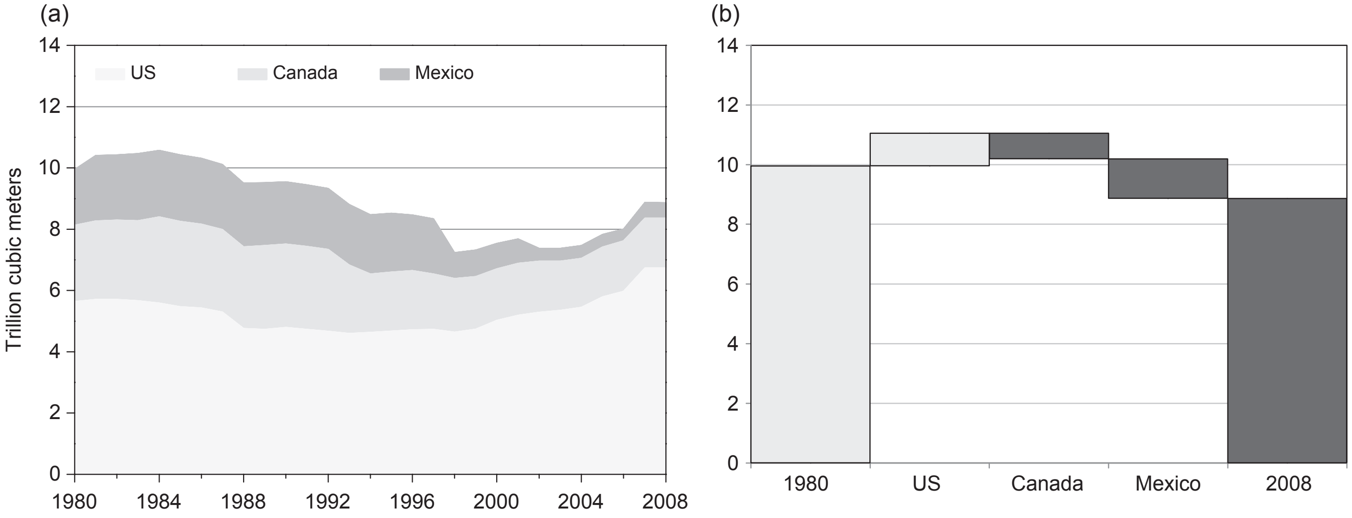


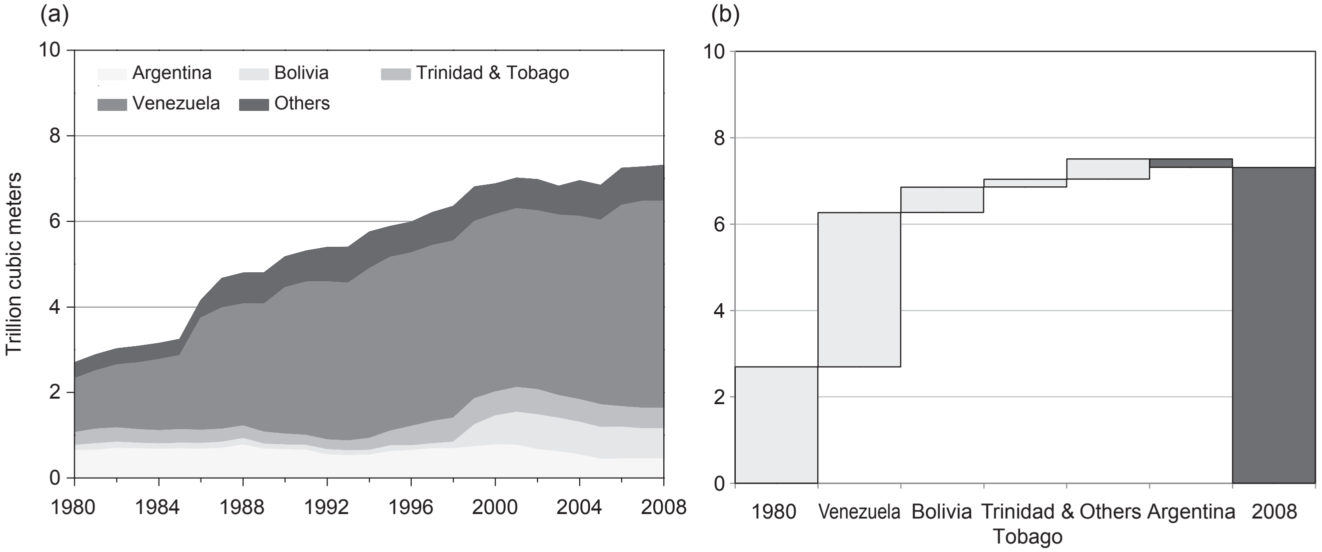
Figure 3.29—World conventional gas reserves (a) evolution and (b) changes 1980–2008 [4].



Middle East

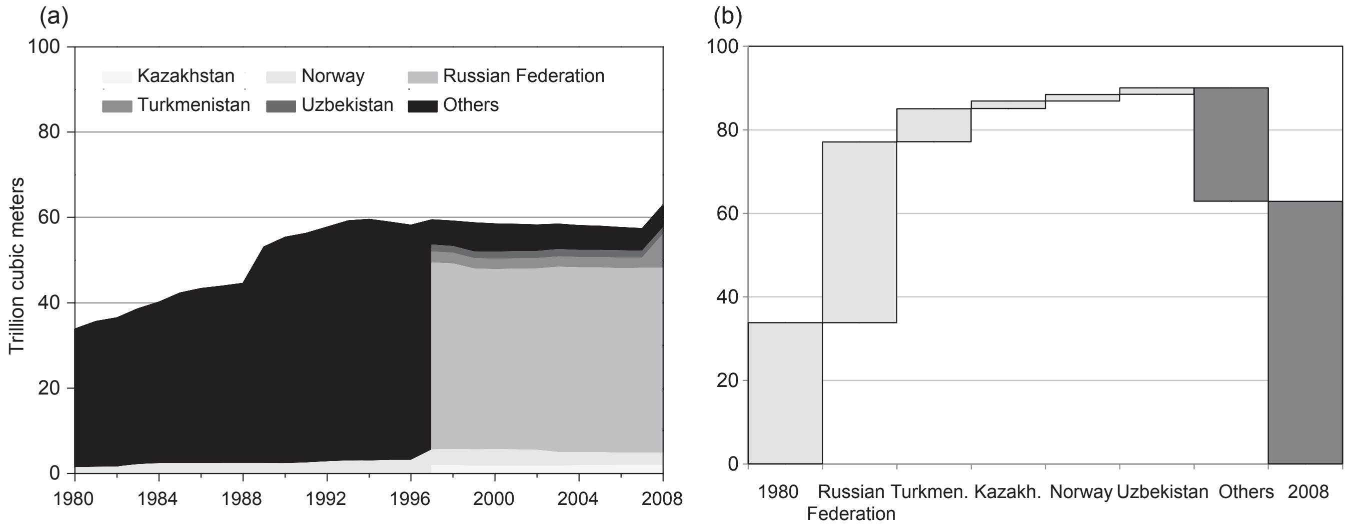


North America

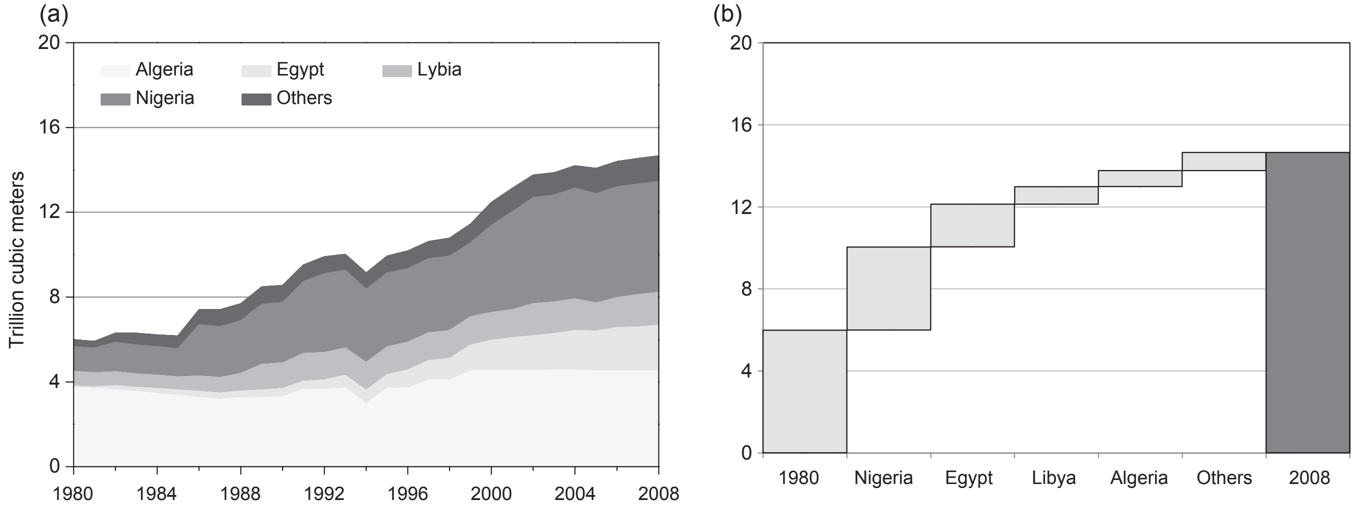


South and Central America

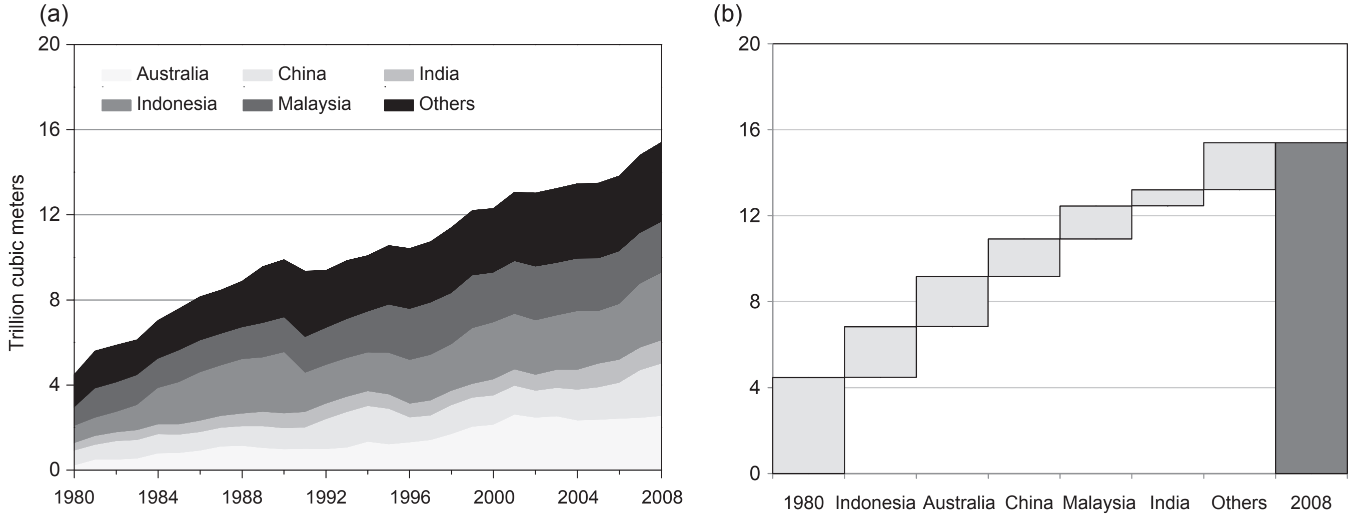
Figure 3.30A—Regional conventional gas reserves (a) evolution and (b) changes 1980–2008 [4].



Europe and Eurasia



Africa



Asia-Pacific

Figure 3.30B—Regional conventional gas reserves (a) evolution and (b) changes 1980–2008 [4].

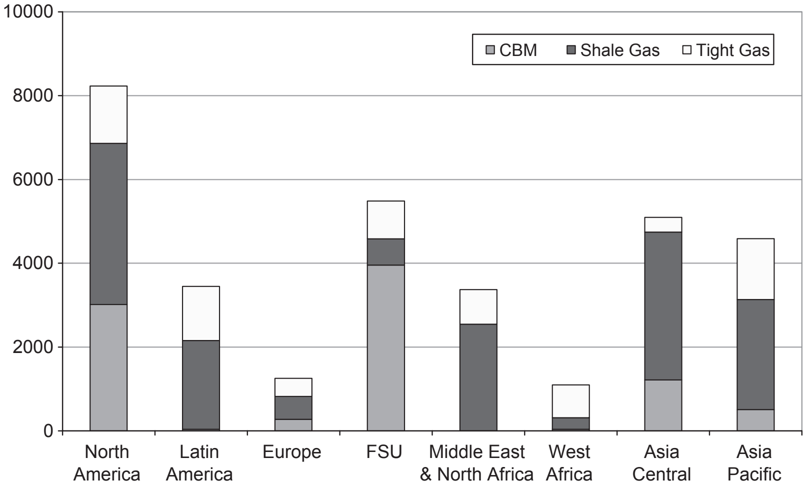


Figure 3.31—Estimated unconventional gas reserves by area [36].

of them agree on the large amount of resources. As a reference [36], a significant number of basins in the world could contain unconventional gas on the order of magnitude of 16,000 trillion ft^3 of shale gas, 7400 trillion ft^3 of tight sand gas, and 9000 trillion ft^3 of CBM. The estimated distribution of these resources by type and geographic area is shown in Figure 3.31. The main contributions would come from North America (>8000 trillion ft^3 between shale gas and CBM), FSU (5500 trillion ft^3, mainly CBM) and Asia Central and Pacific (~5000 trillion ft^3 each, mainly shale gas).

The new approach to unconventional gas started in the United States about a decade ago with small developments in CBM and tight gas. The scenario changed completely with the development of Barnett in the first half of this decade and other main North American gas shales (Haynesville and Marcellus) in recent years [37]. Over the last decade, U.S. shale gas production has almost increased 1 order of magnitude, with 80 billion m^3 of production in 2008, and it is becoming a game changer in North America by significantly reducing requirements for natural gas imports in liquefied natural gas (LNG) form relative to past scenarios.

Other potential sources of natural gas, such as natural gas hydrates (NGHs), are more speculative. Although NGHs have attracted significant attention because estimates indicate potential resources several orders of magnitude larger than present natural gas reserves, significant technical challenges exists to make these resources feasible for exploitation.

3.4 PETROLEUM, NATURAL GAS, COAL, AND BIOFUEL PRODUCTION

In previous parts of this chapter, demand and reserves were discussed; this section deals with production, the third part of the energy equation, through data on oil and gas production and reserves and estimated reserves life in different regions and the world. Most of the presented data, as in previous parts, are taken from the recent data published by EIA [13], IEA [18], and the BP *Statistical Review of World Energy* [4]. The limited flexibility and sensitivity to external factors of the oil market was stated at the beginning of this chapter [15]. Because consumption of oil and gas in a region depends on the availability of alternative sources of energy, production and consumption of coal and biofuels are also presented in this part.

3.4.1 Geographic Distribution and Future Trends

3.4.1.1 CRUDE OIL

Production of crude oil and its projection to 2015 in various regions are presented in Figure 3.32a and for the world in Figure 3.32b [11]. Table 3.5 details the world oil production/consumption balance, showing that excess production relative to internal consumption in the Middle East and Africa covers the deficit in OECD and Asia-Pacific countries. However, relative production rates in some major producers, mainly OPEC countries, are significantly lower than in

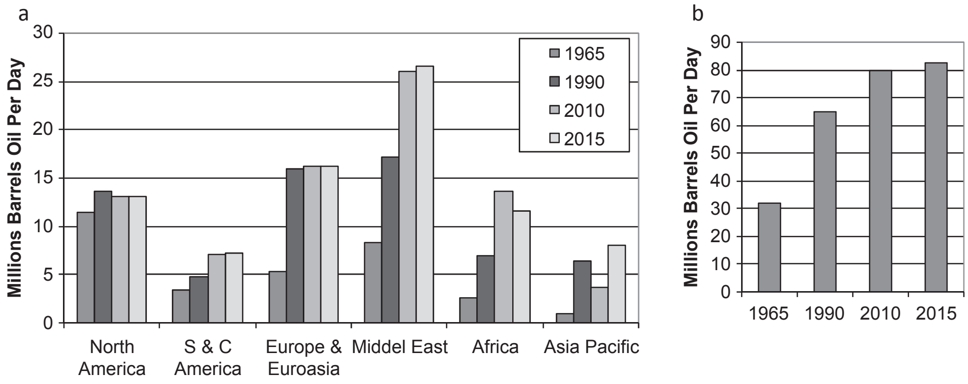


Figure 3.32—Oil production in recent decades and forecast to 2015 (a) by region and (b) in world [11].

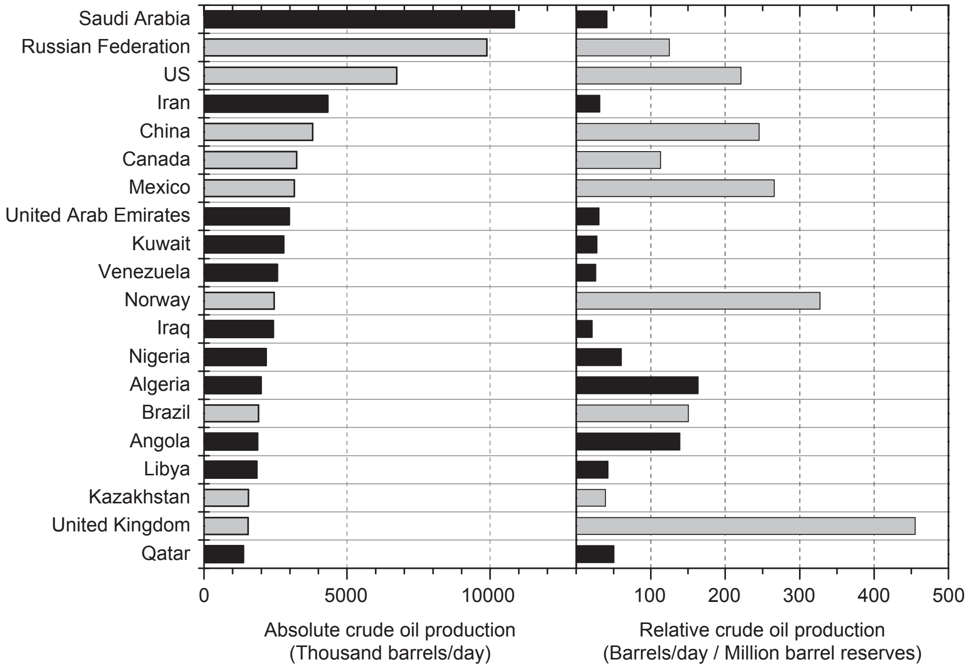


Figure 3.33—Absolute and relative oil production in top 20 producing countries (■ OPEC countries □ non-OPEC countries) [4].

other areas. According to the BP statistical review [4], OPEC countries accounted for 76 % of world oil proven reserves in 2008, whereas in the same period they hardly reached 45 % of world oil production. This difference is shown in Figure 3.33, comparing absolute and relative production rates in the top 20 crude-oil-producing countries. The clear difference between OPEC countries and the rest is probably the result of two main factors: internal compliance with OPEC quotas to stabilize oil prices and less production facilities in some Middle Eastern countries with major oil reserves. This gap will unlikely be sustainable in time because the capability from non-OPEC countries to supply additional oil to the market will be reduced with the depletion of their reserves at a much higher rate than OPEC countries.

Several countries with significant production growth during the last decade depend on high-cost deepwater projects to maintain their increasing production. However, many exploration and development projects that were delayed during the economic crisis, mostly deepwater and heavy-oil projects, are still not economical and wait for sustainable higher oil prices according to Figure 3.27. Some surveys are anticipating challenges to supply the required oil to the market on the basis of the current oil prices scenario, with a probable supply crunch appearing during this decade irrespective of demand level [38].

This risk would be in addition to the warnings received about the world being at a crude-oil production plateau and facing a sharp decline. The debate about this “peak oil” is not new because these widely discussed theories have existed for decades, mainly based on the original Hubbert model forecasts [39]. Most of the studies report peak oil having already occurred during this decade [40], as shown in Figure 3.34. However, these predictions, based on in-depth modeling of every country’s oil production history, are very sensitive to considerations about new discoveries, new technologies, oil prices, and generally any factor allowing moving resources to reserves [41,42]. Recent studies [43] estimate that peak oil was probably July 2008 unless oil prices rise sustainably over $75/bbl. Additional oil price increases would help move more resources to reserves and support enhanced oil recovery (EOR) processes that would significantly delay this peak oil estimate.

3.4.1.2 NATURAL GAS

Major gas producers are in the regions of North America and Eurasia. Russia, Iran, and Qatar combined have 57 % of world natural gas reserves [14]. Production of natural gas and projections to 2030 in various regions and the world are presented in Figure 3.35 [4,17]. Table 3.6 details the world natural gas production/consumption balance, showing that, similar as to what occurs with crude oil, excess production relative to internal consumption in the Middle East and especially Africa covers the deficit in OECD and Asia-Pacific countries. Figure 3.36 compares absolute and relative production rates in the top 20 natural-gas-producing countries, showing trends already observed with crude oil: higher production rates for OECD countries and lower rates for the Middle East. Peak theories also focus on natural gas production, although estimated peak gas is expected to occur with a delay with respect to peak oil according to Figure 3.34.

3.4.1.3 COAL

Consumption of oil and natural gas is related to the consumption of coal in the world. Coal is the second source of energy consumption in the world after oil. The United States and China are the major coal producers and consumers in the world. The major coal-consumer countries in the world and their consumption in 2004 are shown in Figure 3.37 [44]. China consumes more than twice that of the United States because more than 83 % of China’s electricity is produced from coal-burning power plants. According to Germany’s Energy Watch Group [45], coal

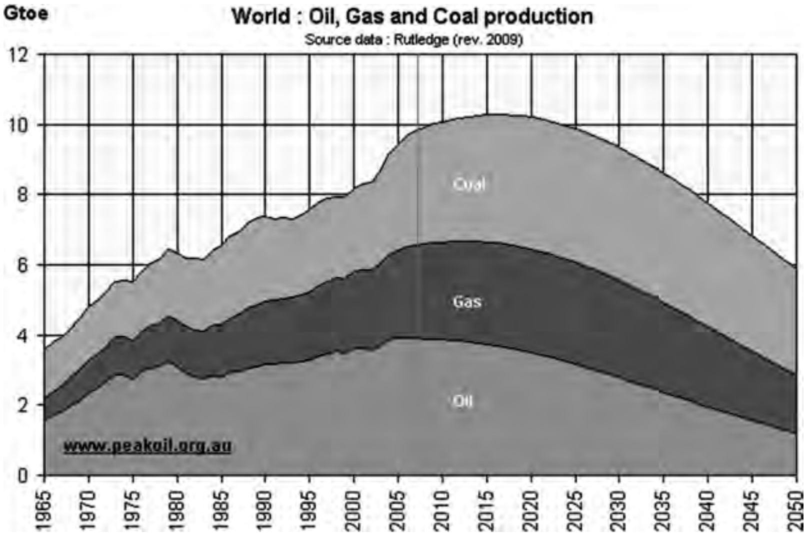


Figure 3.34 —Occurrence of peak oil, gas, and coal [40]. Production rates are in gigatons of oil equivalent (Gtoe). For energy equivalency see Table 3.3.

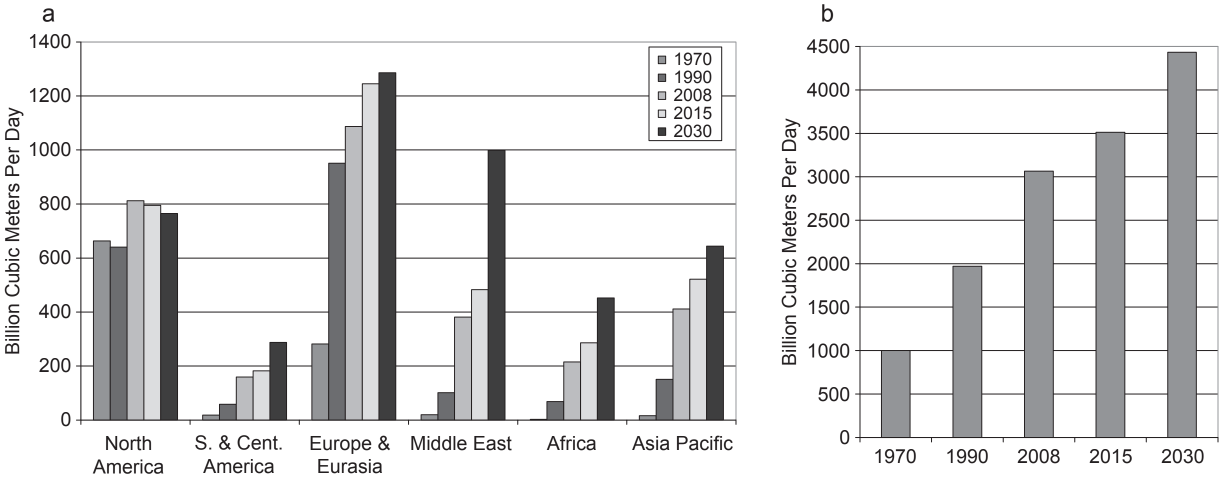


Figure 3.35 —Gas production in recent decades and forecast to 2030 (a) by region and (b) in the world [4,17].

TABLE 3.5—Crude-Oil Production/Consumption Balance in 2008 [4]

Region	Production (10^3 bopd)	Consumption (10^3 bopd)	Oil Balance (Production – Consumption)
North America	13.131	23.753	–10.622
South and Central America	6.685	5.901	784
Europe and Eurasia	17.591	20.158	–2.567
Middle East	26.200	6.423	19.777
Africa	10.285	2.881	7.404
Asia-Pacific	7.928	25.339	–17.411
World (total)	**81.820**	**84.455**	**–2.635**

bopd = barrels of oil per day

production in most producing countries peaks around 2025, as shown in Figure 3.38. A graph of peak oil is shown in Figure 3.34, which shows similar behavior for all three major fossil-type fuels: oil, gas, and coal. Peak oil is followed by peak gas and then peak coal, although these predictions are different from one source to another. Oil reserves are decreasing in many countries, especially in the Asia-Pacific region where consumption of the sources of energy such as coal and gas is increasing. As production of energy from conventional and nonrenewable sources decreases, attempts are being made to produce energy from unconventional oil and renewable energy sources such as biofuel and solar energy [13].

3.4.1.4 BIOFUELS

Biomass is basically organic material made from plants and animals that can be converted to fuels such as ethanol or biodiesel, known as biofuels. Biomass fuels provide 3 % of

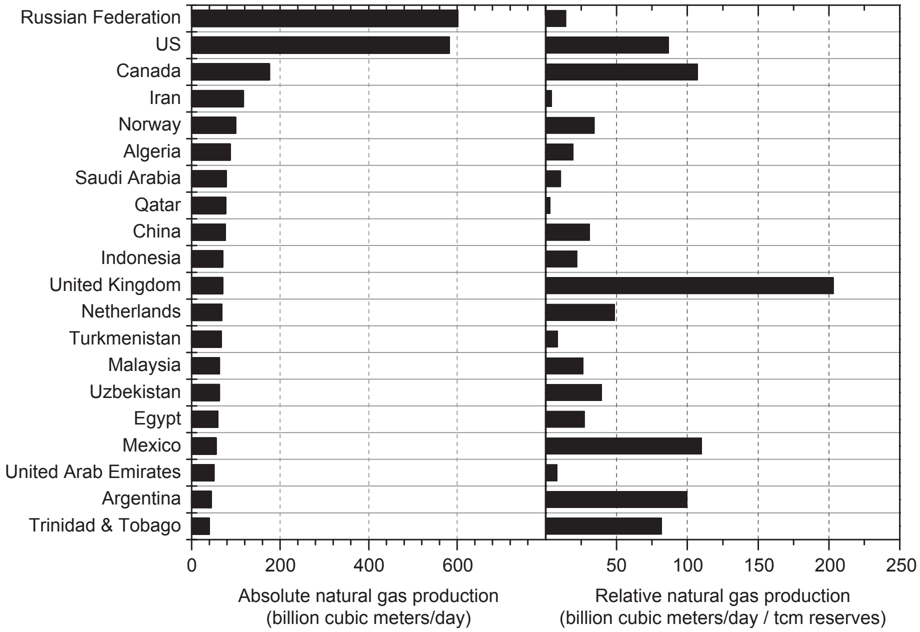


Figure 3.36—Absolute and relative gas production in top 20 producing countries [4].

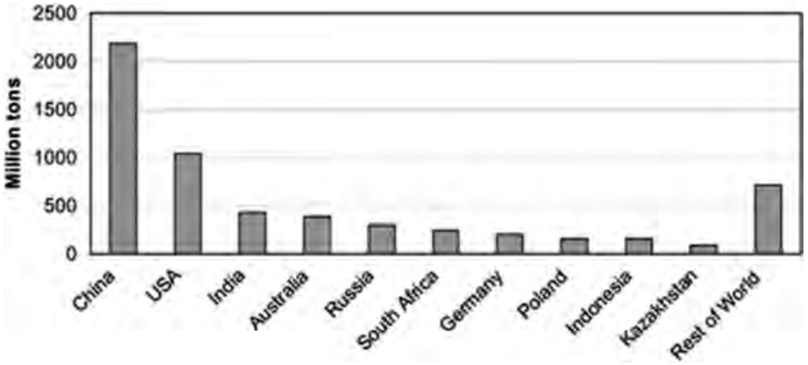


Figure 3.37—Major coal-consuming countries in 2007 [44].

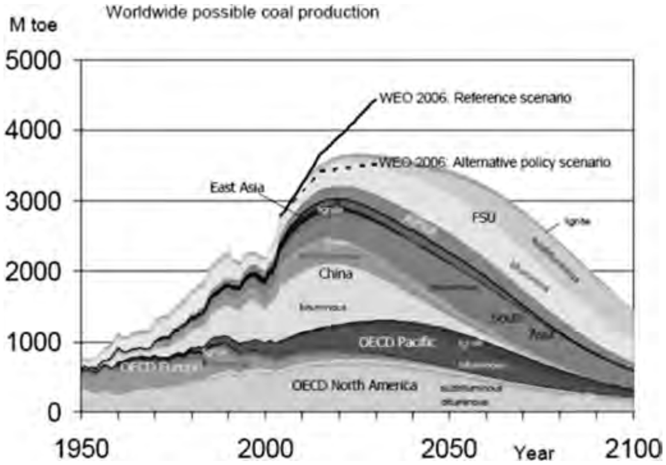


Figure 3.38—World coal production from 1950 and prediction to 2100 [45].

the energy used in the United States and their production is increasing. Biodiesel is one of the fastest growing alternative fuels and can be used in diesel engines. Biomass does not contain sulfur, so when it is burned it does not produce sulfur dioxide (SO_2), a cause of acid rain. However, burning of biomass does produce carbon dioxide (CO_2), a GHG pollutant, but plants use CO_2 in their photosynthesis process.

Different plants produce different amounts of biofuels, as shown below in terms of liters of produced fuel per hectare of required planted land [13,46].

Production of ethanol from different plants:

Plant	Wheat	Corn	Sugar Beet	Sugar Cane
Liters/hectare	2500	3000	5000	6000

Production of biodiesel from different plants:

Plant	Soybeans	Caster Beans	Sunflower Seed	Grape Seed	Jatropha	Palm
Liters/ hectare	600	800	1000	1200	1900	4500

Biofuel production is expected to grow at 8–12 % per year as in 2006 the production rate was 0.86 MBPD (1000 bbl/day), while in 2017 it is expected to be at 2.2–3.0 MBPD. The potential market size is $38 billion/year, or 2.2 million bbl/day

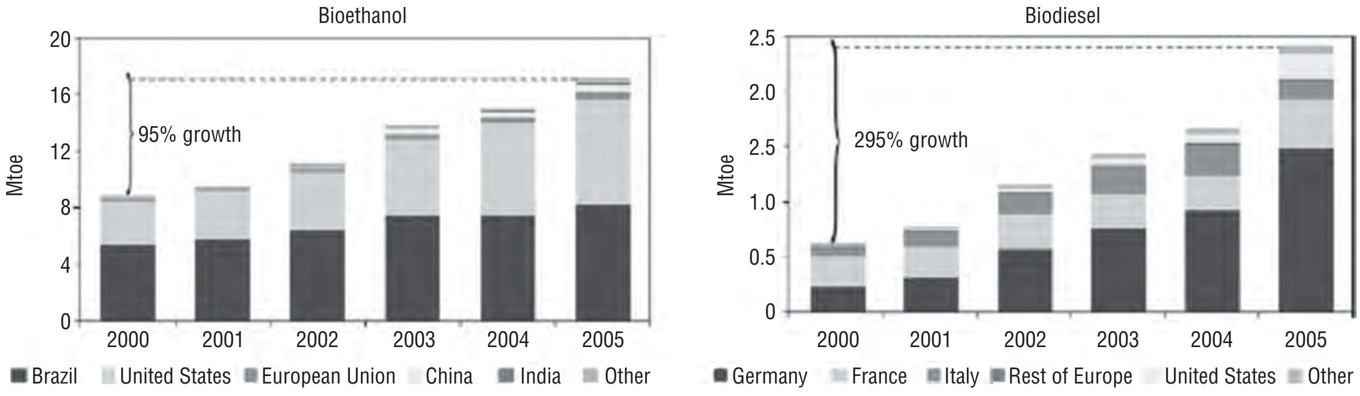


Figure 3.39—Production of bioethanol and biodiesel from 2000 to 2005 in terms of Mtoe [48].

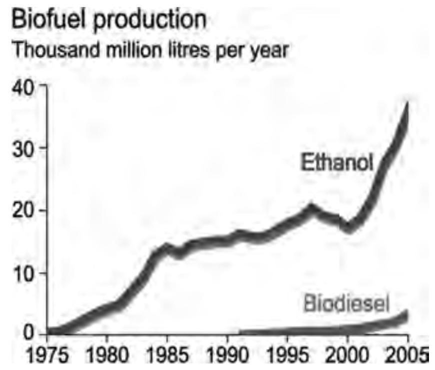


Figure 3.40—Production of bioethanol and biodiesel from 1975 to 2005 [47].

at $50/bbl. Bioethanol is the most common biofuel, accounting for 90 % of total biofuel. Bioethanol can be produced from corn, sugar cane or sugar beets, and potatoes. The world's largest producers of bioethanol are Brazil (from sugar cane) and the United States (from corn). Ethanol is used in low 5–10 % blends with gasoline indicated as E5 and E10, respectively. Figure 3.39 shows the increase in production of bioethanol and biodiesel from 2000 to 2005, which indicates an increase of 95 and 295 %, respectively [47,48]. A similar figure from the U.N. Environment Programme (UNEP) that shows the volumetric annual rate production of bioethanol and biodiesel is presented in Figure 3.40.

The issue of use of biofuel as an alternative energy is controversial because there are some opponents of such energy. For example, in a major cover story article in *Time* magazine, Michael Grunwald argues that politicians who try to substitute oil with biofuel in fact are pushing food prices up and making global warming worse [46]. He argues that all processes in the manufacture of bioethanol are net carbon emitters except those produced from sugar cane. He estimated that the size of the biofuel industry in 2010 would be approximately $100 billion. The state of Iowa produces one third of U.S. ethanol, and in 2007 it produced 7.5 billion L of bioethanol. Brazil is hailed as the global biofuel success and it produced 19 billion L of sugar cane ethanol and supplied 45 % of its transportation fuel in 2007. The United States leads the world in soybean and corn production, and if 100 % of these were converted into fuel, it would provide only 20 % of road vehicle fuels as argued by Grunwald.

3.4.2 Reserves/Production Ratios for Geographical Distribution

The reserves-to-production ratio (R/P) is one of the most widely used parameters when forecasting reserves life. Its simplicity and possibility to be easily determined from limited data available in open literature make it one of the most popular parameters for this type of study. Although this ratio will be used in this section to compare data from different parts of the world, it should be pointed out that these comparisons must be taken with caution and analyzed under proper interpretation. The lifetime of a reservoir determined from this ratio is determined in a certain moment from the ratio of the amount of hydrocarbon remaining in the reservoir to the yearly production rate. Because both parameters (the amount of hydrocarbon in the reservoir and the production rate) change during the field development cycle, these values are expected also to change. The type of reservoir may significantly affect the R/P: highly permeable reservoirs may produce an annual rate of even 15 % of the reserves, whereas low permeability reservoirs cannot provide more than 1–2 % [49]. The ultimate recovery factor may also vary significantly from one reservoir to another depending on parameters such as aquifer support or the presence of water-flooding or EOR processes. On the other hand, production rate depends on the number of wells defined in the field development plan, which may be very different from one field to another or even during the development of the same field.

Even with these limitations, and with the objective of comparison with other published information, the R/P parameter will be used in this chapter. Data presented in this section show the lifetime of oil and gas reservoirs in various regions on the basis of the specified date for the production rate. On the basis of production rate in 2008, the calculated lifetime of conventional oil in the top 20 producing countries are shown in Figure 3.41a. As shown in this figure, the average lifetime of oil reservoirs in OPEC countries, especially the Middle East and Venezuela, are among the highest, as mentioned in the section on production. It is important to mention that these data are calculated on the basis of conventional oil. If unconventional oil reserves are considered, lifetimes in countries such as Canada, Venezuela, or the Russian Federation would greatly exceed what is shown in the figure.

Lifetime of conventional gas reserves in the top 20 producing countries on the basis of 2008 production rates are

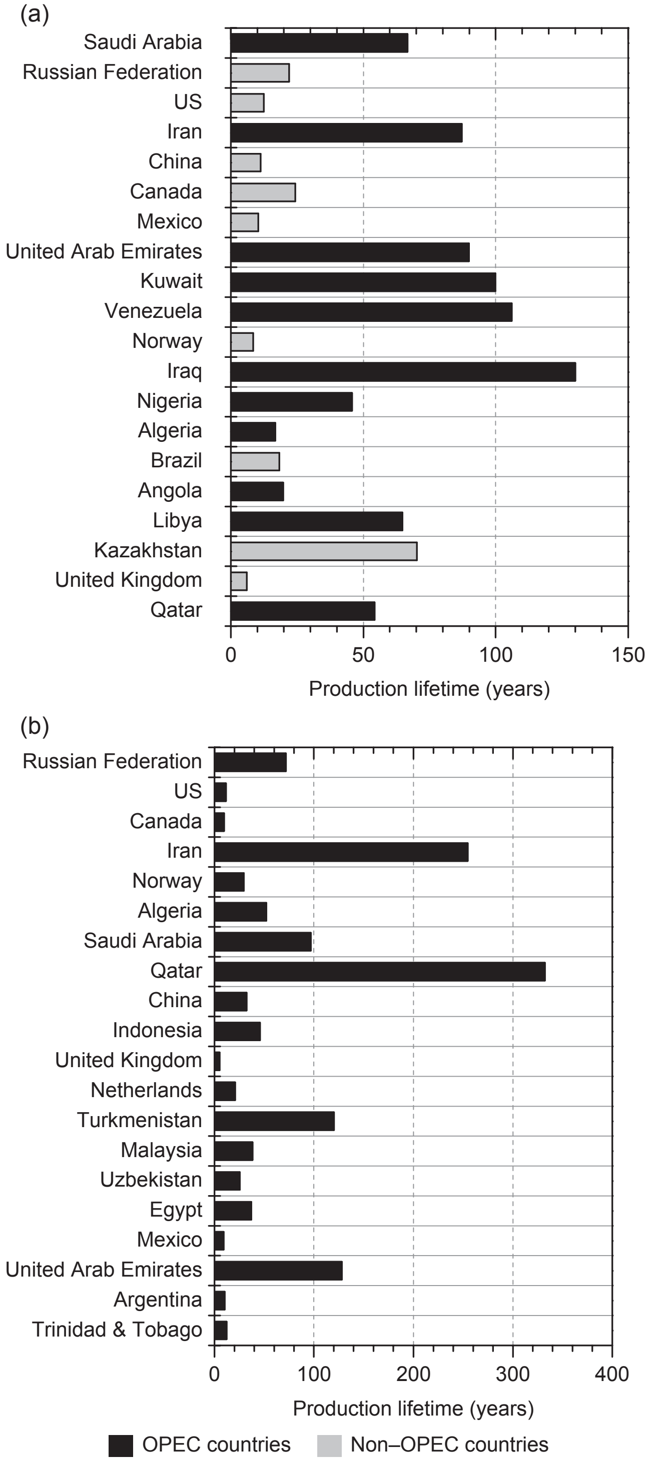


Figure 3.41—Estimated average production lifetime for (a) conventional oil and (b) natural gas for top 20 producing countries (2008) [4].

TABLE 3.6—Natural Gas Production/ Consumption Balance in 2008 [4]

Region	Production (bcm pd)	Consumption (bcm pd)	Gas Balance (Production – Consumption)
North America	812	824	–12
South and Central America	159	143	16
Europe and Eurasia	1.087	1.144	–57
Middle East	381	327	54
Africa	215	95	120
Asia-Pacific	411	485	–74
World (total)	**3.065**	**3.018**	**47**

bcm pd = billion cubic meters per day

TABLE 3.7—Crude Oil and Natural Gas Proven Reserves Average Lifetime Based on 2008 Data [4]

Region	Crude-Oil Reserves Lifetime (years)	Natural Gas Reserves Lifetime (years)
North America	14.8	10.9
South and Central America	50.5	46.0
Europe and Eurasia	22.2	57.8
Middle East	78.9	199.2
Africa	33.5	68.2
Asia-Pacific	14.5	37.4
World (total)	**42.1**	**60.4**

shown in Figure 3.41b. Qatar and Iran have the longest natural gas lifetime. Table 3.7 compares the average lifetime for crude oil and gas proven reserves, confirming that for gas the expected lifetime is longer than for crude oil (60 vs. 42 years).

However, these estimations must be handled with caution. Figure 3.42 shows the change in the average lifetime for crude oil and gas reserves during the last decades. In the case of crude oil, the value has remained almost constant in the range of 40–45 years since the mid-1980s, whereas in the case of natural gas the variations have been similar in the range of 60–70 years, with the exception of a decline in the first part of this decade. The explanation of this phenomenon is related to the definition of the R/P parameter in itself relative to proven reserves. Any movement of resources to reserves (new discoveries, oil price, and technology) affects extending the lifetime, whereas on the production side energy demand is growing mainly in developing countries.

Figure 3.43 shows a projection of oil consumption and production until 2015 (on the basis of data from BP) [50]. The gap in consumption will probably cause an increase of oil prices in the future, and it is one of the reasons that more fuel-efficient cars have been manufactured in recent years to keep consumption under control. One important factor that affects world energy consumption is the rate of population growth in the world. A higher population certainly demands a higher energy consumption rate. The change of population in different regions and the world is demonstrated in Figure 3.44 [51]. As shown in this figure, the world population may reach 10 billion by 2050, a 40 % increase from the current figure of approximately

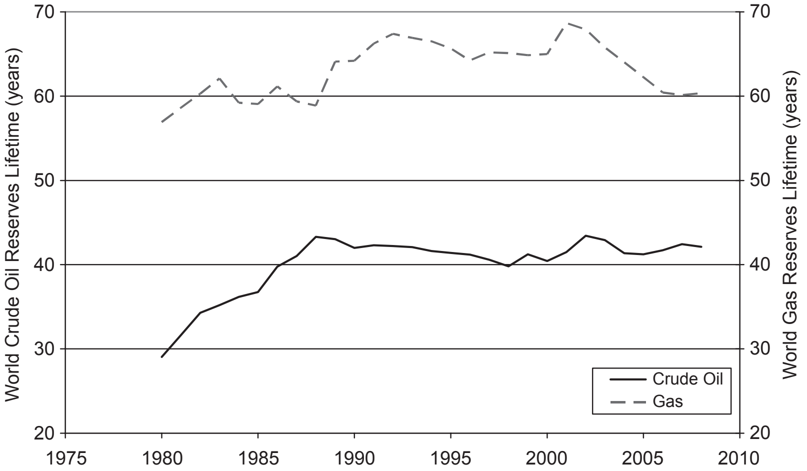


Figure 3.42—Crude-oil and gas proven reserves average lifetime (1980–2008) [4].

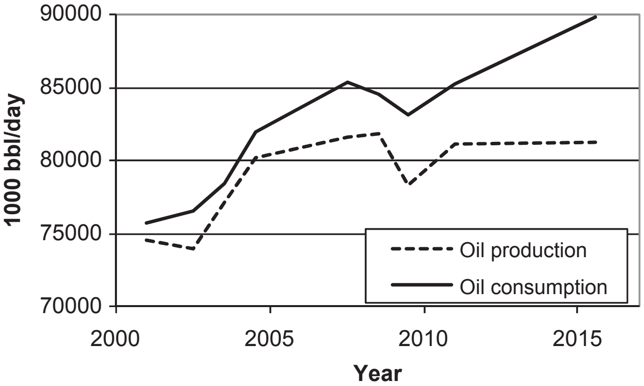


Figure 3.43—Gap between oil consumption and production in the world will increase oil prices on the basis of data from EIA [13].

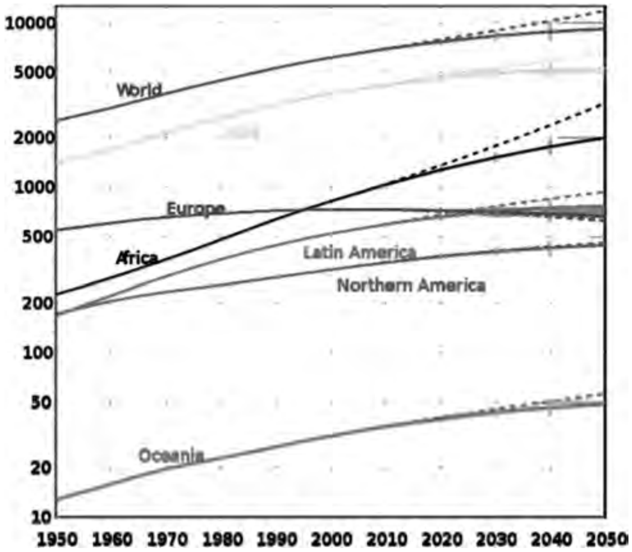


Figure 3.44—Population growth rate until 2050 [51]. *Source:* Reprinted with permission from Oxford Analytica, Ltd. © 2010.

7 billion. Africa shows the largest population growth whereas Europe shows a slight decrease in population over the next 4 decades.

According to estimations from the USGS for the energy demand for the period 2000–2100, the global cumulative demand on crude oil and natural gas will reach 206 Gt. The world proven reserves currently is at approximately 170 Gt, and there are approximately 155 Gt of predicted resources, which puts the total oil and gas reserves at 325 Gt. If only 50 % of these resources are recoverable with existing technology, then total production by 2100 would be approximately 162 Gt, which indicates there would be a 62 % deliverability gap for oil and gas [17]. This shortage will need to be compensated for by other sources such as renewable energies.

3.5 REFINING OF PETROLEUM AND PROCESSING OF NATURAL GAS

3.5.1 Worldwide Refinery Capacity

Petroleum refining is a continuously changing process that varies with consumer demand. Included in the downstream processing refinery capacities are the production of finished petroleum products and the distribution, marketing, and shipping of the products. Refining processes fractionate the various components of crude oil and process these fractions with diverse operation to minimize the heavier fraction, lower-value products (e.g., residual fuel oil) in favor of lighter, higher-value products (e.g., gasoline) [52]. On the other hand, refining margins are defined as the difference in value between the products produced by a refinery and the value of the crude oil used to produce them. Refining margins will thus vary from refinery to refinery and depend on the price and characteristics of the crude [53]. Petroleum refining processes and operations can be separated into three basic areas: fractionation (distillation), conversion (changing the molecular size, structure, or both), and treatment (removal of undesirable contaminants). There are some other processes such as blending and mixing of different fractions of petroleum that are widely used in the refinery [13,54–56]. Refiners face tough challenges when they adapt or design refineries for heavy- or extra-heavy crude-oil processing. The most common configuration includes distillation, thermal cracking, catalytic cracking, hydrocracking, and hydrotreating. The selection of one or more refinery processes is based on the best possible combination for obtaining a clean and valuable fossil fuel (natural gas, oil, and coal) energy source to suit the market demand.

The global refineries' capacities are extending in a big way, as evident in the record increase in recent years despite a decreasing trend in the observed number of refineries because larger refineries are being built whereas others are being closed because of economic reasons such as low refining margins, small local markets, high operating costs (because of small size), and poor yields. In the last decade more than 100 refineries have closed—typically smaller, less-efficient ones. It is obvious that strong decreasing trends in western and central Europe and North America caused a global decrease in refinery numbers. The global refinery utilization rate will continue to decline to an average 78 % of capacity in 2015, compared with 84 % in 2008 and approximately 81 % in 2009. For 2010, a survey indicated total capacity to be more than 88 million bbl/day in 662 refineries, an increase of 1 million bbl/day from the 2009 figure of 87 million bbl/day for 661 refineries. In Figure 3.45 an increase of more than 1.6 million bbl/day over 2008 is reported. In 2009, capacity growth surpassed the total growth for the previous 3 years: 2008 (300,000 bbl/day), 2007 (130,000 bbl/day), and 2006 (52,000 bbl/day). On the other hand, worldwide demand (2009) averaged 86.3 million bbl/day, rebounding from the 2008 average of 84.9 million bbl/day and nearly reaching the 2007 average of 86.5 million bbl/day. The output of oil has increased since 2009 to an average 86 million bbl/day compared with 84.9 million bbl/day last year and 86.4 million bbl/day 2 years ago. A worldwide list of the top 20 refineries is reported in Table 3.8, which includes refinery, location, and crude-oil daily processing capacity. The new Reliance refinery has now become the petroleum hub of the world in Asia by increasing to 1.24 million bbl/day for crude processing capacity. Reliance is the single largest refining complex (Jamnagar) in the world, which is equivalent to 1.6 % of the global capacity or one third of India's capacity, which globally places it among the top 10 private refineries. The largest petroleum processing companies are reported in Figure 3.46, along with their process capacity [4,13,54,57–59]. Major changes in the refiners' position have occurred among Valero, Chevron, Total, and Marathon, whereas others generally move up and down the list by one or two positions. There are approximately 700 refineries all over the world (currently operating ~662 refineries). The regional distribution of worldwide total refineries is shown in Figure 3.47. The utilization of installed refinery capacities by region are particularly displayed with number and their percentage rank in the region.

A chronological development in refinery capacities is reported in Table 3.9. The first step of the refinery is to separate the crude-oil component using thermal fractional distillation, in which the oil is heated and then broken down according to different boiling points. Figure 3.48 shows the total capacity of atmospheric and vacuum distillation as a function of time (1970–2010) and region. The distillation process is the most important and is available in most refineries. A regional distribution of atmospheric and vacuum distillation in different refinery capacities is shown in Figure 3.49. The global refining crude-oil distillation is expected to increase from 9 million bbl/day in 2009 to 99 million bbl/day in 2015. The largest increase will come from Asia and the Middle East. Most refineries worldwide never work at their full capacity; an example of a U.S. distillation unit capacity is given in Figure 3.50. Utilization of refinery capacities in practice is necessarily functionally related to installed capacities and is equally proportionate for the same periods, but not with the same intensity in all regions, nor with equal enunciation. In general, the differences in utilization of installed refinery capacities by region are high in the Middle East, North and Latin America, western and central Europe, Asia, and the Pacific. This is followed by Africa, whereas east Europe and central Asia are at the end of the list. Not only that, eastern European (<17), African (<20), and Middle Eastern (<22) refineries have the lowest average complexity ratios in comparison to refineries in western and central Europe (<36), Latin

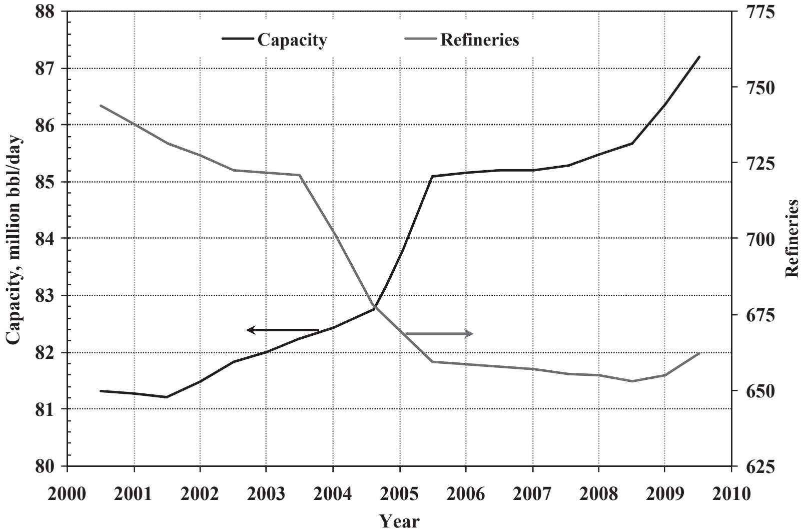


Figure 3.45—Worldwide trend in operable refineries and their capacities [54].

TABLE 3.8 —World's Largest Refineries, Their Locations, and Their Processing Capacity [54]

Rank	Location	Company	Crude Capacity (b/cd)
1	Jamnagar, India	Reliance Industrial, Ltd.	1,240,000
2	Cordon/Judibana, Falcon, Venezuela	Paraguana Refining Center	940,000
3	Ulsan, South Korea	SK Corporation	817,000
4	Yeosu, South Korea	GS Caltex Corporation	730,000
5	Jurong/Pulau Ayer Chawan, Singapore	ExxonMobil Refining and Supply Co.	605,000
6	Baytown, TX	ExxonMobil Refining and Supply Co.	576,000
7	Onsan, South Korea	S-Oil Corporation	565,000
8	Ras Tanura, Saudi Arabia	Saudi Arabian Oil Co. (Saudi Aramco)	550,000
9	Mailiao, Taiwan	Formosa Petrochemical Co.	540,000
10	Baton Rouge, LA	ExxonMobil Refining and Supply Co.	504,000
11	St. Croix, Virgin Islands	Hovensa LLC	500,000
12	Mina Al-Ahmadi, Kuwait	Kuwait National Petroleum Co.	466,000
13	Pulau Bukom, Singapore	Shell Eastern Petroleum Co.	462,000
14	Texas City, TX	BP PCL	451,000
15	Lake Charles, LA	Citgo Petroleum Corporation	440,000
16	Garyville, LA	Marathon Petroleum Co. LLC	436,000
17	Pernis, The Netherlands	Shell Netherlands Raffinadenj BV	404,000
18	Zhenhai, China	Sinopec	403,000
19	Rabigh, Saudi Arabia	Saudi Arabian Oil Co. (Saudi Aramco)	400,000
20	Yanbu, Saudi Arabia	Saudi Aramco-Mobil	400,000

b/cd = barrels per calendar day

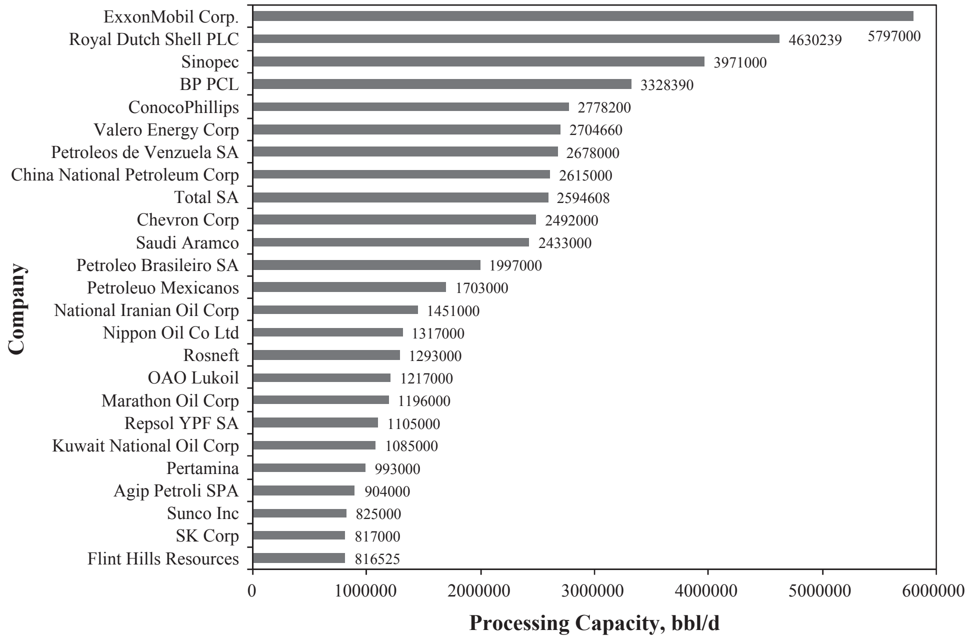


Figure 3.46—World largest refineries rank (January 1, 2009) with their processing capacity [54].

America (<44), Asia-Pacific (<45), and North American (<75), respectively. The complexity ratio (reported in the parentheses) as a percentage of the refinery conversion capacities of the total refinery (distillation) capacity is reported by world regions for 2008. The refinery complexity is an effort to describe the investment cost of a refinery in terms of the process operation being conducted. However, this applies only to the process unit cost of the refinery, not to the total refinery cost. The processing capacity of specialized processes such as thermal, catalytic cracking, and

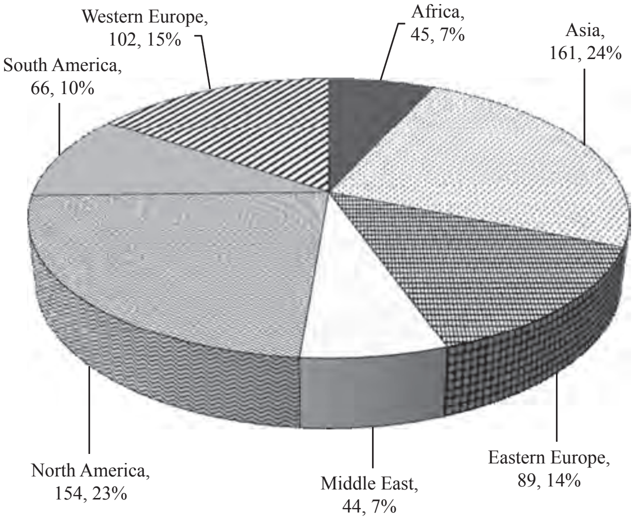


Figure 3.47—Regional breakdown of worldwide refineries (numbers) and their percentage distribution [13].

reforming are compared in Figure 3.51. These processes have endured over 60 years and remain the workhouse of the refinery. Catalytic reforming has similar distinction in its very important place; however, in recent years alkylation and isomerization promise to become more significant in the reformulated era because of advancement in those techniques. In the 1970s or early 1980s, refiners put more effort on hydroprocessing, particularly the removal of sulfur. Catalytic hydrocracking also offers flexibility in the product yield and specification, but at a higher process price. The worldwide regional distribution and comparison is shown in Figure 3.52 and is mainly dominated by North American refineries.

3.5.1.1 GLOBAL REFINING TREND

The stricter fuel standards and more efficient fuel and combustion engines are required to protect our climate. Nowadays, we have many vehicles—the "two SUVs in every driveway syndrome"—thus the high value (ultraclean fuel) demand for gasoline and diesel is at priority for all countries. On the other hand, most countries do not fulfill their demand with respect to raw petroleum (crude oil), capacity to process, and efficient method to obtain clean fuel. Therefore, these countries require a huge amount of export-import to accomplish their demand. Hence, the gap between product demand and domestic refining capacity indicates the need for imports, whereas the lack of refineries or low capacity force them to refine their crude to import and buy back for their necessary use. The product import situation suggests more taxes, transportation, and other duties. The refined product regional distribution and total import-export per day is shown in Figure 3.53, indicating their demand for the particular year 2006. It is also reported in the previous section that the Middle East is the largest oil-producing region, whereas most refining takes place in the United States, Europe, or Asia. The largest refining capacity is in North America (in fact, the United States), accounting for approximately one quarter of the crude-oil distillation capacity worldwide. The growth in demand for light products such as gasoline and diesel has been matched by the growth in emissions control and the emissions' effects on the environment, as shown in Figure 3.54, indicating that hydroprocessing is the most significant area of the refining processing. The U.S., Japanese, and EU sulfur specifications drive toward lower sulfur content (<10 ppm), which is a concept that has spread to the developing countries of South America, Africa, and the Middle East and Asia-Pacific regions.

3.5.1.2 REFINING CHALLENGES AND LIMITATIONS

The crude-oil scenario is changing every year as it becomes heavier with higher contaminants such as higher sulfur, nitrogen, and metal contents, which require more severe refining conditions or catalysts to produce cleaner and valuable finished products [59–65]. The worldwide production of light crude oil is rapidly dwindling, whereas extra-heavy crude-oil production is increasing [66,67]. Thus, processing of such crudes poses different challenges for today's refiners. In addition, the understanding of such feedstock is limited or difficult to characterize at its molecular level. The heaviest fraction of heavy crude oil is represented by asphaltenes. Asphaltenes are the precursors of most heteroatoms (S, N, etc.) and metals (Ni and V). An asphaltene molecule may be 4–5 nm in diameter, which

TABLE 3.9—A Chronological Development in Oil Refinery

Period	Refinery Configuration
1960s and before	Distillation; thermal processing; pretreatment; reforming
1970s	Vacuum distillation; catalytic cracking; hydrocracking/hydrotreating; visbreaking; residue fuel oil (low S, N, etc.)
1980s	Elimination of Pb in gasoline; lowering S in gasoline and diesel; fluid catalytic cracking; reduction in SO_x/NO_x
1990s	Isomerization; MTBE, ETBE, TAME, etc.; alkylation
2000s	Hydrocracking (multistage reactor); inhibition effect (H_2S, NH_3, N compounds, aromatics, etc.); capacity increase, esterification, etc.; deep hydrodesulfurization (<50 ppm)
2010 and beyond	ULDS (<5 ppm); separation of N compounds before ULDS; alternative methods for ultradeep desulfurization (desulfurization by adsorption, removal of N compounds by adsorption); feed blending technology and its composition; selective conversion of bottom-of-barrel; industrial application of nanotechnology

SO_x, oxides of sulfur; NH_3, ammonia; MTBE, methyl tert-butyl ether; ETBE, ethyl tert-butyl ether; TAME, tert-amyl methyl ether; ULDS, ultralow deep hydrodesulfurization.

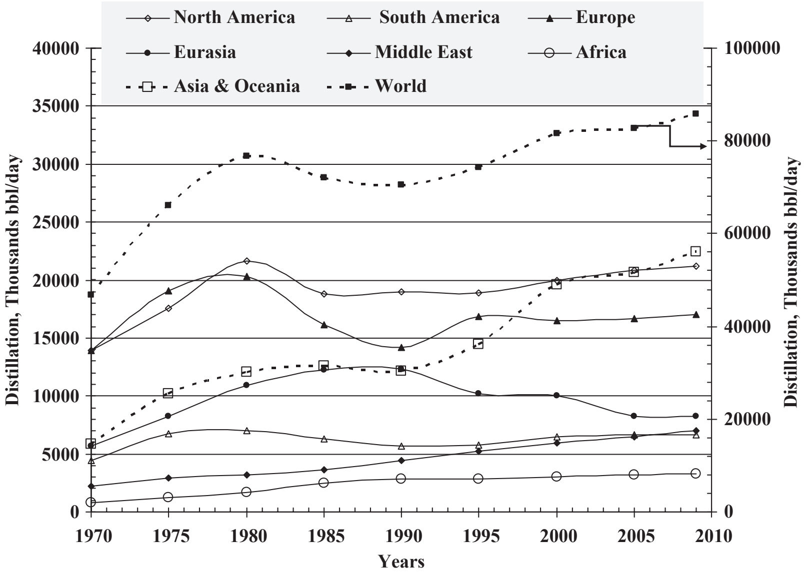


Figure 3.48—Geographical evolution of crude-oil distillation process within 4 decades [13].

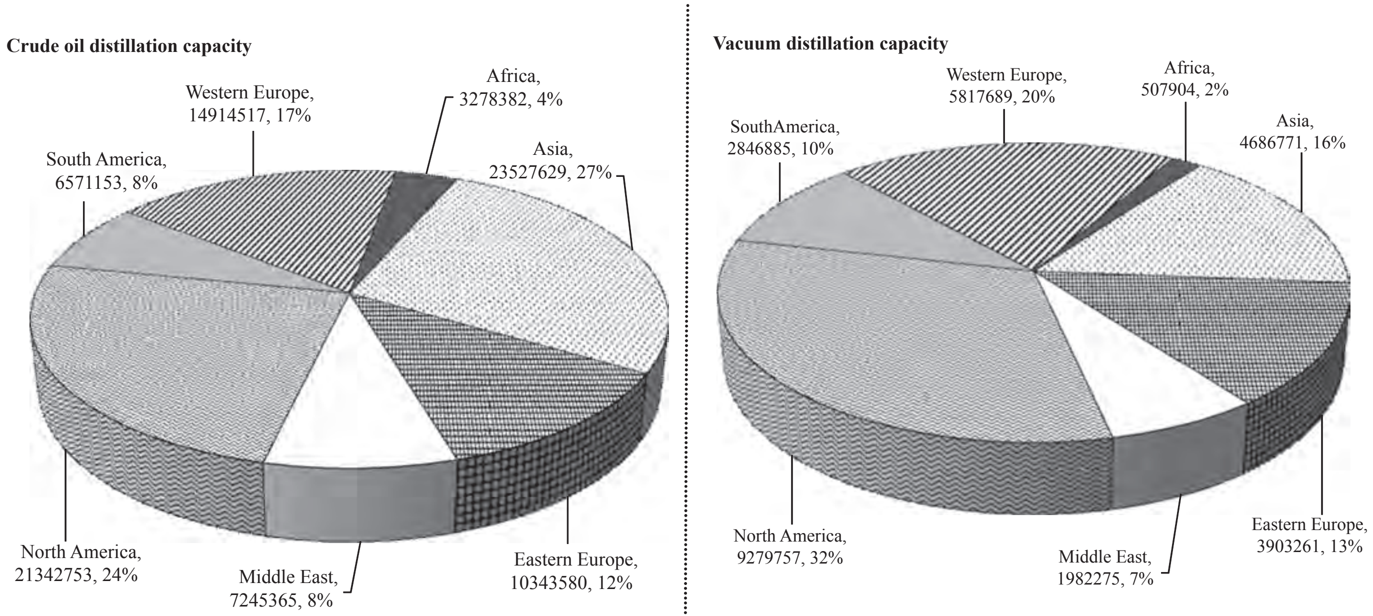


Figure 3.49—Regional breakdown of atmospheric and vacuum distillation capacities and worldwide refinery distribution (bbl/day) and their percentage.

is difficult to process in a refinery by catalytic systems [68,69]. Metals in the asphaltene aggregates are believed to be present as organometallic compounds associated with asphaltene sheets, making the asphaltene molecule more complex. Asphaltenes are usually problems during exploration, processing, and transportation because of their polar and unstable (precipitation and sediment formation) nature within processed or unprocessed streams. Hence, a high content of asphaltenes creates a refining problem that is not easy to solve. Therefore, it is mandatory for researchers to understand the chemistry of the complex fossil fuel feedstocks that are required to design suitable catalysts and conditions for processing. The processing complexity of the feedstock is further enhanced when coupled with the demand for ultraclean fuels (diesel and gasoline). The worldwide energy oil demand is projected to continue with a high level of refining capability [4]; however, one should be confident that refineries will meet the increasingly stringent product specifications and have the ability to meet future demands.

3.5.2 Worldwide Products Distributions

3.5.2.1 DEMAND FOR PETROLEUM PRODUCTS AND TRANSPORTATION FUEL

Demand for petroleum products is inevitably increasing, particularly in developing countries such as India, China, and Brazil. Their demand is centered on gasoline and distillates (transportation fuel) because these countries are growing in their middle-class population. Thus, conversion technologies become a key driver in improving refinery

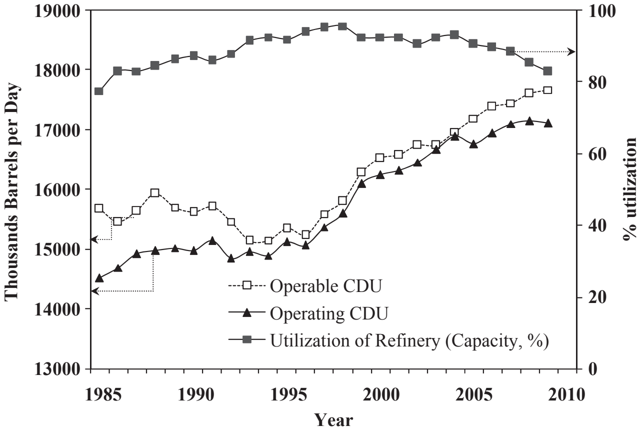


Figure 3.50—U.S. operable crude distillation units (CDU) capacity and its utilization (thousand bbl/day) [13].

profitability. The demand for middle distillates is growing steadily, as shown in Figure 3.55a. According to a recent estimate by IEA, distillates (jet fuel, kerosene, diesel, and other gas oils) will continue to be the main growth driver of world oil demand for the next few years [58,70,71]. Moreover, the latest forecast by IEA indicated that global oil demand will increase approximately 0.6 %/year during 2009–2015. According to the IEA projection, approximately 48 % of the global product demand growth over the next 5 years will be concentrated in middle distillate fuels, which are dominated by diesel. This trend is likely to continue for many more years. It appears that petroleum refining capacity, demand, and consumption are mainly oriented around the middle distillate. Within the middle distillate demand for passenger cars, sport utility vehicles, light trucks, buses, and heavy-goods vehicles was 13.5 million bbl/day in 2008, which will increase approximately 24 % within next 12 years (i.e., 2020) as shown in Figure 55, b and c.

Since 2000, North America (United States, Canada, and Mexico) enhanced its diesel desulfurization capacity by 3.7 %, whereas naphtha desulfurization capacity was augmented by 0.7 %. The regional consumption of refined group products is shown in Figure 3.56. The gasoline demand in the United States is gradually growing whereas in Europe it has been declining since 2000. Gasoline demand in Europe has declined at an average 2.1 %/year since 2000, and diesel demand has increased by 2 %. The decline in European demand for gasoline can be a benefit for U.S. refiners because it makes more gasoline supplies available to the world market.

3.5.2.2 ULTRALOW SULFUR DIESEL SUPPLY AND DEMAND

Producing low-emissions transportation fuels is one of the highest priorities for the petroleum industry. Thus, sulfur removal from petroleum feedstocks is a forefront issue in the refinery industry because of recently enacted environmental protection laws. Reducing the level of sulfur in diesel fuel will increase the durability and performance of aftertreatment technologies used in automobiles to satisfy the stringent clean air standards established globally. Sulfur in fuels is a pollutant, and reduction of sulfur beyond current requirements is beneficial from an air quality and pollution control equipment standpoint. U.S. Environmental Protection Agency (EPA) rules required that 80 % of highway diesel supplies contained no more than 15 ppm sulfur for the period 2006–2010. After 2011, all highway diesel fuel will be required to contain less than 15 ppm sulfur, at least in the United States and EU. The need to find a solution for this considerable problem has led to a worldwide search for appropriate hydrodesulfurization catalysts.

Only a few refineries currently produce diesel with sulfur in the 15-ppm range. However, the worldwide existence of the requisite technology does not ensure that all refineries will have that technology in place in time to meet the new ultralow sulfur diesel (ULSD) standards. Widespread production of ULSD in the future will require many refineries

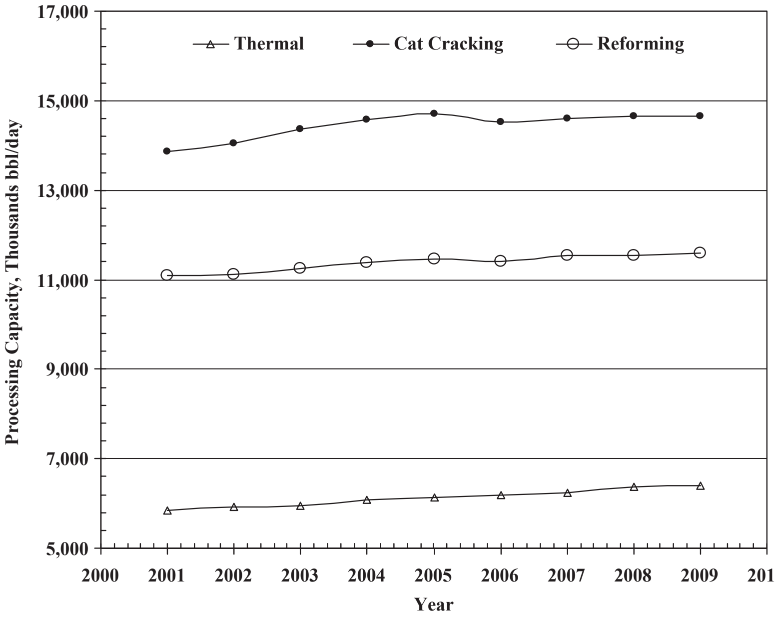


Figure 3.51—Chronological processing capacity of different processes [13].

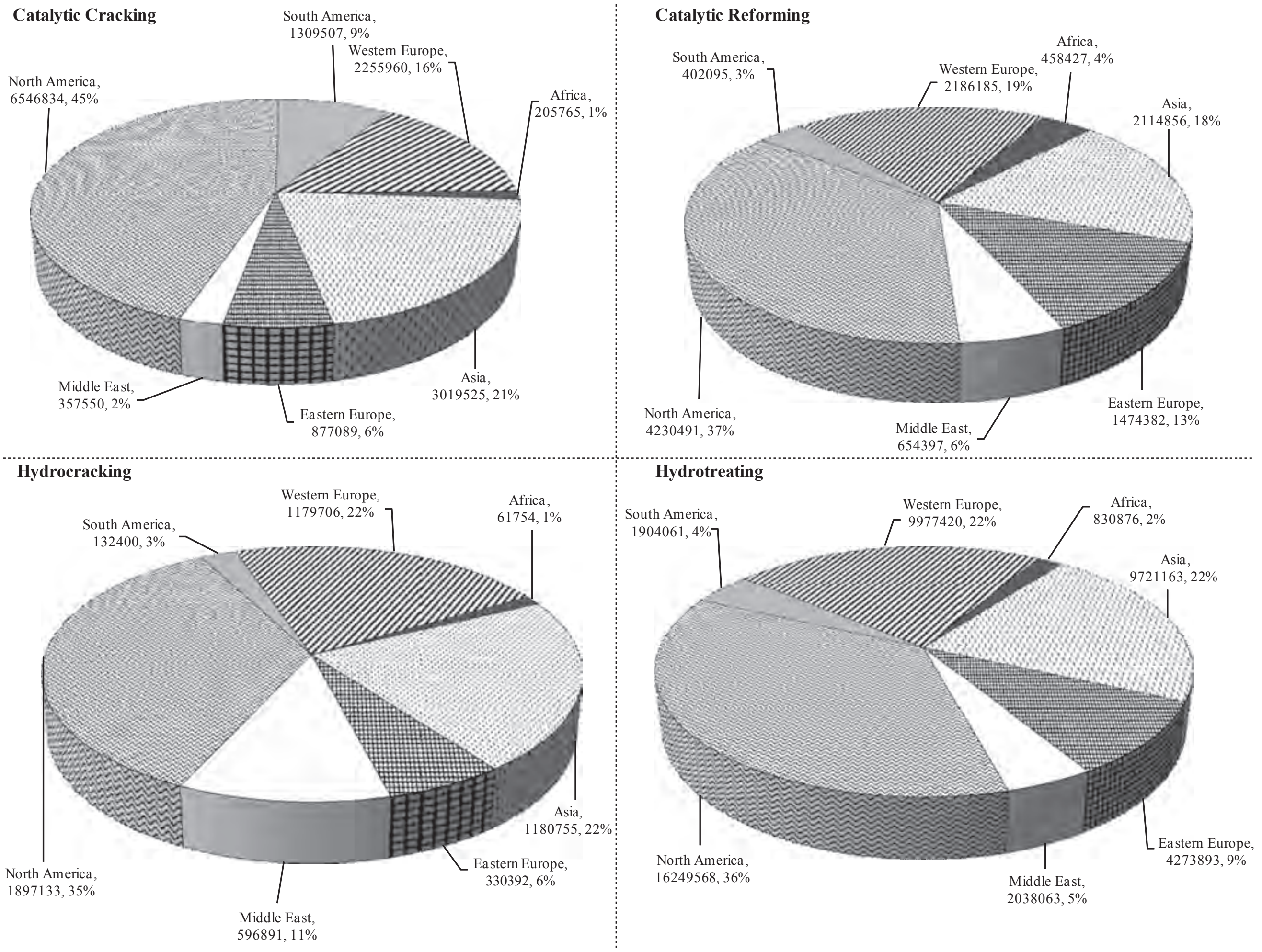


Figure 3.52—Regional glance at worldwide refining operations for different processes [13].

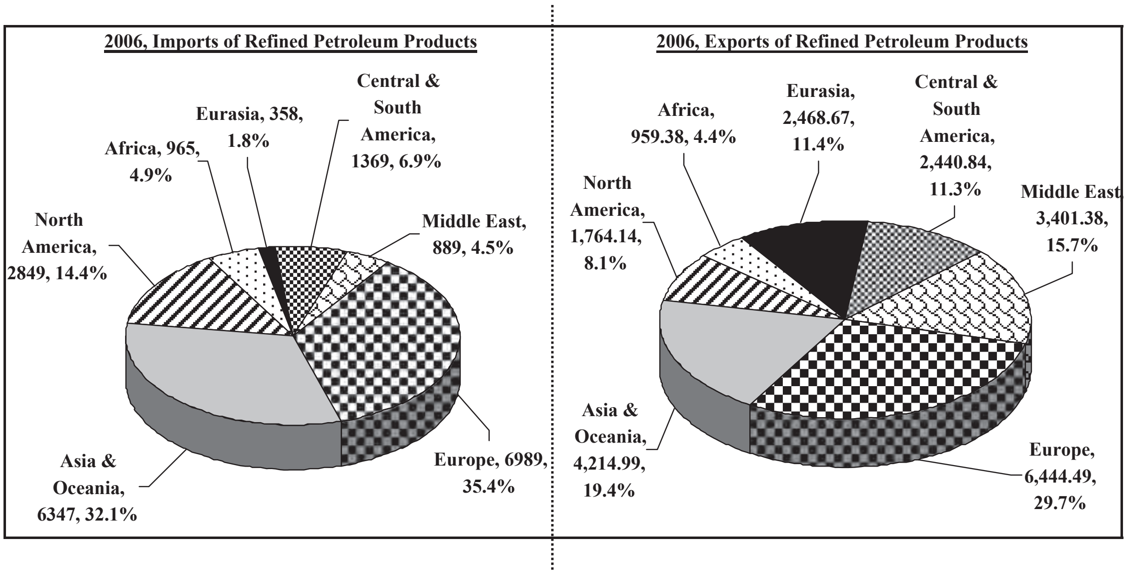


Figure 3.53—Geographical regions and total import-export of petroleum products [13].

to invest in major revamps or construction of new units. Very-low-sulfur diesel products have been available commercially in some European countries, Japan, and the United States. Sweden was the first to impose very strict quality specifications for diesel fuel, requiring a minimum 50 cetane, 10 ppm sulfur, and 5 % aromatic contents. To meet these specifications, the refinery at Scanraff, Lysekil, near the west coast of Sweden, installed a hydrotreating facility that

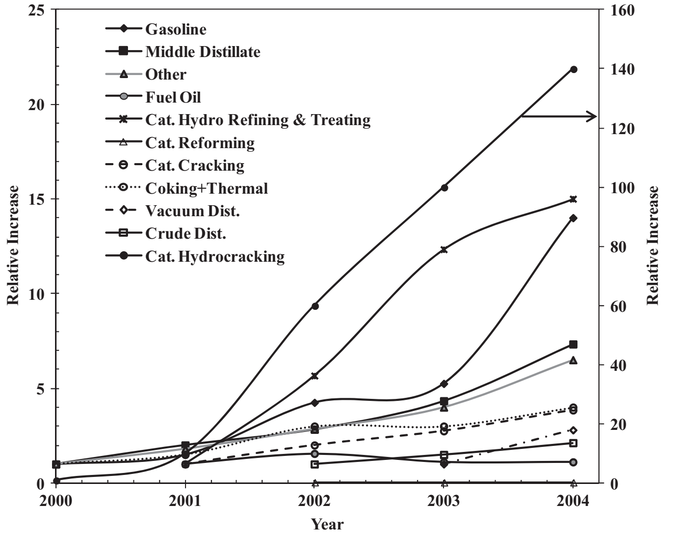


Figure 3.54—Relative increase in world refining capacity and product demand between 2000 and 2004 (year 2000 is taken as base) [4].

is based on SynTechnology. Therefore, hydroprocessing has been far and away the most significant processing investment over the past few years [65]. It is generally believed that a two-stage deep desulfurization process will be required by most, if not all, refiners to achieve a diesel product with less than 10 ppm sulfur. In some cases the first stage could be a conventional hydrotreating unit with moderate adjustments to the operation parameters. Recent advances in higher activity catalysts also help in achieving a higher sulfur removal rate [72,73]. The second stage would require substantial modification of the desulfurization process, primarily through using higher pressure, increasing hydrogen pressure, reducing space velocity, and choice of catalyst. Hydrogen consumption is the largest operating cost in hydrotreating, and minimizing hydrogen use is a key objective in hydrotreating for sulfur removal. In general, 10-ppm sulfur diesel would require 25–45 % more hydrogen consumption than would 500-ppm sulfur diesel, in addition to improved catalysts. On the other hand, removal of nitrogen or partial hydrogenation of aromatic rings before deep desulfurization are also possible for removal of refractory sulfur compounds in a more cost-effective way than hydrogenation.

3.5.2.3 SYNTHETIC DIESEL

3.5.2.3.1 Gas-to-Liquid Technologies (Fischer–Tropsch Synthesis)

High-quality diesel fuel (high cetane and low sulfur) can be synthesized by a Fischer–Tropsch (FT) reaction [61,64]. Gas-to-liquid (GTL) technologies potentially offer a supply of very-high-quality middle distillates, particularly when demand for diesel fuel and jet kerosene is forecasted to grow strongly with increasingly stringent quality specifications. GTL facilities have been operated commercially in recent years, including the Moss gas plant in South Africa with

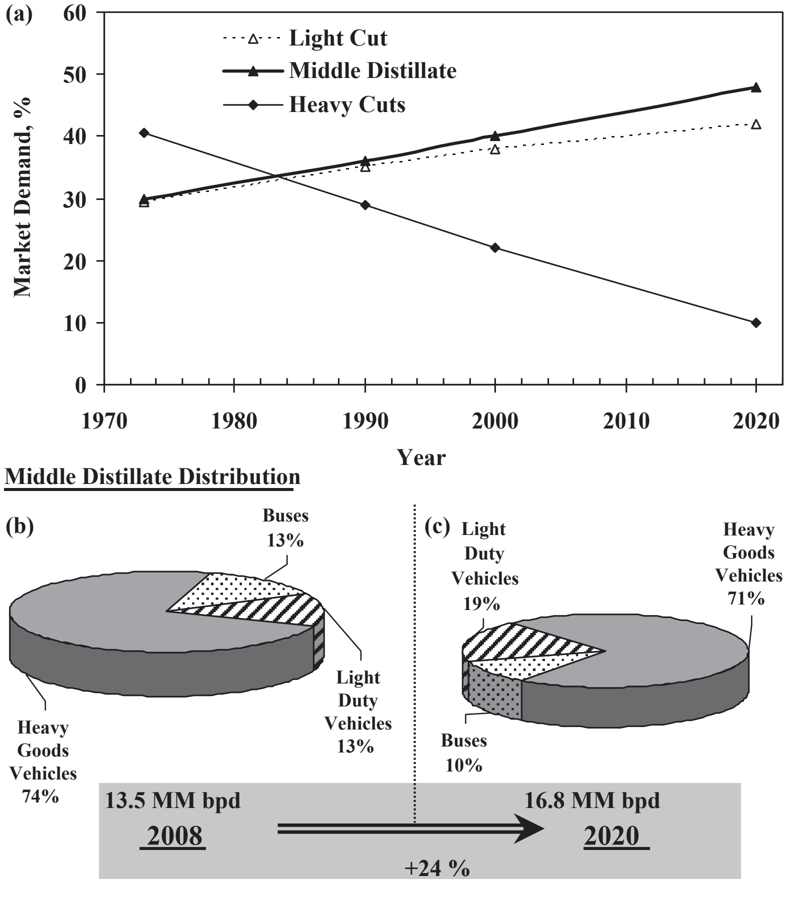


Figure 3.55—Refining issue: (a) World market trend of petroleum products, (b) worldwide middle distillate demand distribution of on-road fuel in 2008, and (c) projected demand for 2020.

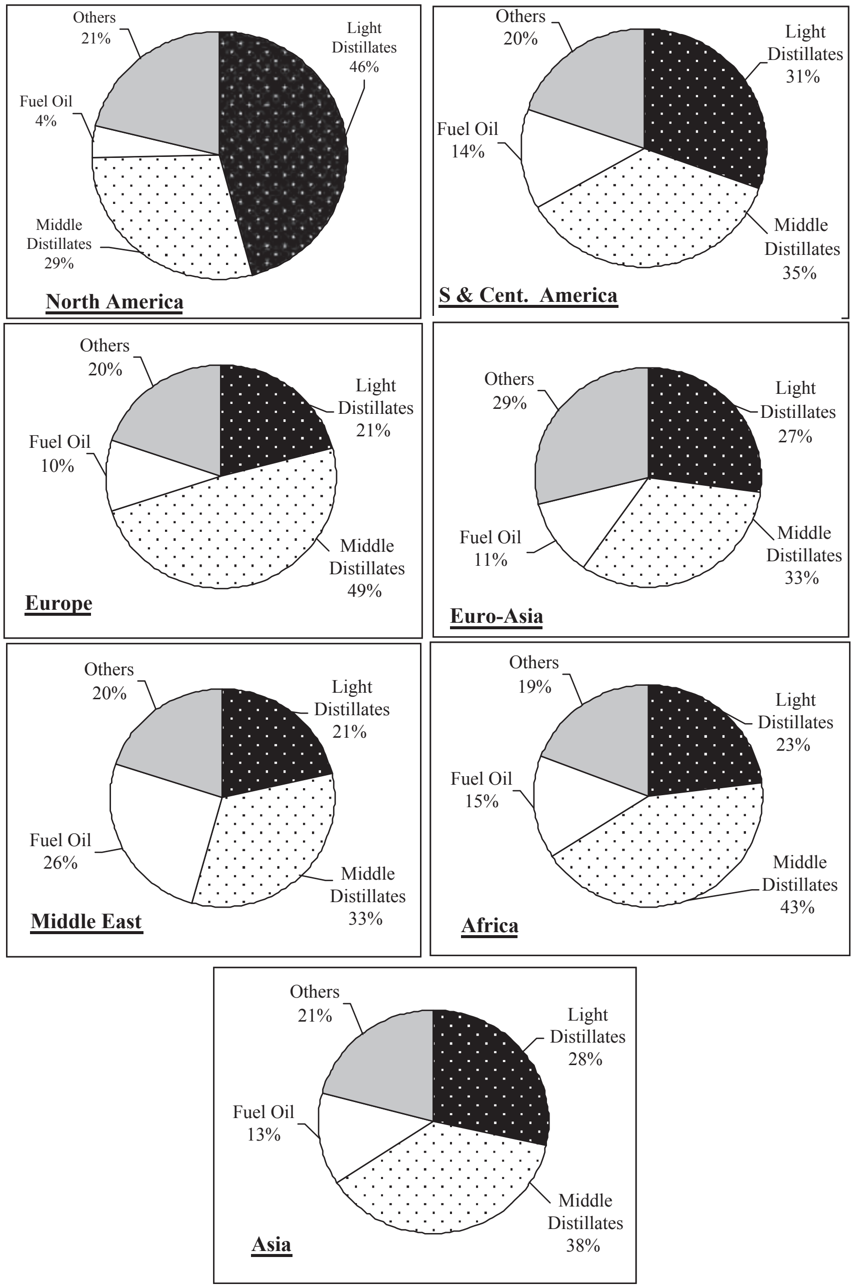


Figure 3.56—Regional consumption of refined products (2008) and their distribution in different regions [13].

an output capacity of 23,000 bbl/day and the Shell Bintulu plant in Malaysia with an output capacity of approximately 12,500 bbl/day. Natural gas GTL technology can be cost-competitive only if investors are confident that crude-oil prices will stay in the low range. The focus of GTL technology is to develop a clean viable route to make liquid transportation fuels from natural gas and carbon dioxide.

3.5.2.3.2 Biodiesel

Considerable interest has recently been focused on the further development and expansion of a domestic biofuels industry. The reasons for growing interest in biodiesel include its potential for reducing noxious emissions, its potential contributions to rural economic development as an additional demand center for agricultural commodities, and its potential to reduce our dependence on petroleum oil. It has also been established that exhaust emissions from biodiesel are substantially less than those from petroleum-based diesel, which would reduce emissions [particulate matter (PM), carbon monoxide (CO), and hydrocarbons] up to 75 %; however, oxides of nitrogen (NO_x) emissions are slightly increased in the case of biodiesel [4,13,57]. Figure 3.57 indicates the chronological development (from 2000 to 2008) in world biofuel production and consumption. Biofuel production and consumption increased approximately 7-fold from 300,000 bbl/day in 2000 to at least 1,500,000 bbl/day in 2008 (Figure 3.57a). The regional distribution of biofuel consumption showed dramatic changes, particularly in North America, the leading region since 2005, where capacity increased by 15 times (Figure 3.57, b and c). Table 3.10

indicates the top 10 countries for biofuel production in the last decade. Apart from these countries, no other countries produce an excess amount of biofuel for commercial export.

3.5.2.3.3 Natural Gas as Transportation Fuel

Promoting sustainable development and combating climate change have become integral aspects of energy planning. The level and growth of CO_2 emissions (Figure 3.58a) and their source and geographic distribution (Figure 3.58b) will be essential to lay the foundation for a global agreement and continue fossil fuel-based energy development. Natural gas is often described as the cleanest fossil fuel, producing less CO_2 per joule delivered than coal or oil and far fewer pollutants than other fossil fuels, as shown in Figure 3.58c. However, it does contribute substantially to global carbon emissions, and this contribution is projected to grow with its use. Natural gas can be used as automobile fuel in the form of compressed natural gas (CNG) as an alternative to gasoline and diesel. In addition, the energy efficiency of using natural gas (octane number of 120–130) is equal to that of gasoline

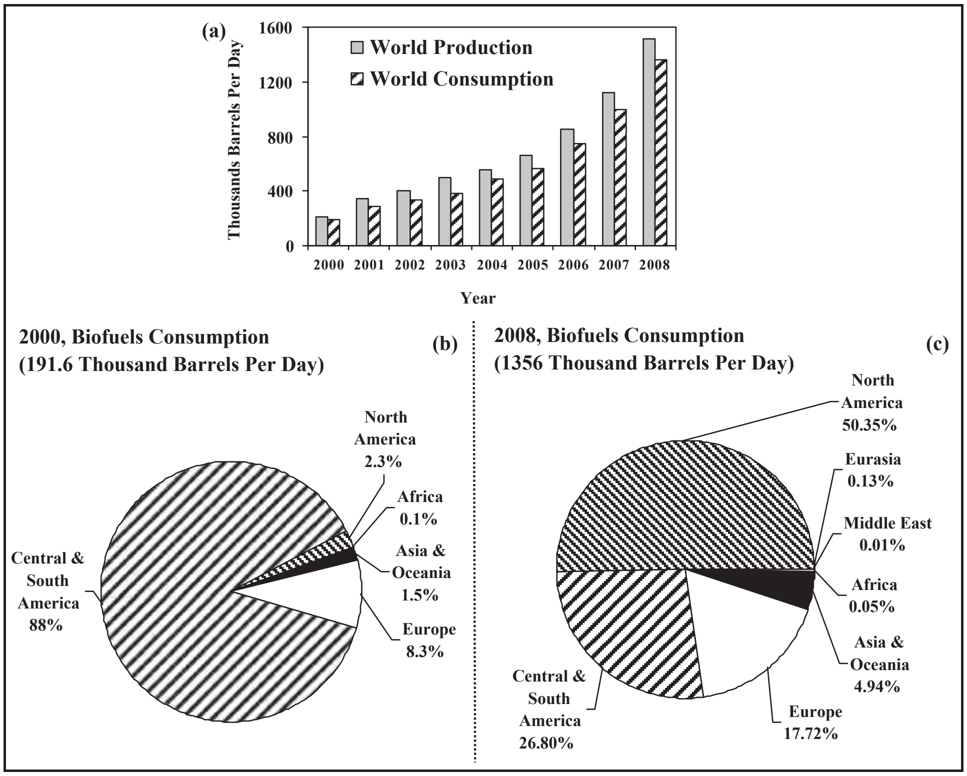


Figure 3.57—Advances in alternative fuel (biofuel) and (a) their per-day world total production and consumption and regional consumption in (b) 2000 and (c) 2008 [13].

TABLE 3.10—Biofuel Consumption Variation with Time and Top 10 Countries That Have High Capacity to Consume Biofuel [13]

	Total Biofuel Consumption (thousand bbl/day)					
Rank	**Country**	**2000**	**Country**	**2005**	**Country**	**2008**
1	Brazil	166.9	United States	270.7	United States	656.8
2	France	8.0	Brazil	182.0	Brazil	355.1
3	Germany	4.9	Germany	44.4	Germany	68.1
4	Canada	4.5	China	21.5	France	56.5
5	India	2.9	France	9.5	China	37.5
6	Spain	1.6	Spain	7.1	Canada	25.8
7	Czech Republic	1.4	Canada	6.0	United Kingdom	18.7
8	Cuba	1.1	Sweden	5.1	Spain	15.5
9	Malawi	0.2	Italy	4.1	Thailand	12.9
10	Argentina	0.1	India	3.9	Italy	12.5

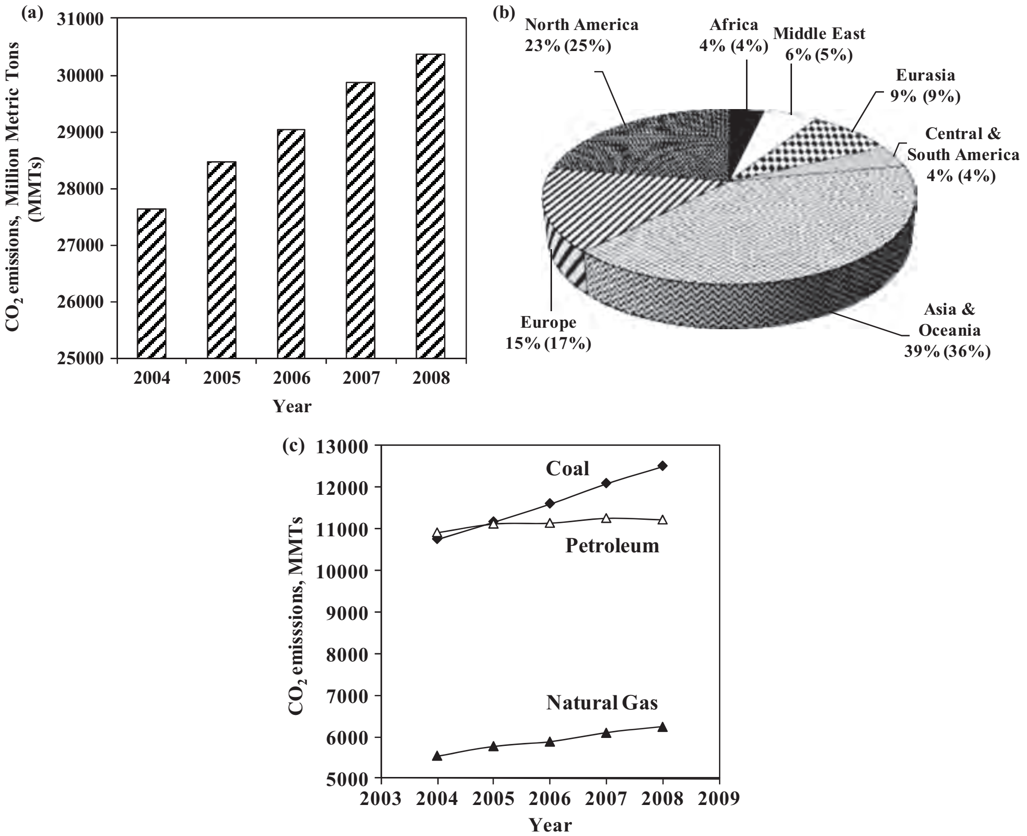
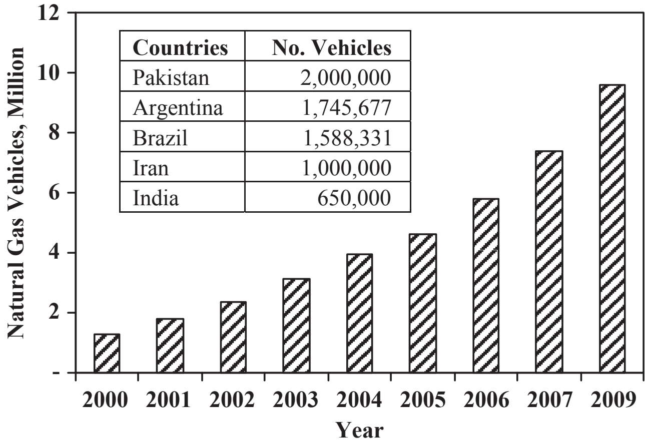


Figure 3.58—(a) CO_2 emission by using fossil fuel, (b) 2008 regional distribution (data for 2004), and (c) effect of type of fossil fuel on CO_2 production [13].



Countries	No. Vehicles
Pakistan	2,000,000
Argentina	1,745,677
Brazil	1,588,331
Iran	1,000,000
India	650,000

Figure 3.59—Worldwide natural gas vehicles used and top five countries (inset) that use natural gas vehicles.

engines but is lower than that of modern diesel engines. Worldwide, approximately 9.6 million natural gas vehicles were running in 2009, mostly led top user as shown in Figure 3.59. In addition to displacing petroleum fuels with natural gas, one of the primary benefits is the potential to reduce exhaust emissions of harmful pollutants such as SO_x, NO_x, and PM. Studies have shown that NO_x reductions of 50–80 % and PM reductions of 80–95 % are possible when heavy-duty vehicles are operated on natural gas instead of diesel fuel.

3.5.2.4 REFINING COSTS AND PROFITS

The price variation in refined petroleum products mainly depends on fuel qualities such as octane or cetane numbers, sulfur levels, aromatic contents, and other fuel parameters. However there are no precise correlations between price and properties. Fuel quality recently changed, mainly because of environmental issues. For example, in the EU, the diesel sulfur level was 350 ppm in 2004, but by 2008 a significant portion of diesel contained only 10 ppm sulfur and the rest was 5 ppm sulfur. Sulfur removal adds to the cost of refining; therefore, comparison of diesel prices in Europe between 2004 and 2008 reflects more than oil price increases during the intervening years. However, 2008 was a dramatic year in which prices reached a maximum limit ($148/bbl, July 2008) and dropped rapidly with a record margin at the end of year ($35/bbl, December 2008).

Nevertheless, as every driver knows, filling up your tank can be an expensive task. What is not generally known is just where most of that money goes. Figure 3.60 attempts to shed some light on this issue and indicates a wide regional variation in the prices (U.S. $/L) of different oil products for 2008. However, these price variations are not due to differences in crude-oil prices, but to varying levels of taxation in the major consuming nations. The figure shows how much of the price for each liter of oil goes to oil producers (including cost of production and other related expenses), the industry margin (includes transport, insurance, and other costs), and the amount that goes to national government taxes. The graph indicates that tax levels range from relatively low levels in the United States to very high levels in many EU countries. In the United Kingdom, the government generates considerably more money from taxation than OPEC member countries receive from the sale of their oil. Thus, it is clear that the real cost

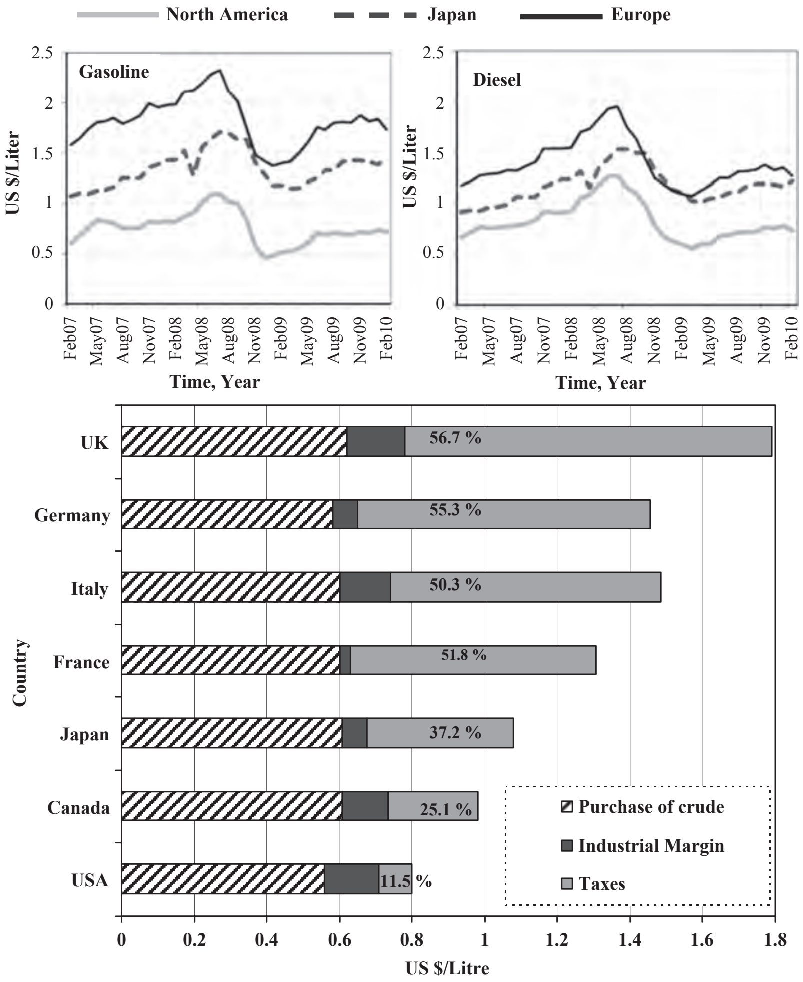


Figure 3.60—Price of a liter of oil in different countries and the percentage of money that contributes to total market price [70].

burden on end-users is from the oil taxes imposed on customers by their government.

3.5.2.5 REGIONAL REFINERY BACKGROUND AND THEIR CAPACITIES

The worldwide cumulative refining capacity expansion is expected to contribute approximately 44 % to global refining capacity additions during 2012–2015. The Middle East and India plan to transform themselves into major refining and petroleum product exporting-importing hubs, whereas Central and South America are expanding their refining capacity, mainly to process their domestic heavy crude oil, the production of which is rapidly increasing. However, refining margins will remain modest because the demand for products in the major consuming markets is expected to remain low. A new trend is approaching that the national oil companies (majority) are adding refining capacities—either to supply to the domestic refined products need or to transform their countries into global refining hubs. For example, national oil companies in the Middle East are investing in refineries to process domestic heavy crude oil and reduce the import of light and middle distillates. Considering the regulatory constraints to build green-field refineries in North America and Europe, the Middle East can become a major petroleum product supplier to these countries instead of just a crude-oil supplier. Thus, in the near future, most refinery capacity expansion is expected to come from Asia and the Middle East by adding new and expanding existing refineries to meet the anticipated market demand in the region. In fact, the net Asian refining capacity increased approximately 1 million bbl/day for 2009, followed by North America with more than 0.393 million bbl/day and the Middle East with more than 0.200 million bbl/day.

Overall, it is expected that at the end of 2020, refinery capacity worldwide will increase from 84.6 million bbl/day to 102 million bbl/day. At the same time, demand for crude oil is expected to increase from 82.6 million bbl/day in 2004 to 90.4 million bbl/day. Thus, refinery capacity is 9.3 million bbl/day whereas demand is approximately 7.8 million bbl/day. The United States has been operating their refineries at approximately 90 % capacity since 1992, which has a negative effect on the economy. The world is currently operating at close to 88 % capacity for refineries.

3.5.2.6 REFINING IN AFRICA

In Africa before 1954 there were no refineries. After 50 years (2005), approximately 48 refineries were built in Africa. The foremost African refineries were built in 1954 in Algiers (CFP/Total) and Durban (Socony/Mobil). These were followed by the building of the Luanda refinery (Petrofina) in 1958 and refineries in Kenya (Shell/BP), Ghana (ENI/Agip), and Senegal (consortium) in 1963. In the 1960s, refineries were also built in Cote d'Ivoire, Gabon, Tanzania, Nigeria (Port Harcourt I), and Capetown. In the 1970s and 1980s, after nationalization of the oil industry in many countries, several state-controlled refineries were built. In the last decade, there have been several modernization projects, but the only new refineries built in the past 10 years have been Khartoum in 2001 and MIDOR in Egypt in 2002. Apart from the refineries, there are also three synfuel plants (coal and gas feedstock) in South Africa. The total active distillation capacity for the continent is approximately 3 million bbl/day, an average of 79,000 bbl/day per refinery. The major refining capacities in Africa are in South Africa, Nigeria, Egypt, and Algeria. The largest refinery in Africa is the Skikda refinery in Algeria (300,000 bbl/day), whereas the second largest is the Ras Lanuf plant in Libya (220,000 bbl/day). The African oil refining industry has been impacted seriously because of the poor management of the political situation during recent years, and production has been an average of 65 % below capacity.

3.5.2.7 REFINING IN THE MIDDLE EAST

The name "Middle East" has been associated with oil refining since the middle of the last century, and oil has been the backbone of the economy in this region for the past, present, and possibly for many decades to come. The region produces approximately two thirds of the world's oil consumption, whereas Middle Eastern natural gas reserves are approximately one tenth of the world's proven reserves as of January 1, 2009 [13]. The economy of oil-producing countries in the Middle East/North Africa region heavily (80–90 %) depends on oil revenues, yet some 70 % of businessmen in this region do not consider environmental issues in their business practices. The main areas of refinery capacity in the Middle East are reported in Figure 3.61, indicating saturation in the process operations. Middle Eastern countries are also thinking of enhancing total refining capacity by 2015 for downstream refining capacity at home as well as abroad. The new capacity plan is mainly in the area of distillation and hydrotreating. Major plans are underway to construct new refineries and increase the capacity of existing ones to attain production of cleaner fuel with market demand.

The Middle East currently operates approximately 44 refineries for crude-oil distillation (7.2 million bbl/day), vacuum distillation (1.9 million bbl/day), catalytic cracking (0.35 million bbl/day), catalytic reforming (0.65 million bbl/day), hydrocracking (0.59 million bbl/day), and hydrotreating (2.0 million bbl/day). Refining markets in the Middle East are mainly controlled by the Gulf Cooperation Council (GCC), which offers comprehensive information on the refining markets in Saudi Arabia (eight refineries), the United Arab Emirates (three refineries), Kuwait (three refineries), Qatar (one refinery), Oman (one refinery), and Bahrain (one refinery). GCC refining capacity increased from 1.7 million bbl/day in 1980 to 3.1 million bbl/day in 1995, which was further targeted to 4 million bbl/day by 2010. The cumulative refining capacity of these countries accounted for 4.9 % of the global refining capacity and 41 % of the total refining capacity of the Middle East in 2008. New refineries and expansion in existing refineries will increase the refining capacity in the GCC to 6.8 million bbl/day by 2013, and GCC will contribute 6.4 % to the global refining capacity. The average size of refineries in the GCC countries at 11.4 million metric tons per annum (MMTPA) is above the global average of 6.7 MMTPA.

3.5.2.8 REFINING IN NORTH AMERICA

In petroleum refining, North America, in particular the United States, plays an important role because it is the first to import and export petroleum. Moreover, North America has approximately 200 petroleum refineries within North and South America, including 600 defined areas and over 3900 operating units. Most of the units have distillation, whereas others have just downstream processes such as fluid catalytic cracking, hydrotreaters, reforming, thermal cracking, etc. The United States has approximately 108 refineries, Canada has approximately 26 refineries at different places, and Mexico has 6 refineries (~1.5 million-bbl/day capacity), all of which are controlled by PEMEX (Petróleos Mexico). However, Mexico exports a huge amount of crude oil, but it imports expensive gasoline from U.S. refineries. Thus, adequate planning and investments available for refining capacity are required to set up a new refinery and revamp their existing refineries. North American refinery

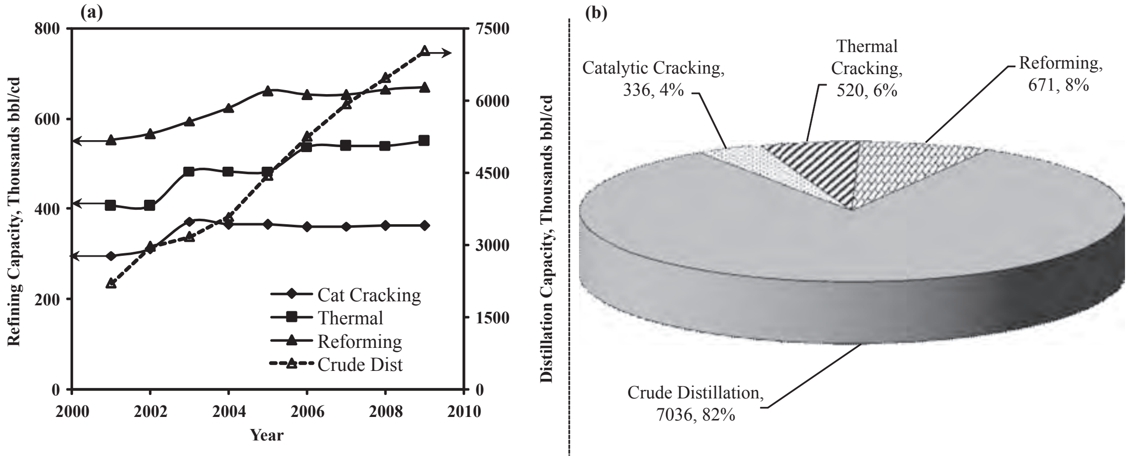


Figure 3.61—Middle Eastern refinery capacity variation since 2000 and its distribution [13].

capacity of crude-oil distillation is at approximately 16 million bbl/day of operable capacity. The new capacities are coming up mostly with hydrotreating to meet the tighter product specifications. Therefore, expansion of refining capacity in North America will primarily be through addition of secondary conversion units. Recent U.S. refineries' capacity for various processes and the variation of capacity in recent years are shown in Figure 3.62. Figure 3.62 indicates that, except for hydrotreating, North America's refining capacity remained virtually flat. In the United States, ConocoPhillips (2.22 million bbl/day), Valero (2.20 million bbl/day), and ExxonMobil (2.06 million bbl/day) own the top-most positions. In late 2009, Marathon Oil Corporation completed an expansion in Garyville, LA, and started a refinery in early 2010 with the capacity of 180,000 bbl/day. Apart from this, Saudi Arabia and Kuwait have made offers to build new refineries in the United States because the big oil companies have not stepped up to the plate.

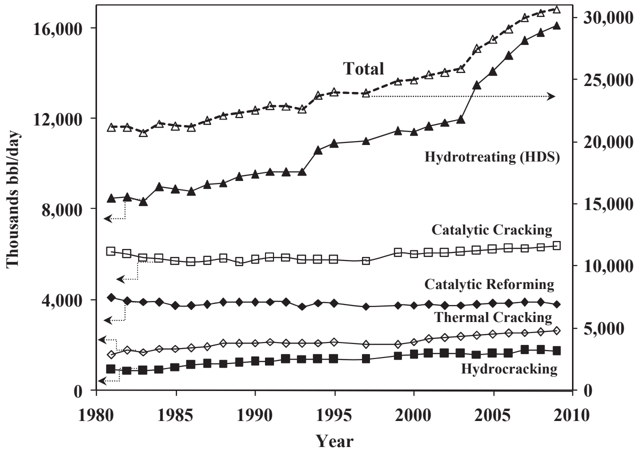


Figure 3.62—U.S. refineries' capacity for various processes and its variation in recent years [13].

3.5.2.9 REFINING IN SOUTH AMERICA

The total number of refineries available and their operating capacity for South America are reported in Table 3.11. The table indicates that Petroleos de Venezuela (PdVSA) and Petrobras are the two main refining components in South America, and they have domestic and foreign interests. PdVSA operates one of the largest refineries (940,000 bbl/day) at the Paraguana refining complex. Domestic refinery capacity stands at 1.28 million bbl/day, whereas its overall crude-oil refinery capacity is over 3 million bbl/day when including the Caribbean, United States, and Europe. One third of Venezuela's refined product is exported to U.S. markets, particularly for reformulated gasoline, which is distributed mainly by the Tulsa-based Citgo Corporation. PdVSA has been looking for partners to increase the company's ability to refine Venezuela's heavy and extra-heavy crude to increase production in coming years. PdVSA currently has two main refining joint ventures in Europe: AB Nynäs Petroleum (Sweden) and Ruhr Oel GmBH (Germany). The partnership gives PdVSA access to five refineries in Europe. In addition, regional oil industry internationalization strategic (energy integration and corporate) alliances are under discussion, the enterprises of which may have significant effects on the economic and energy integration processes in South America. The internationalization of the oil markets in this region have occurred with the arrival of major companies (Exxon-Mobil, Chevron-Texaco, and Shell), and more particularly the companies established through the privatization of European state-run enterprises (Repsol-YPF, ENI-Agip, Elf-Total-Fina, and British Petroleum-Amoco) [74].

3.5.2.10 REFINING IN EUROPE

The European (EU) refining industries are facing a tough slog of market conditions because of their new regulatory commitment and inclusion of biofuel. The petroleum refining industry is a key sector in the EU framework facing the foremost challenges. These include supply and demand

TABLE 3.11—South America Refineries and Their Capacity

	Oil Refining Profiles		
Country	**Number of Refineries**	**Total Capacity (bbl/day)**	**Comments**
Venezuela	6	3 million	Domestic six-refinery capacity stands at 1.28 million bbl/day
Brazil	13	2 million	98 % of refineries (10) are controlled by Petrobras; plans to build a new refinery with a capacity of 200,000 bbl/day
Chile	3	194,990	Controlled by ENAP (merger of Petrox and Biobio). New refinery at Biobio that will be able to produce diesel with low S content
Peru	2–4	192,950	Repsol (two refineries) controls the largest facility in the country, whereas the other four refineries are controlled by Petroperu
Ecuador	3	176,000	Ecuador has one of South America's largest markets for LPG
Argentina	3	82,000	Repsol accounts for approximately half of the country's total crude-oil refining capacity; Shell and Esso also share small part
Bolivia	5	67,000	Petrobras operates through its affiliate Empresa Boliviano de Refinación (EBR)
Suriname	1	–	Staatsoile's refinery

Data compiled from several sources.

imbalances, flat demand, expected low margin, and competition from other regions. Because of the legislation in fuel, Europe faces a major supply and demand imbalance because it is importing approximately 27 million t of middle distillate from Russia and exporting 31 million t of gas to the United States. Europe has been most impacted by falling demand in 2009, which is not forecast to recover quickly. Moreover, growing interest in biofuel will further depress oil product demand. New European capacity is primarily hydrocracking units, and some coking is expected in 2010, particularly in Spain. In addition, because of an increasing number of vehicles using diesel fuel, the largest amounts of gasoil are imported by France, Germany, and Spain. France has diversified its import sources (Russia, 18 %; the United Kingdom, Italy and Germany, 11 % each), Germany imports over half of its diesel from the Netherlands, whereas Spain imports close to 40 % of its imports from Italy. The main gasoline exporter is the Netherlands, exporting more than twice the amount of the second exporter (United Kingdom). The Netherlands supplies most of its high-specification surplus to Germany, followed by Belgium and the United States. Germany also acts as a major gasoline supplier to Switzerland, the United States, and Austria.

In Europe, refineries are found in most countries other than Luxembourg, and there are areas in Europe where there are multiple refineries at the same location (e.g., Rotterdam and Antwerp). In 2004, approximately 104 refineries were in operation in 27 EU countries, and their total refinery breakdown is shown in Figure 3.63 along with the most important processes. The EU refining industry continues investment to meet increasingly stringent emission standards. European refiners have invested an average of $6 billion each year over the past 20 years in desulfurization capacity of distillates and gasoline, the upgrading of production facilities, emission abatement equipment, and energy savings. EU overall demand for refined products is on a downward trend. However, trends vary for different types of refined products, but overall, the expected representation is of a 20 % drop in demand by 2030 compared with 2006.

3.5.2.11 REFINING IN ASIA

In the Asian region, demand and supply have recently changed in a wider spectrum than any other part of the world. In this region, two major countries (China and India) play a leading role in petroleum consumption with their enormous populations. The demand is increasing particularly for middle distillate or transportation fuel. Moreover, most countries (except China) in this region have a lack of petroleum supply and must rely on crude-oil import. The world's top refineries are installed (Reliance I and II, India), and they have the capacity to process approximately 1.24 million bbl/day. This refinery has a huge processing capacity, particularly of crude oil that has a very high amount of bottom-of-barrel. *Petroleum Intelligence Weekly* reports that nearly 1.8 million bbl/day of new refining capacity is slated in 2012, a 59 % increase in India's current processing capacity (~3 million bbl/day). The domestic product demand of 2.24 million bbl/day is forecast to increase by 2.9 % to 4.5 % over the period 2010–2015. India's refiners are looking at increasing refined product exports to the Middle East, particularly Iran, the Asia-Pacific region, Europe, and Latin America. It is expected that approximately 76 % refining capacity will be added in China and 15 % in India. Thus, China's capacity will reach more than 15 million bbl/day by 2020, and India's capacity will overtake that of Japan by 2012 to become the second-largest refiner in Asia.

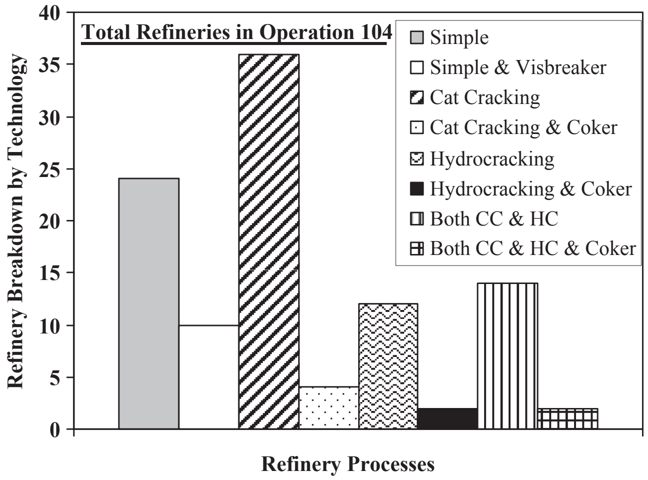


Figure 3.63—2004 refinery breakdown in Europe by technology [13].

Within 12 Asian countries, approximately 145 refineries operate at approximately 84 % refinery capacity. The major problem in Asian refineries is that out of 145 refineries, 113 do not have hydrotreating or hydrocracking capacity. Within this, 15 have hydrotreating unit capacity only in the 8–10 % range, whereas 9 have hydrocracking units working with capacity in the 12–30 % range. Only five refineries have hydrotreating and hydrocracking units with a total capacity of approximately 25 %. Therefore, significant investment is required to meet Euro III or Euro IV type transportation fuel across the region. Several new refineries are to be built in Asia over the next 5 years, particularly in China and India, whereas more developed nations are upgrading their existing facilities to meet stricter fuel standards. A total account of Asian refinery structure by country along with percentage capacity is reported in Table 3.12. China and India will continue to account for the many major projects to build new refineries or upgrade existing ones. China (Sinopec, 50 %) plans to work in a joint venture with Kuwait (KPC, 50 %) to set up their alliance in Guangdong province. China's largest oil company (PetroChina Company) recently started its new 20,000-bbl/day refinery at the port city of Qinzhou, having a 70,000-bbl/day heavy residue catalytic cracker, a 44,000-bbl/day hydrocracking unit, and a 44,000-bbl/day continuous reforming unit. On the other side, HPCL, India upgraded (mainly for ULSD) its two refineries to meet the Euro IV emission standard. Overall, in 2009 Asia added 2.2 million bbl/day of refining capacity, the largest distillation capacity addition in the region's history. In 2010, estimated demand in the Asia-Pacific region grew strongly at 1.1 million bbl/day, whereas net refining capacity additions reached only 820,000 bbl/day.

3.5.2.12 REFINERY IMPACTS ON GHG EMISSIONS (ENVIRONMENTAL ISSUE)

In general, petroleum refining is a capital-intensive business that must conform to the stringent environmental regulations of the processing industry and deal with declining refining margins, political instability, increasing

TABLE 3.12—Asian Refinery Structure by Country in Percent Capacity

Country	Number of Refineries	Thermal Cracking	Coking	Catalytic Cracking	Hydrocracking	Hydrotreating
China	47	–	6.7	20.5	2.8	1.1
Japan	29	–	–	–	–	–
India	19	4.4	2.1	7.9	2.6	3.8
Indonesia	10	5.9	3.3	10.2	10	1.2
Thailand	7	2.6	–	11.8	2.9	14.3
Malaysia	6	–	3.7	–	5.5	6.1
Pakistan	6	–	–	–	–	–
South Korea	5	–	–	–	–	–
Singapore	3	16.4	–	5.1	7.4	20.7
Philippines	3	5.2	–	5.8	–	23.7
Burma	3	–	–	–	–	–
Myanmar	2	–	16.3	–	–	–
Brunei	1	–	–	–	–	–
Bangladesh	1	30.3	–	–	3.6	–
Sri Lanka	1	26.7	–	–	–	4.2

Data collected compiled from several sources.

risk of war, and terrorist attacks. Higher pressures have recently been exerted on refiners to optimize performance and find the best combination of feed and processes to produce stable products that meet the stricter product specifications. For example, an increase in desulfurization will result in increased refinery GHG emissions, but these increases are required to achieve near-zero-sulfur transportation fuel. The production of low-sulfur fuels is generally more energy-intensive, often requiring higher temperatures and pressures and more hydrogen consumption. Moreover, the hydrocarbons conversion process is extremely CO_2-intensive, creating 8–15 t of CO_2 for every ton of hydrogen used [75]. In addition, removal of sulfur from diesel (350–50 ppm) results in an approximately 3 % increase in refinery emissions. To get to even lower sulfur levels (50–10 ppm), CO_2 emissions were increased by an additional 4.3 % for gasoline refining and 1.8 % for diesel. The literature data suggested that the total impact on refinery emissions for production of gasoline and diesel at 10 ppm sulfur would be worse than additive, with a 12.9 % increase in CO_2 emissions to achieve 10 ppm sulfur diesel and gasoline [76].

3.5.2.13 ROLE OF CATALYTIC CONVERSION AND REFINERY CAPACITY

In refining, catalysis has undoubtedly played a very important role since the mid-20th century and the development of the refining and petrochemical industries. Some limited but important dates are reported in Figure 3.64, indicating the catalyst development and the catalyst type used in the refinery [59]. The mounting concerns over the environment and the growing need to process heavier/dirtier crude oils will make it mandatory to develop new catalysts for producing high-quality, ultraclean fuels. Thus, new refining goals are emerging. The efficient economical conversion of these feedstocks requires improvements in the control of the individual reactions, better management of hydrogen, and more selective removal of heteroatoms. Development of a next generation of catalysts and processes for heavy feedstocks requires molecular-scale understanding of the crude components, including the interactions between large, complex molecules such as asphaltene, resin, metal-porphyrines, etc. Since petroleum is composed of complex hydrocarbon mixtures, it is not easy to identify each individual component and its catalytic reaction chemistry. Therefore, it is desirable to understand what the feedstocks components are, how they interact with catalysts, how partial conversions (such as hydrogenation) affect the reactant species and their interactions, and how construction of the aggregates takes place and affects the reactivities of the molecules.

3.5.3 Worldwide Natural Gas Conversion and Liquefaction Plants

3.5.3.1 NATURAL GAS OVERVIEW

Figure 3.65 shows the latest assessment of natural gas as a function of regional distribution. The top consumer of natural gas is the United States. The natural gas consumption in the non-OECD countries grows more than twice as fast as in the OECD countries. Production increases in the non-OECD region account for more than 80 % of the growth in world production. The worldwide demand (consumption) is gradually increasing, particularly in Europe, the Middle East, and Asia, whereas in North America and Africa its growth remains constant, as shown in Figure 3.66.

Natural gas generally contains 70–90 % methane at its natural source point. The balance of the gas is usually ethane, propane, butane, water, nitrogen, CO_2, and hydrogen sulfide (H_2S). Natural gas from different wells is widely different in composition. The main undesirable

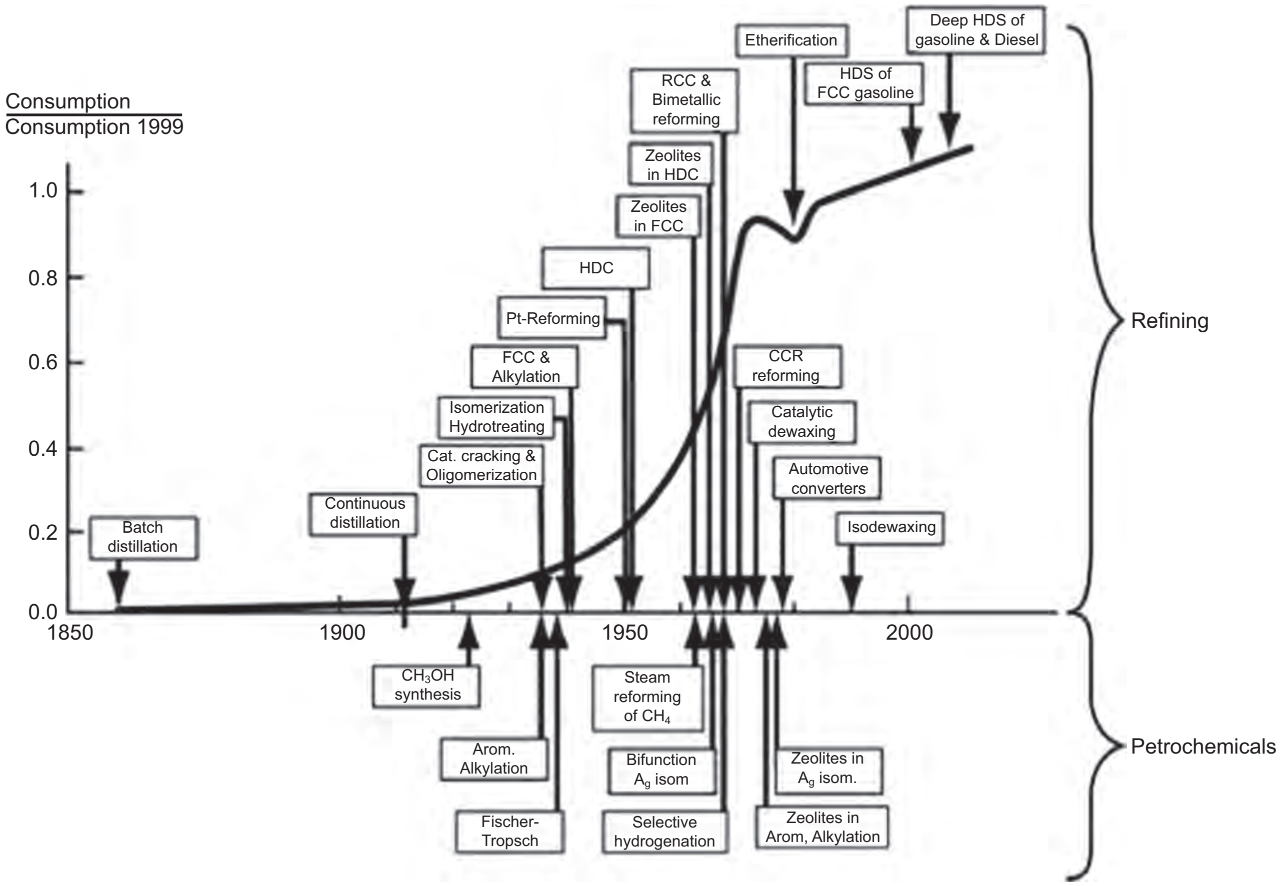


Figure 3.64—Some important dates in the development of the refining and petrochemical industries. Alkyl, alkylation; A8, C8 aromatics; Arom., aromatics; Bifunct., bifunctional; CCR, continuous catalyst regeneration; FCC, fluid catalytic cracking; HDC, hydrocracking; HDS, hydrodesulfurisation; RCC, residual catalytic cracking [59].

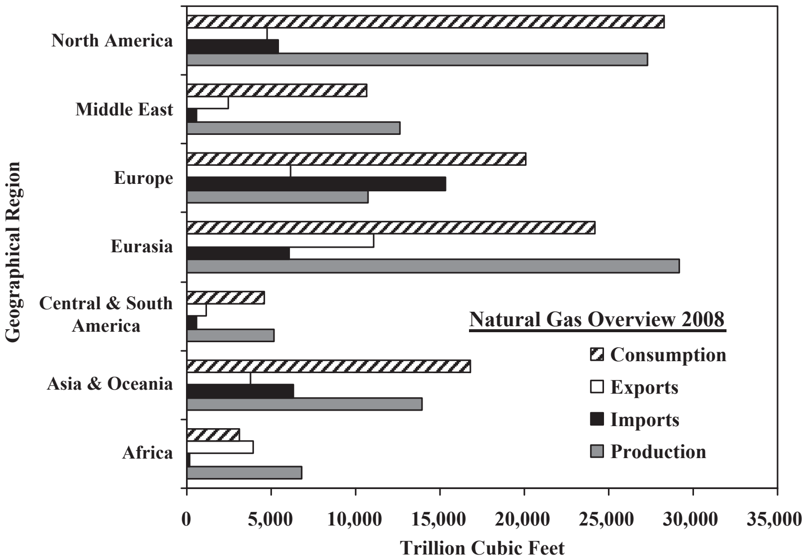


Figure 3.65—An overview of natural gas as a function of geographical region [13].

impurities are CO_2 and H_2S. The former does not need to be completely removed, but the latter is highly poisonous and needs to be removed to a concentration of less than 1 ppm. The standard technology applied for removing natural gas contaminants is by saturation of natural gas into a solution, usually with an amine-based solvent, although use of membranes to process natural gas is a rapidly growing area of technology.

After purification, natural gas is carried on-board as a cryogenic liquid (LNG) or in the form of high-pressure

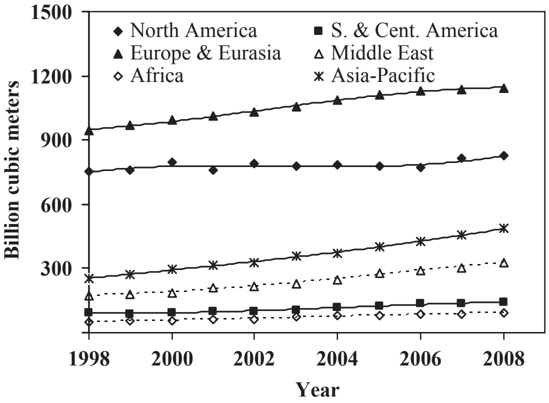


Figure 3.66—Natural gas consumption [13].

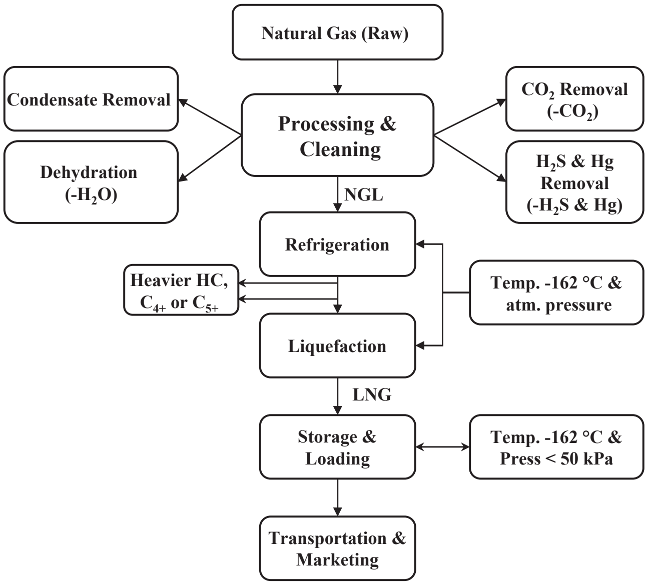


Figure 3.67—A typical integrated NGL and LNG processing plant in which the NGL and LNG are purified by removing any condensates such as water, oil, and mud as well as other gases such as CO_2 and H_2S and sometimes solids as such as mercury. The gas is then cooled down in stages (–35, –90, and –155°C) until it is liquefied. LNG is finally stored in storage tanks and can be loaded and shipped.

compressed gas (CNG). Because LNG fuel tanks are much more expensive than CNG tanks, vehicles usually carry natural gas fuel as CNG rather than as LNG. Thus, LNG offers an energy density comparable to petrol and diesel fuels and produces less pollution, but its production is relatively higher cost and it must be stored in expensive cryogenic tanks, which prevents its widespread use in commercial applications. A schematic flow diagram of natural gas liquid separation from its base components is shown in Figure 3.67. The global LNG industry has seen dramatic growth since the late 1990s. According to BP, global LNG trade has increased from 113 million t/year (MMtpy) in 2000 to 154 MMtpy in 2006. The same source expects LNG trade to reach 524 MMtpy by 2030. In 2008, a combined liquefaction capacity of 207.01 MMtpy was provided by 31 terminals in 17 countries supplying LNG to 59 regasification terminals with a combined capacity of 402.15 MMtpy in 19 countries [4].

3.5.3.2 NATURAL GAS PROCESSING

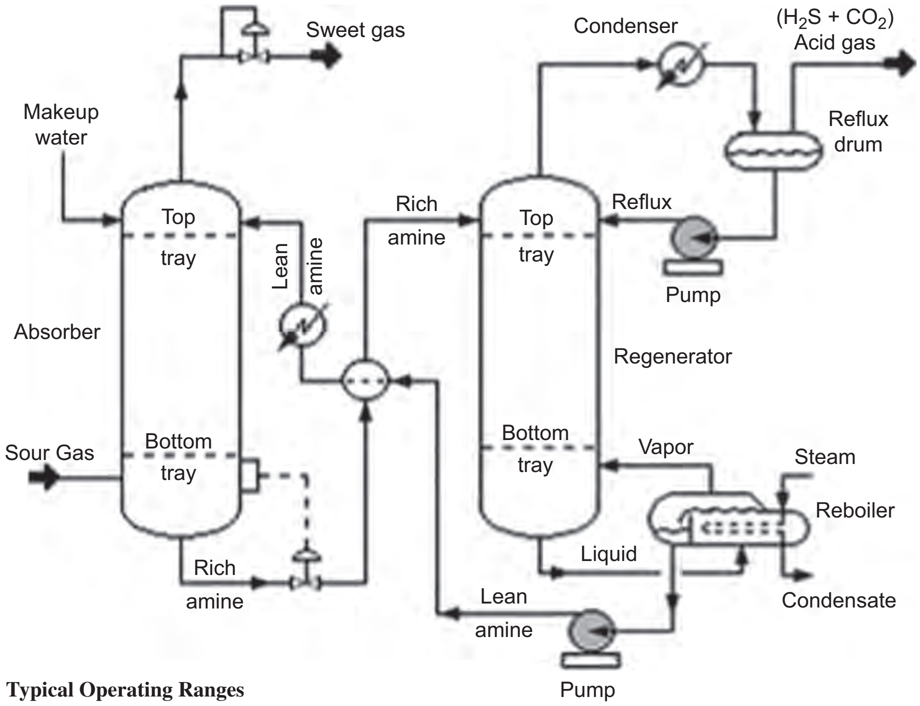
Natural gas processing refers to the removal of ethane, propane, butane, and heavier components from a gas stream. Various conventional separation methods are presently being used to remove acid gases such as CO_2 and H_2S from crude natural gas [77,78]. These methods include gas absorption in liquid solvents, adsorption on solid adsorbents, and chemical conversion.

3.5.3.2.1 Conventional Process for Natural Gas Processing

The selective removal of impurities may depend on the acid-base reaction. The selection of the best amine/solvent for gas treating is not a trivial task. Amine gas treating, also known as gas sweetening and acid gas removal, refers to a group of processes that uses aqueous solutions of various alkylamines to remove H_2S and CO_2 from gases. There are several amines available to remove contaminants such as CO_2, H_2S, and organic sulfur compounds from sour gas streams, as shown in Figure 3.68. The most commonly used amines are methanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diglycolamine (DGA), diisopropanolamine (DIPA), and triethanolamine (TEA). A mixture of amines can also be used to customize or optimize the acid gas recovery. However, selection of amine composition and its type also depend on the temperature, pressure, and source gas composition, and purity requirements must be considered. Primary amines are more effective at atmospheric pressure conditions, and MEA can remove H_2S to less than 4 ppm, but it is effective up to 100 ppm for CO_2 removal. DGA is another primary amine that is typically used for the removal of CO_2, H_2S, carbonyl sulfide (COS) gas, and mercaptanes. Secondary amines (e.g., DEA) remove CO_2 and H_2S, but they generally require higher pressure than MEA to meet overhead specifications. Because DEA is a weaker amine than MEA, it requires less energy for stripping. Tertiary amines such as MDEA are often used to selectively remove H_2S, especially for cases with high CO_2-to-H_2S ratios as in natural gas. MDEA can remove H_2S to 4 ppm but maintain 2 % or less CO_2 in the treated gas using relatively less energy for regeneration than that for DEA. Because MDEA is not prone to degradation, corrosion is thus low and a reclaim is unnecessary. Operating pressure can range from atmospheric (typical of a tail-gas-treating unit) to over 70 bar. With mixed solvents, the solvent can be adapted to optimize the sweetening process; for example, adding a primary and secondary amine to MDEA can increase the rate of CO_2 absorption without compromising the advantages of MDEA. Advantages of using such solvents are usually increased mercaptane pickup, lower regeneration energy, and selectivity to H_2S. Apart from the amine, it is also possible to use solid desiccant (e.g., iron sponges) to remove the sulfide and CO_2 from the natural gas.

3.5.3.2.2 Membrane Separation Process for Natural Gas Processing

Membrane separation processes are a relatively new development over the last 2 decades as a promising alternative to conventional separation processes and offer several important advantages [78–80]. These membranes are made of



Typical Operating Ranges
Absorber: 35–50 °C and 5-205 atm of absolute pressure
Regenerator: 115–126 °C and 1.4–1.7 atm of absolute pressure at tower bottom

Figure 3.68—Process flow diagram of a typical amine sweetening unit used in industrial plants.

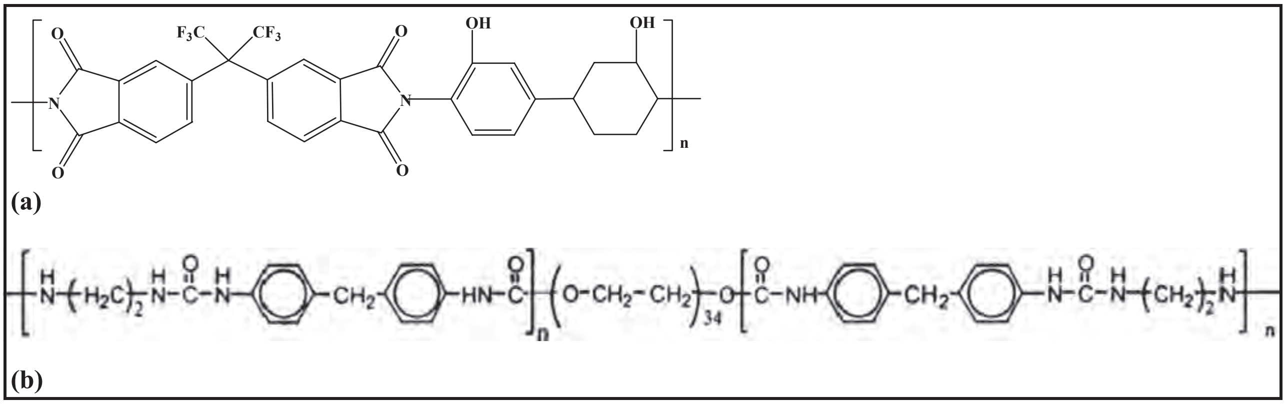


Figure 3.69—Type of natural gas separation membrane structure for selective removal of CO_2: (A) fluorine-containing polyimide 6FDA-HAB-glassy polymer and H_2S and (B) poly(ether urethane urea) (PEUU)-rubbery polymer [81].

polymeric-type materials, the structure of which is shown in Figure 3.69. Generally, polymer membranes are used commercially to separate CO_2 and H_2S from natural gas. The membrane permeation is a pressure-driven process. The partial pressure difference between the feed side and the permeate side has the greatest impact on the performance of a membrane separator. This pressure difference directly influences the membrane area required to achieve the desired separation at given feed conditions. Another important characteristic of the process is the ratio of feed pressure to permeate pressure, which has to be established in accordance with the membrane selectivity to achieve an efficient separation. The gas purity can be increased by the installation of more membrane (one stage or multistage) area or the increase of the pressure ratio (feed pressure to permeate pressure). Higher feed flow rates reduce the purity but increase the permeate concentration of the faster-permeating compound. The upgrading of low-quality natural gas by membrane separation processes has been reported by simultaneously or separately operating two different types of polymer membranes that exhibit high CO_2/methane (CH_4) and H_2S/CH_4 selectivities along with process design, optimization, and economic assessment studies [81].

3.5.3.3 NATURAL GAS DEMAND AND SUPPLY

The natural gas sector has been a tight supply and demand balance, with rising energy prices followed by demand weakening and spot-price plummeting. After a 1 % increase in 2008, OECD gas demand fell by 4 % during 2009 and 2010. In the United States, natural gas demand increased 0.7 % in 2008 to 23.2 trillion ft3. Domestic natural gas production increased 7.7 % in 2008 over 2007, the largest increase since 1984. Demand for natural gas depends highly on the time of year and is highest during the winter and lowest in the summer.

3.5.4 Worldwide Coal Conversion and Gasification-Liquefaction Plants

3.5.4.1 COAL OVERVIEW

Among the fossil fuels, natural gas is the cleanest whereas coal is the most difficult hydrocarbon source. Coal is a hard, black-colored, rock-like substance. It is made up of carbon, hydrogen, oxygen, nitrogen, and varying amounts of sulfur. There are three main types of coal: anthracite (hardest), bituminous, and lignite (softest). It is expected that coal could become the dominant fuel by the middle of the 21st century. Approximately 40 % of the global electricity generated comes from coal. Coal is predominantly used by the electricity-generation sector, which uses more than 3 times as much coal as other industries, particularly the steel industry. The use of coal has recently been growing faster than oil or gas use, particularly in China and India. Therefore, the price of coal has gone up approximately 1.5 times within the last 10 years ($30 per short ton in 2000 to ~$150 per short ton as of September 2008); however, at the end of 2008, the price per short ton had declined to $111.5. The most important countries that have more than two thirds of the world's coal reserves are China, Russia, the United States, and India [13]. China and India have plans to construct a new coal-fired plant, whereas the United States generated approximately 150 new plants in 2007. It is possible that coal's prospects in Europe are also currently undergoing some kind of resurgence, especially given the large reserves in the region's biggest producer—Poland. Indeed, across the EU, 50 new coal-fired plants are being considered for construction over the next few years.

3.5.4.2 COAL GASIFICATION AND LIQUEFACTION

Coal gasification can be used to produce syngas, a mixture of CO and hydrogen (H_2) gas. This syngas can then be converted into transportation fuels such as gasoline and diesel by using the FT process. During gasification, the coal is mixed with oxygen and steam (water vapor) while also being heated and pressurized. During the reaction, oxygen and water molecules oxidize the coal into CO and H_2. This process has been conducted in underground coal mines and in coal refineries.

$$\text{(Coal)} + O_2 + H_2O \rightarrow H_2 + CO \text{ (syngas)} \tag{3.1}$$

On the basis of refiner desire, the syngas is collected and processed in a FT reaction for gasoline yield; if hydrogen is the desired end product, then the syngas is fed into the water gas shift reaction in which more hydrogen is liberated.

$$CO + H_2O \text{ (syngas)} + \text{FT reaction} \rightarrow \text{gasoline pool (liquefaction)} \tag{3.2}$$

$$CO + H_2O \text{ (syngas)} + \text{water shift reaction} \rightarrow CO_2 + H_2 \tag{3.3}$$

In the past, coal was converted to make coal gas, which was piped to customers to burn for illumination, heating, and cooking.

3.5.4.3 COAL PROCESSING INTO NATURAL GAS

The natural gas cost of production is expected to be significantly lower than current prices of new drilled natural gas and imported LNG that meets all high-grade, natural-gas-quality specifications.

The hydromethanation process is an elegant and highly efficient process by which natural gas is produced through the reaction of steam and carbonaceous solids in the presence of a catalyst. The process enables the conversion of low-cost feedstock such as coal, petroleum coke, and biomass into clean, high-purity CH_4. The chemistry of catalytic hydromethanation involves water steam and carbon to produce CH_4 and CO_2.

$$2C + 2H_2O \rightarrow CH_4 + CO_2 \tag{3.4}$$

Thus, hydromethanation is an economic and clean process for the production of natural gas by using an environmentally friendly process.

3.6 CONCLUSIONS

The main source of energy remains fossil fuel, which will continue for the next several decades. After this, the global economy will have to transition from oil to renewable energy, such as solar, wind, ethanol, and hydrogen. The world continues with the current energy-related policies, with heavier and complex crude-oil processing capacities. Thus, refinery obligations are to enhance their capacity to convert black gold into usable consumer products, which is essential for transforming crude into gasoline, diesel, or household fuel. The refiners are facing two dimensional problems: (1) the refining industry's need for upgrading capacity (i.e., upgrading oil from sour to sweeter crudes rather than primary distillation capacity in refining); and (2) most important are the increasingly tightening environmental specifications on transportation fuels. High oil prices are still being propped up by a shortage of refinery capacity, and there is little sign of the bottleneck easing at the present time. For the coming decades, the use of heavy and unconventional oils, natural gas, biofuel, and coal will increase while in many parts of the world resources for conventional oil diminish. The Middle East will remain as the main supplier of crude oil and natural gas for many years to come. Toward the middle of the century, the use of renewable sources of energy will increase and refineries should focus on providing feeds to petrochemical industries rather than fuels for motor vehicles.

ACKNOWLEDGMENTS

The permission to use some graphs and charts by various organizations is greatly appreciated. In particular, I am grateful to the Commonwealth Copyright Administration of the Government of Australia, the Survey of Energy Resources, World Energy, the EWG, Oxford Analytica, Ltd., the BP Economics Team, and the EIA of the U.S. Department of Energy.

REFERENCES

[1][Mansoori, G.A., "A Unified Perspective on the Phase Behavior of Petroleum Fluids," *Int. J. Oil, Gas Coal Technol.*, Vol. 2, 2009, pp. 141–167.

[2] Horn, M.K., "Giant Fields 1868–2004 (CD-ROM)," in *Giant Oil and Gas Fields of the Decade, 1990–1999*, AAPG/Datapages Miscellaneous Data Series, version 1.2, American Association of Petroleum Geologists, Houston, TX, 2004.

[3] Riazi, M.R., Alhadad, A., and Mansoori, G.A., "An Update on the Developments in Petroleum Production Research in the Middle East," *J. Petrol. Sci. Eng.*, Vol. 55, 2007, pp. 1–6.

[4] "BP Statistical Review of World Energy," http://www.bp.com/statisticalreview (accessed June 22, 2009).

[5] "Energy Security," Institute of the Analysis of Global Security, Potomac, MD, 2003, http://www.iags.org/n1020032.htm.

[6] "Official Energy Statistics from the U.S. Government, International Energy Outlook 2009, Natural Gas," http://www.eia.gov/forecasts/archive/ieo09/index.html.

[7] "Worldwide Look at Reserves and Production," *Oil Gas J.*, Vol. 106, 2008, pp. 22–23.

[8] Kramer, A.E., "Russian Will Lead Gas Exporting Alliance," *New York Times*, December 9, 2009, http://www.nytimes.com/2009/12/10/business/energy-environment/10gas.html?_r=1.

[9] Jojarth, C., "The End of Easy Oil: Estimating Average Production Costs for Oil Fields around the World," Working Paper No. 81, Center on Democracy, Development, and the Rule of Law, Stanford University, Palo Alto, CA, 2008, http://iis-db.stanford.edu/pubs/22150/No_81_Christine_Jojarth_-_Cost-Model_PESD080312.pdf.

[10] Madden, C., Voyt, T., "The End Of 'Easy Oil': How IT Is Critical to Maintaining Successful E&P Operations," Hart Webinar Series, April 22, 2011, https://secure.oilandgasinvestor.com/webinars/?eventid=48.

[11] Riazi, M.R., "Energy, Economy, and Environment and Sustainable Development in the Middle East and North Africa," *Int. J. Oil, Gas Coal Technol.*, Vol. 3, 2010, pp. 201–244.

[12] "World Population Prospects: The 2008 Revision," Population Division of the Department of Economic and Social Affairs of the United Nations Secretariat, http://www.un.org/esa/population/publications/wpp2008/wpp2008_highlights.pdf.

[13] "International Energy Outlook 2010," U.S. Energy Information Administration, http://www.eia.gov/forecasts/archive/ieo09/index.html.

[14] "US Energy Consumption," Maxwell School, Syracuse University, Syracuse, NY, 2009, http://wilcoxen.maxwell.insightworks.com/pages/804.html.

[15] Labastie, A., "16 Facts about Energy, Oil & Gas and SPE," paper presented at the Repsol Conference, Madrid, Spain, 2009.

[16] Makarov, A., "New Energy Consumption and Supply Trends (Worldwide and Russia)," 19th World Energy Congress, Sydney, Australia, September 5–9, 2004.

[17] Lakatos, I., "Global Oil Demand and Role of Chemical EOR Methods in the 21st Century," *Int. J Oil, Gas and Coal Technol.*, Vol. 1, 2008, pp. 46–64.

[18] "World Energy Outlook 2009," International Energy Agency, Paris, 2009.

[19] "Annual Energy Outlook 2009 (with Projections to 2030)," U.S. Energy Information Administration, Washington, DC, 2009, http://www.eia.gov/forecasts/archive/aeo09/index.html.

[20] "Total Primary Energy Consumption," ENER 26, European Environmental Agency, Copenhagen, Denmark, 2009, http://eea.eionet.europa.eu/Public/irc/eionet-circle/energy/library.

[21] "Annual Energy Review 2008," U.S. Energy Information Administration, Washington, DC, 2009, http://www.eia.gov/FTPROOT/multifuel/038408.pdf.

[22] Zabel, G., "Peak People: The Interrelationship between Population Growth and Energy Resources," *Energy Bulletin*, April 20, 2008, www.energybulletin.net/node/48677.

[23] "Reserves and Production Show Little Change in 2008," *World Oil*, September 2009, pp. 51–52.

[24] "Final Energy Consumption Intensity," ENER 21, European Environmental Agency, Copenhagen, Denmark, 2009, http://eea.eionet.europa.eu/Public/irc/eionet-circle/energy/library.

[25] German Advisory Council on Global Change, Berlin, 2003, www.rtcc.org/2009/html/renew-solar-1.html or http://www.wbgu.de/en/home.

[26] "Comparison of Selected Reserves and Resource Classifications and Associated Definitions," Society of Petroleum Engineers, Oil and Gas Reserves Committee, http://www.spe.org/industry/docs/OGR_Mapping.pdf.

[27] "Why a Universal Language for Evaluating Reserves Is Needed," Society of Petroleum Engineers, Oil and Gas Reserves Committee, 2006, http://www.spe.org/industry/docs/Reserves_White_Paper.pdf.

[28] "Petroleum Resources Management System," Society of Petroleum Engineers/American Association of Petroleum Geologists/WPC/SPEE, http://www.spe.org/industry/docs/Petroleum_Resources_Management_System_2007.pdf.

[29] Raut, B., Patil, S.L., Dandekar, A.Y., Fisk, R., Maclean, B., and V. Hice, "Comparative Study of Compositional Viscosity Prediction Models for Medium-Heavy Oils," *Int. J. Oil Gas Coal Technol.*, Vol. 1, 2008, pp. 229–249.

[30] "Resources to Reserves—Oil and Gas Technologies for the Energy Markets of the Future," International Energy Agency, Paris, 2005, www.iea.org/press/pressdetail.asp?PRESS_REL_ID=159.

[31] Kovarik, B., "The Oil Reserve Fallacy: Proven Reserves Are Not a Measure of Future Supply," Radford University, http://radford.edu/~wkovarik/oil/.

[32] *BBC World News TV*, "China Invests in Canada Oil Sands," October 31, 2009, http://news.bbc.co.uk/2/hi/business/8231006.stm.

[33] "Heavy Oil, Understanding Heavy Oil," Schlumberger, Houston, TX, 2009, http://www.slb.com/services/industry_challenges/heavy_oil.asp.

[34] "Resources to Reserves 2010," International Energy Agency, Paris, 2010, http://www.iea.org/papers/2010/Flyer_RtoR2010.pdf.

[35] "Heavy Oil," Topic Paper #22, in *Facing the Hard Truths about Energy: A Comprehensive View to 2030 of Global Oil and Natural Gas*, National Petroleum Council, Washington, DC, 2007, http://www.npc.org/Study_Topic_Papers/29-TTG-Unconventional-Gas.pdf.

[36] "Unconventional Gas," Topic Paper #29, in *Facing the Hard Truths about Energy: A Comprehensive View to 2030 of Global Oil and Natural Gas*, National Petroleum Council, Washington, DC, 2007, http://www.npchardtruthsreport.org/topic_papers.php.

[37] Newell, R.G., "Shale Gas: A Game Changer for U.S. and Global Gas Markets?" Flame, European Gas Conference, March 2, 2010, Amsterdam, The Netherlands.

[38] Larson, D., 2009, "The Financial Crisis and Its Impact on the Energy Industry," Society of Petroleum Engineers Research and Development Conference March 3–4, 2009, Lisbon, Portugal.

[39] Hubbert, M.K., "Nuclear Energy and the Fossil Fuels," American Petroleum Institute, San Antonio, TX, 1956, pp. 7–25.

[40] "US All States: Oil Production," Peak Oil Australia, 2009, www.peakoil.org.au.

[41] Nashawi, I.S., Malallah, A., and Al-Bisharah, M., "Forecasting World Crude Oil Production Using Multicyclic Hubbert Model," *Energy Fuels*, Vol. 24, 2010, pp. 1788–1800.

[42] Graefe, L., "Federal Reserve Bank of Atlanta Economic Review, The Peak Oil Debate," Vol. 94, No. 2, 2009.

[43] "Peak Oil Production and Reserves—Peak Oil July 2008," Special Reports 118, Energy Insight, 2009, www.energyinsights.net/.

[44] Strahan, D., "Coaled Comfort," The Geological Society, 2008, http://www.geolsoc.org.uk/gsl/geoscientist/features/page3338.html.

[45] Energy Watch Group, "Wind Power in Context–A Clean Revolution in the Energy Sector," Germany's Energy Watch Group, Berlin, 2009, http://www.energywatchgroup.org/fileadmin/global/pdf/2009-01_Wind_Power_Report.pdf.

[46] Grunwald, M., "The Clean Energy Scam," *Time*, April 7, 2008.

[47] "Biofuel Production," U.N. Environment Programme, 2009, http://maps.grida.no/go/graphic/biofuel-production.

[48] Holmgren, J., “Biofuels: Unlocking the Potential,” presented at the Joint American Chemical Society/American Institute of Chemical Engineers Meeting, Chicago, IL, January 24, 2008.

[49] Feygin, M., and Satkin, R., “The Oil Reserves-to-Production Ratio and Its Proper Interpretation,” *Natl. Resourc. Res.*, Vol. 13, 2004, pp. 57–60.

[50] “The World Fact Book,” Central Intelligence Agency, Washington, DC, 2009, https://www.cia.gov/library/publications/the-world-factbook/.

[51] Buster, J., “Overpopulation,” Oxford Analytica, New York, 2007, http://www.oxan.com.

[52] Heinrich, H., “Introduction to Refining,” in *Crude Oil Petroleum Products Process Flow Sheets*, J.-P. Wauquier, Ed., Technip IFP, Paris, France, 1995.

[53] Maples, R.E., *Petroleum Refining Process Economics*, PennWell Books, Tulsa OK, 1993.

[54] Warren R.T., and Leena K., “Special Report: Global Refining Capacity Advances; US Industry Faces Uncertain Future,” *Oil Gas J.*, Vol. 107, 2009, http://www.ogj.com/index/article-tools-template/_printArtic...l/volume-107/issue-47/processing/special-report_global.html.

[55] “OSHA Technical Manual: Section IV: Chapter 2, Petroleum Refining Processes,” Occupational Safety & Health Administration, http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.

[56] *Biodiesel Handling and Use Guidelines*, 4th ed., National Renewable Energy Laboratory: Innovation for Our Energy Future, (NREL/TP-540-43672), 2009, U.S. Department of Energy, Washington, D.C.

[57] “World Oil Outlook 2009,” Organization of the Petroleum Exporting Countries, Vienna, Austria, www.opec.org.

[58] “Petroleum & Other Liquids,” U.S. Energy Information Administration, 2008, http://www.eia.doe.gov/oil_gas/petroleum/info_glance/petroleum.html or http://www.eia.doe.gov/oiaf/aeo/index.html.

[59] Marcilly, C., “Present Status and Future Trends in Catalysis for Refining and Petrochemicals,” *J. Catal.*, Vol. 216, 2003, pp. 47–62.

[60] Ramírez, J., Rana, M.S., and Ancheyta, J., “Characteristics of Heavy Oil Hydroprocessing Catalysts,” in *Hydroprocessing of Heavy Oil and Residua*, J. Ancheyta and J.G. Speight, Eds., Taylor & Francis, New York, 2007.

[61] Courty, P., and Gruson, J.F., “Refining Clean Fuels for the Future,” *Oil Gas Sci. Technol.*, Vol. 56, 2001, pp. 515–524.

[62] Ancheyta, J., and Rana, M.S., “Future Technology in Heavy Oil Processing,” in *Encyclopedia of Life Support Systems (EOLSS)*, Developed under the Auspices of the U.N. Educational, Scientific, and Cultural Organization, EOLSS Publishers, Oxford, United Kingdom, 2008.

[63] Ancheyta, J., Rana, M.S., and Furimsky, E., “Hydroprocessing of Heavy Petroleum Feeds: Tutorial,” *Catal. Today*, Vol. 109, 2005, pp. 3–15.

[64] Chaumette, P., Courty, P.R., and Raimbault, C., “Synthetic or Reformulated Fuels: A Challenge for Catalysis,” *Oil Gas Sci. Technol.*, Vol. 54, 1999, pp. 357–363.

[65] “The Emerging Oil Refinery Capacity Crunch, A Global Clean Products Outlook,” ICF Consulting, Fairfax, VA, 2005, pp. 1–9.

[66] Rana, M.S., Samano, V., Ancheyta, J., and Diaz, J.A.I., “A Review of Recent Advances on Process Technologies for Upgrading of Heavy Oils and Residua,” *Fuel*, Vol. 86, 2007, pp. 1216–1231.

[67] Ancheyta, J., and Speight, J.G., Eds., *Hydroprocessing of Heavy Oil and Residua*, Taylor & Francis, New York, 2007.

[68] Larson, O.A., and Beuther H., “Processing Aspects of Vanadium and Nickel in Crude Oils,” *Prepr. Am. Chem. Soc. Div. Pet. Chem.*, Vol. 11, 1966, pp. B95–B103.

[69] Ancheyta, J., Trejo, F., and Rana, M.S., *Asphaltenes: Chemical Transformation during Hydroprocessing of Heavy Oils*, Taylor & Francis, New York, 2010.

[70] “End-Use Petroleum Product Prices and Average Crude Oil Import Costs,” International Energy Agency, Paris, 2010.

[71] Stanislaus, A., Marafi, A., and Rana, M.S., “Recent Advances in the Science and Technology of Ultra Low Sulfur Diesel (ULSD) Production,” *Catal. Today*, Vol. 153, 2010, pp. 1-68.

[72] “ULSD Hydrotreating Catalysts,” Albemarle Diesel, http://www.albemarle.com/Products_and_services/Catalysts/HPC/Hydrotreating_catalysts/Mid_distillate/DieselULSD/.

[73] Topsøe, H., Hinnemann, B., Nørskov, J.K., Lauritsen, J.V., Besenbacher, F., Hansen, P.L., Hytoft, G., Egeberg, R.G., and Knudsen, K.G., “The Role of Reaction Pathways and Support Interactions in the Development of High Activity Hydrotreating Catalysts,” *Catal. Today*, Vol. 12, 2005, pp. 107–108.

[74] Campos, A.F., Tolmasquim, M.T., and Alveal, C., “Restructuring the Oil Segment in South America: Public Policy, Private Capital and Energy Integration,” *Oil Gas Sci. Technol.*, Vol. 61, 2006, pp. 415–431.

[75] Martino, G., and van Wechem, H., “Current Status and Future Developments in Catalytic Technologies Related to Refining and Petrochemistry,” paper presented at the 17th World Petroleum Congress, Rio de Janeiro, Brazil, September 1–5, 2002.

[76] Fredriksson, M., “Impact of a 10 ppm Sulphur Specification for Transport Fuels on the EU Refining Industry,” Report No. 00/54, Concawe, Brussels, Belgium, 2000.

[77] Kohl, A., and Nielson, R., *Gas Purification*, 5th ed., Gulf Publishing Company, Houston, TX, 1997.

[78] Spillman, R.W., “Economics of Gas Separation Membrane Processes,” in *Membrane Separation Technology, Principles and Applications*, R.D. Noble and S.A. Stern, Eds., Elsevier, Amsterdam, 1995, pp. 589–667.

[79] Zolandz, R.R., and Fleming, G.K., “Gas Permeation,” in *Membrane Handbook*, W.S.W. Ho and K.K. Sirkar, Eds., Van Nostrand Reinhold, New York, 1992, pp. 54–101.

[80] Koros, W.J., and Fleming, G.K., “Membrane-Based Gas Separation,” *J. Membr. Sci.*, Vol. 83, 1993, pp. 1–80.

[81] Hao, J., Rice, P.A., and Stern, S.A., “Upgrading Low-Quality Natural Gas with H_2S and CO_2-Selective Polymer Membranes, Part I. Process Design and Economics of Membrane Stages without Recycle Streams,” *J. Membrane Sci.*, Vol. 209, 2002, pp. 177–206.

4

Properties, Specifications, and Quality of Crude Oil and Petroleum Products

M.R. Riazi[1] and Semih Eser[2]

ABBREVIATIONS

API	American Petroleum Institute
CH	Carbon to hydrogen weight ratio
CR	Carbon residue
CN	Cetane number
DAO	Deasphalted oil
EP	End point (same as FBP)
FBP	Final boiling point
FVI	Fuel volatility index
GC	Gas chromatography
IBP	Initial boiling point
IP	Institute of Petroleum (UK Petroleum Standards)
ISO	International Organization of Standards
LC	Liquid chromatography
MS	Mass spectrometry
PNA	Paraffins, naphthenes, and aromatics content of a petroleum mixture
RVP	Reid vapor pressure
SD	Simulated distillation
SEC	Size exclusion chromatography
SG	Specific gravity
SUS	Saybolt universal second
TBP	True boiling point
TCD	Thermal conductivity detector
TVP	True vapor pressure
ULSD	Ultra low sulfur diesel
UOP	Universal oil products
VGC	Viscosity gravity constant

4.1 BOILING POINT AND DISTILLATION DATA

The boiling point of a pure compound is the temperature at which vapor and liquid exist together at equilibrium. Boiling point varies with pressure, and the temperature at which a liquid's vapor pressure equals 1 atm is called the "normal boiling point" or simply the "boiling point." The boiling point decreases with decreasing pressure. The boiling point of pure hydrocarbons increases with the increasing carbon number and molecular weight. Naphthenic and aromatic compounds have higher boiling points than those of paraffins with the same carbon number. Boiling points of heavy hydrocarbons are usually measured at low pressures (i.e., 1, 10, and 50 mmHg) and reported as atmospheric pressure equivalent boiling points because at these temperatures they may go through thermal decomposition.

Whereas for pure compounds the boiling point is a single temperature, for mixtures such as petroleum products the boiling point covers a range from initial boiling point (IBP) to a final boiling point (FBP) or end point (EP) when the highest-boiling compounds evaporate. Measurement of FBP is not very accurate and usually boiling points at 95 vol % distilled are reported. The difference between FBP and IBP is called the "boiling range," and for crude oils this difference may exceed 1000 °F (> 550 °C). For petroleum products the boiling range may vary from 25 °C for narrow boiling range to 200 °C for wide boiling range fractions [1].

The simplest method of measuring boiling point of petroleum fractions is by the ASTM D86 method, in which boiling points are measured at 10, 30, 50, 70, and 90 vol % vaporized samples of 100 cm^3. In many cases boiling points at 0, 5, and 95 % are also reported. For temperatures reported in the ASTM D86 method in which they are above 250 °C (480 °F), correction because of cracking may be needed [2]. Although the ASTM method is very simple and convenient, it is not consistent or reproducible. As an alternative method, distillation data can be obtained by gas chromatography (GC), in which boiling points are reported versus the weight percent of sample vaporized. This test method described in ASTM D2887 is also called simulated distillation (SD). This method is applicable to petroleum fractions with FBPs of less than 538 °C (1000 °F) and a boiling range greater than 55 °C (100 °F). It is not applicable to gasoline.

SD curves are very close to actual boiling points known as true boiling points (TBPs). TBP curves are determined by distillation of sample in a distillation column with 15–100 theoretical plates and relatively high reflux ratio (i.e., ~1–5). The IBP of a TBP curve is less than the IBP from ASTM D86, whereas the FBP by a distillation curve is greater than that of ASTM D86. In the TBP curve the IBP is the vapor temperature that is observed at the instant that the first drop of condensate falls from the condenser. Details of various distillations curves and their interconversions are discussed in ASTM Manual 50 [2].

The newest methods for determining boiling points of heavy hydrocarbons and heavy oils by SD are described in ASTM D6352 and D7169, which are widely used because the instruments are finally robust and cost-competitive. It is possible to determine boiling points of heavy oil up to C_{100} [3]. Normal boiling points of n-alkanes up to n-C_{100} as given in ASTM D6352 [4] are shown in Figure 4.1, indicating that the boiling point approaches a finite value for very heavy hydrocarbons. These data are consistent with predicted values from methods described in ASTM Manual 50 for the boiling points of heavy hydrocarbons [2].

---

[1] Kuwait University, Kuwait

[2] The Pennsylvania State University, University Park, PA, USA

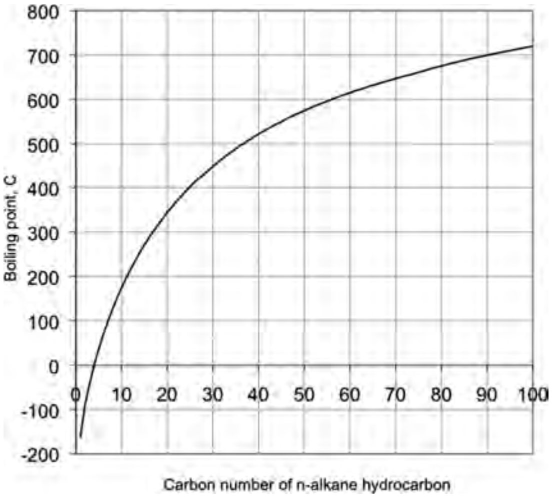


Figure 4.1—Normal boiling point of n-alkanes: Data taken from ASTM D6352 [4].

4.2 DENSITY, SPECIFIC GRAVITY, AND API DEGREE

Density is defined as mass per unit volume of a fluid. Liquid densities decrease as temperature increases, but the effect of pressure on liquid densities at moderate pressures is usually negligible. The density of petroleum fractions is measured at 15.5 °C (60 °F) or 20 °C (68 °F) and at atmospheric pressure. Liquid density for hydrocarbons is usually reported in terms of specific gravity (SG) or relative density, defined as

$$SG = \frac{density\ of\ liquid\ at\ temperature\ T}{density\ of\ water\ at\ temperature\ T} \qquad (4.1)$$

Because the standard conditions adopted by the petroleum industry are 60 °F (15.5 °C) and 1 atm, normally SG values of liquid hydrocarbons are reported at these conditions. At a reference temperature of 60 °F (15.5 °C), the density of liquid water is 0.999 g/cm^3 (999 kg/m^3) or 8.337 lb/gal (U.S.). Therefore, for a hydrocarbon or a petroleum fraction, the SG is defined as

$$SG\ (60\ ^\circ\mathrm{F}/60\ ^\circ\mathrm{F}) = \frac{density\ of\ liquid\ at\ 60\ ^\circ\mathrm{F}\ in\ g/cm^3}{0.999\ g/cm^3} \qquad (4.2)$$

The density of water at 60 °F is 0.999, or approximately 1 g/cm^3; therefore, values of SG are nearly the same as the density of liquid at 15.5 °C (289 K) in g/cm^3. SG defined by the above equation is slightly different from the SG defined in the SI system as the ratio of the density of hydrocarbon at 15 °C to that of water at 4 °C, designated by d_4^{15}. Note that density of water at 4 °C is exactly 1 g/cm^3 and therefore d_4^{15} is equal to the density of liquid hydrocarbon at 15 °C in g/cm^3. The relation between these two SGs is approximately given as $SG = 1.001\ d_4^{15}$

In the early years of the petroleum industry, the American Petroleum Institute (API) defined the API gravity (°API) to quantify the quality of petroleum products and crude oils. The API gravity is defined as [5]

$$API\ Gravity = \frac{141.5}{SG\ (\mathrm{at}\ 60\ ^\circ\mathrm{F})} - 131.5 \qquad (4.3)$$

Liquid hydrocarbons with lower SGs have higher API gravities. Aromatic hydrocarbons have higher SG (lower API gravity) than paraffinic hydrocarbons. For example, benzene has a SG of 0.8832 (API of 28.72) whereas *n*-hexane with the same carbon number has a SG of 0.6651 (API gravity of 81.25). A liquid with SG of 1 has an API gravity of 10.

The definition of SG for gases is somewhat different. It is defined as the relative density of gas to the density of air at standard conditions. In addition, the density of gases is a strong function of pressure. Because at standard conditions (15.5 °C and 1 atm) the density of gases is estimated from the ideal gas law, the gas SG is proportional to the ratio of the molecular weight of gas (M_g) to the molecular weight of air (28.97).

$$SG_g = \frac{M_g}{28.97} \qquad (4.4)$$

Therefore, to obtain the SG of a gas, only its molecular weight is needed.

4.3 MOLECULAR WEIGHT

Molecular weight is another bulk property that is indicative of molecular size and structure. This is an important property that laboratories usually do not measure and fail to report when reporting various properties of petroleum fractions. This is perhaps because of the low accuracy in the measurement of the molecular weight of petroleum fractions, especially for heavy fractions. However, it should be realized that the experimental uncertainty in reported values of molecular weight is less than the errors associated with predictive methods for this very useful parameter. Because petroleum fractions are mixtures of hydrocarbon compounds, mixture molecular weight is defined as an average value called the "number average molecular weight" or simply "molecular weight of the mixture," and it is calculated as $M = \sum_i x_i M_i$, where x_i and M_i are the mole fraction and molecular weight of component *i*, respectively. Molecular weight of the mixture, *M*, represents the ratio of the total mass of the mixture to the total moles in the mixture. Exact knowledge of molecular weight of a mixture requires the exact composition of all compounds in the mixture. For petroleum fractions such exact knowledge is not available because of the many components present in the mixture. Therefore, experimental measurement of mixture molecular weight is needed in lieu of the exact composition of all compounds in the mixture.

There are three methods that are widely used to measure the molecular weight of various petroleum fractions. These are *cryoscopy*, the *vapor pressure* method, and the *size exclusion chromatography* (SEC) method. For heavy petroleum fractions and asphaltenic compounds the SEC method is commonly used to measure the molecular weight distribution in the fraction. The SEC method is mainly used to determine molecular weights of polymers in the range of 2000 to 2×10^6. This method is also called "gel permeation chromatography" (GPC) and is described in the ASTM D5296 test method. In the GPC method, by comparing the elution time of a sample with that of a reference solution, the molecular weight of the sample can be determined. The SEC experiment is usually performed for heavy residues and asphaltenes in crude oils and gives the weight percent of various constituents versus molecular weight

The vapor pressure method is based on the measurement of the difference between vapor pressure of the sample and that of a known reference solvent with a vapor pressure greater than that of the sample. This method is described by the ASTM D2503 test method and is applicable to oils with an IBP of greater than 220 °C. The third and most widely used method of determining the molecular weight of an unknown petroleum mixture is by the cryoscopy method, which is based on freezing point depression. Further details of experimental methods to measure molecular weight of various petroleum products are given in ASTM Manual 50 [2].

4.4 REFRACTIVE INDEX

Refractive index, or the refractivity for a substance, is defined as the ratio of velocity of light in a vacuum to the velocity of light in the substance (fluid) and is a dimensionless quantity shown by n. In other words, when a light beam passes from one substance (air) to another (a liquid), it is bent or refracted because of the velocity difference, and the refractive index indicates the degree of this refraction. Because the velocity of light in a fluid is less than the velocity of light in a vacuum, the refractive index of a fluid is greater than unity. Liquids have higher refractive index values than do gases. For gases, the values of refractive index are very close to unity. Usually the refractive index of hydrocarbons is measured by the sodium D-line at 20 °C and 1 atm. The refractive index is a very useful characterization parameter for pure hydrocarbon and petroleum fractions, especially in relation to molecular-type composition.

Refractive indices of hydrocarbons vary from 1.35 to 1.60; however, aromatics have refractive index values greater than naphthenes., which in turn have refractive indices greater than paraffins. Paraffinic oils have lower refractive index values. For mixtures, refractive index is a bulk property that can be easily and accurately measured by an instrument called a *refractometer*. Refractive index can be measured by digital refractometers with a precision of ±0.0001 and temperature precision of ±0.1 °C. The amount of sample required to measure refractive index is very small, and ASTM D1218 provides a test method for clear hydrocarbons with values of refractive indices in the range of 1.33–1.5 and the temperature range of 20–30 °C. In the ASTM D1218 test method, the Bausch and Lomb refractometer is used. Refractive index of viscous oils, with values up to 1.6, can be measured by the ASTM D1747 test method. Samples must have clear color to measure their refractive index; however, for darker and more viscous samples in which the actual refractive index value is outside of the range of measurement by a refractometer, a light solvent can dilute samples to measure the refractive index of the solution. From the composition of the solution and refractive indices of the pure solvent and that of the solution, the refractive index of viscous samples can be determined. Because of the simplicity and importance of the refractive index, it would be very useful for laboratories to measure and report its value at 20 °C for a petroleum product, especially if the composition of the mixture is not reported.

4.5 COMPOSITIONAL ANALYSIS

Petroleum fractions are mixtures of many different types of hydrocarbon compounds. A petroleum mixture is well defined if the composition and structure of all compounds present in the mixture are known. Because of the diversity and number of constituents of a petroleum mixture, the determination of such exact composition is nearly impossible. Hydrocarbons can generally be identified by their carbon number or by their molecular type. Carbon number distribution may be determined from fractionation by distillation or by molecular weight. However, for narrow-boiling-range petroleum products and petroleum cuts in which the carbon number range is quite limited, knowledge of the molecular type of compounds is very important. After distillation data, molecular type composition is the most important characteristic of petroleum fractions. On the basis of the nature of petroleum mixture, there are several ways to express the composition of a petroleum mixture. Some of the most important types of composition are

- PONA (paraffins, olefins, naphthenes, and aromatics)
- PNA (paraffins, naphthenes, and aromatics)
- PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics)
- SARA (saturates, aromatics, resins, and asphaltenes)
- Elemental analysis (C, H, S, N, O)

Because most petroleum fractions are free of olefins, the hydrocarbon types can be expressed in terms of only PINA, and if paraffins and isoparaffins are combined into a single fraction, they are simply expressed in terms of PNA composition. This type of analysis is useful for light and narrow-boiling-range petroleum products such as distillates from atmospheric crude distillation units. The SARA analysis is useful for heavy petroleum fractions, residues, and fossil fuels (i.e., coal liquids) that have high contents of aromatics, resins, and asphaltenes. Elemental analysis gives information on hydrogen and sulfur contents as well as the carbon-to-hydrogen ratio, which is indicative of the quality of petroleum products.

Generally three techniques may be used to analyze petroleum fractions:

1. Separation by solvents
2. Chromatography methods
3. Spectroscopic methods

Method of separation by solvent is particularly useful for heavy petroleum fractions and residues containing asphaltenes, resins, and saturate hydrocarbons. For example, if n-heptane is added to a heavy oil, asphaltenes precipitate whereas the other constituents form a solution. If the solvent is changed to propane, because of the greater difference between the structure of the solvent and the high-molecular-weight asphaltenes, more asphaltenic compounds precipitate. Similarly, if acetone is added to a deasphalted oil (DAO), resins precipitate whereas low-molecular-weight hydrocarbons remain soluble in acetone.

One of the disadvantages of all of the solvent separation techniques is that in some instances a very low temperature (0–10 °C) is required, which causes inconvenience in a laboratory operation. Another difficulty is that in many cases large volumes of solvent may be required and that the solvent must have a sufficiently low boiling point to allow its complete removal from the product. ASTM [1] provides several methods based on solvent separation to determine amounts of asphaltenes. For example, in the ASTM D4124 method asphaltene is separated by n-heptane. Asphaltenes are soluble in liquids with a surface tension greater than 25 dyne/cm, such as pyridine, carbon disulfide, carbon tetrachloride, and benzene [6].

Chromatography methods are commonly used in the petroleum industry to identify compounds or to determine boiling distribution. If the mobile phase in the chromatography column is gas, the instrument is a gas chromatograph, whereas for liquid mobile phase it is a liquid chromatograph. Components can be separated by their boiling points through GC analysis. In advanced petroleum refineries, automatic online GCs are used for continuous analysis of various streams to control the quality of products. A stream may be analyzed every 20 min and automatic adjustment can be made to the refinery unit. In crude assay analysis, distillation is being replaced by chromatography techniques. The liquid chromatography (LC) method is used for less volatile mixtures such as heavy petroleum fractions and residues. Use of LC in separation of saturated and aromatic hydrocarbons is described in the ASTM D2549 test method. Various forms of chromatography techniques have been applied to a wide range of petroleum products for analysis such as PONA, PIONA, PNA, and SARA. One of the most useful types of LC is *high-performance liquid chromatography* (HPLC), which can be used to identify different types of hydrocarbon groups. One particular application of HPLC is to identify asphaltene and resin-type constituents in nonvolatile feedstocks such as residua. The total time required to analyze a sample by HPLC is just a few minutes. One of the main advantages of HPLC is that the boiling range of the sample is immaterial.

The accuracy of chromatography techniques mainly depends on the type of detector used [6]. Flame ionization detectors (FID) and thermal conductivity detectors (TCD) are widely used in GC. For LC, the most common detectors are refractive index detectors (RID) and wavelength ultraviolet (UV) detectors. UV spectroscopy is particularly useful to identify the types of aromatics in asphaltenic fractions. Another spectroscopy method is conventional *infrared* (IR) spectroscopy, which yields information about the functional features of various petroleum constituents. For example, IR spectroscopy aids in the identification of N-H and O-H functions, in the nature of polymethylene chains (C-H), and in the nature of any polyaromatic hydrocarbon (PAH) systems [6].

Another analysis used to identify molecular groups in petroleum fractions is *mass spectrometry* (MS). In general, there is a difference between spectroscopy and spectrometry methods although in some references this difference is not acknowledged. Spectroscopy refers to the techniques where the molecules are excited by various sources such as UV and IR and they return to their normal state. Spectrometry refers to the techniques where the molecules are actually ionized and fragmented. Evolution of spectroscopic methods comes after chromatography techniques, nonetheless, and in recent decades they have received considerable attention. While volatile and light petroleum products can be analyzed by GC, heavier and nonvolatile compounds can be analyzed and identified by spectrometric methods. One of the most important types of spectrometry techniques in analysis of petroleum fractions is MS. In this method, masses of molecular and atomic components, which are ionized in the gaseous state by collision with electrons, are measured. The advantage of MS over other spectrometric methods is its high reproducibility of quantitative analysis and information on molecular type in complex mixtures. MS can provide the most detailed quantitative and qualitative information about the atomic and molecular composition of organic and inorganic compounds. However, use of MS is limited to organic compounds that are stable up to 300 °C (570 °F). At higher temperatures, thermal decomposition may occur and the analysis will be biased [6]. Through MS analysis, hydrocarbons of similar boiling points can be identified. In the MS analysis, molecular weight and chemical formula of hydrocarbons and their amounts can be determined. The most powerful instrument to analyze petroleum distillates is combination of a GC and an MS, called a GC-MS instrument, which separates compounds through boiling point and molecular weight. For heavy petroleum fractions containing high-boiling-point compounds, an integrated LC-MS unit may be suitable for analysis of mixtures; however, use of LC-MS is more difficult than GC-MS because in LC-MS the solvent must be removed from the elute before it can be analyzed by MS.

Another type of separation is by SEC or GPC, which can be used to determine molecular weight distribution of heavy petroleum fractions. Fractions are separated according to their size and molecular weight, and the method is particularly useful to determine the amount of asphaltenes. Asphaltenes are polar multiring aromatic compounds with molecular weights greater than 1000, and it is assumed that in this molecular weight range only aromatics are present in a petroleum fraction.

4.5.1 Elemental Analysis

The main elements present in a petroleum fraction are carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S). The most valuable information from elemental analysis that can be obtained is the C/H ratio and sulfur content of a petroleum mixture, from which one can determine the quality of oil. As boiling points of fractions increase or their API gravity decrease, the C/H ratio, sulfur content, nitrogen content, and the amount of metallic constituents increase, signifying a reduction in the quality of an oil. Sulfur content of very heavy fractions can reach 6–8 % and the nitrogen content can reach 2.0-2.5 wt. %. There are specific methods to measure these elements individually. However, instruments do exist that measure these elements all together, and these are called elemental analyzers. ASTM test methods for elemental analysis of petroleum products and crude oils include hydrogen content (ASTM D1018, D3178, D3343), nitrogen content (ASTM D3179, D3228, D3431), and sulfur content (ASTM D129/IP 61, D1266/IP 107, D1552, D4045). Usually carbon dioxide, water, and sulfur dioxide are detected by infrared detectors (IRDs) whereas N_2 is determined by the TCD method.

Another group of heteroatoms found in petroleum mixtures are metallic constituents. The amounts of these metals are in the range of few hundreds to thousand parts per million and their amounts increase with increase in boiling points or decrease in the API gravity of oil. Even a small amount of these metals (particularly nickel, vanadium, iron and copper) in the feedstocks for catalytic cracking have negative effects on the activity of catalysts and result in increased coke formation. Metallic constituents are associated with heavy compounds and mainly appear in residuas. There is no general method to determine the composition of all metals at once, but ASTM [1] provides test methods for determination of various metallic constituents (i.e., ASTM D1026, D1262, D1318, D1368, D1548). Another method is to burn the oil sample in which metallic compounds appear in inorganic ashes. The ash should be digested by an acid and the solution is examined for metal species by atomic absorption spectroscopy [6].

4.6 VAPOR PRESSURE, VAPOR-TO-LIQUID RATIO, AND VOLATILITY INDEX

In a closed container, the vapor pressure of a pure compound is the force exerted per unit area of walls by the vaporized portion of the liquid. Vapor pressure can also be defined as a pressure at which vapor and liquid phases of a pure substance are in equilibrium with each other. The vapor pressure is also called "saturation pressure" and the corresponding temperature is called "saturation temperature." In an open air under atmospheric pressure, a liquid at any temperature below its boiling point has its own vapor pressure that is less than 1 atm. When vapor pressure reaches 1 atm, the saturation temperature becomes the normal boiling point. Vapor pressure increases with temperature and the highest value of vapor pressure for a substance is its critical pressure, in which the corresponding temperature is the critical temperature.

Vapor pressure is a very important thermodynamic property of any substance and it is a measure of the volatility of a fluid. Compounds with a higher tendency to vaporize have higher vapor pressures. At a fixed temperature, vapor pressure decreases with increase in molecular weight or carbon number. Vapor pressure is a useful parameter in calculations related to hydrocarbon losses and flammability of hydrocarbon vapor in the air. More volatile compounds are more ignitable than heavier compounds. For example *n*-butane is added to gasoline to improve its ignition characteristics. Low vapor pressure compounds reduce evaporation losses and chance of vapor lock. Therefore, for a fuel there should be a compromise between low and high vapor pressure. Vapor pressure is also needed in the calculation of equilibrium ratios for phase equilibrium calculations. Methods of calculation of vapor pressure are given in detail in ASTM Manual 50 [2].

For crude oils, petroleum fractions, and hydrocarbon mixtures, the method of Reid is used to measure vapor pressure at 100 °F. Reid vapor pressure (RVP) is the absolute pressure exerted by a mixture at 37.8 °C (311 K or 100 °F) at a vapor-to-liquid volume ratio of 4. The RVP is one of the important properties of gasolines and jet fuels and it is used as a criterion for blending of products. RVP is also a useful parameter for estimation of losses from storage tanks during filling or draining. For example, according to the Nelson method, losses can be approximately calculated as $losses$ (vol %) = $(14.5RVP - 1)/6$, where RVP is in bar [2]. The apparatus and procedures for standard measurement of RVP are specified in ASTM D323 or the Institute of Petroleum (IP) 402 test methods. In general, true vapor pressure (TVP) is higher than RVP because of light gases dissolved in liquid fuel; however, RVP is approximately equivalent to vapor pressure at 100 °F (38 °C).

The RVP and boiling range of gasoline governs ease of starting, engine warm-up, mileage economy, and tendency toward vapor lock [7]. Vapor lock tendency is directly related to RVP, and at ambient temperature of 21 °C (70 °F), the maximum allowable RVP is 75.8 kPa (11 psia), whereas this limit at 32 °C (90 °F) reduces to 55.2 kPa (8 psia). RVP can also be used to estimate TVP of petroleum fractions at various temperatures as shown in reference 2. TVP is important in the calculations related to losses and rate of evaporation of liquid petroleum products. Because RVP does not represent TVP, the current tendency is to substitute RVP with more modern and meaningful techniques. The more sophisticated instruments for measurement of TVP at various temperatures are discussed in the ASTM D4953 test method. This method can be used to measure the RVP of gasolines with oxygenates, and measured values are closer to actual vapor pressures [1].

Once RVP is known, it can be used to determine two other volatility characteristics—the vapor-to-liquid (V/L) ratio and fuel volatility index (FVI), which are specific characteristics of spark-ignition engine fuels such as gasolines. V/L ratio is a volatility criterion that is mainly used in the United State and Japan whereas FVI is used in France and Europe [8]. The V/L ratio at a given temperature represents the volume of vapor formed per unit volume of liquid initially at 0 °C. The procedure of measuring the V/L ratio is standardized as ASTM D2533. The volatility of a fuel is expressed as the temperature levels at which the V/L ratio is equal to certain values. A simple relation to calculate $T_{(\mathrm{V/L})20}$ is given in terms of RVP and distillation temperatures at 10 and 50 % [2]:

$$T_{(\mathrm{V/L})20} = 0.2T_{10} + 0.17T_{50} - 33RVP \qquad (4.5)$$

where T_{10} and T_{50} are temperatures at 10 and 50 volume 5 distilled on the ASTM D86 distillation curve. All temperatures are in degrees Celsius and RVP is in bar. Several petroleum refining companies in the United States such as Exxon and Mobil use the critical vapor locking index (CVLI), which is also related to the volatility index [2].

FVI is a characteristic of a fuel for its performance during hot operation of the engine. In France, specifications require that its value be limited to 900 in summer, 1000 in fall/spring, and 1150 in the winter season. Automobile manufacturers in France require their own specifications that the value of FVI not to exceed 850 in summer [8].

4.7 FLASH POINT

Flash point for a hydrocarbon or a fuel is the minimum temperature at which vapor pressure of the hydrocarbon is sufficient to produce the vapor needed for spontaneous ignition of the hydrocarbon with the air with the presence of an external source (i.e., spark or flame). From this definition, it is clear that hydrocarbons with higher vapor pressures (lighter compounds) have lower flash points. Flash point generally increases with an increase in boiling point. Flash point is an important parameter for safety considerations, especially during storage and transportation of volatile petroleum products (i.e., liquefied petroleum gas, light naphtha, gasoline) in a high temperature environment. The surrounding temperature around a storage tank should always be less than the flash point of the fuel to avoid the possibility of ignition. Flash point is used as an indication of the fire and explosion potential of a petroleum product.

Flash point is related to the volatility of a fuel and the presence of light and volatile components, with higher vapor pressure corresponding to lower flash points. Generally for crude oils with RVP greater than 0.2 bar, the flash point is less than 20 °C [8]. Flash point is an important characteristics of light petroleum fractions and products under high temperature environment and is directly related to the safe storage and handling of such petroleum products. There are several methods of determining flash points of petroleum fractions. The Closed Tag method (ASTM D56) is used for petroleum stocks with flash points below 80 °C (175 °F). The Pensky–Martens method (ASTM D93 or ISO 2719) is used for all petroleum products except waxes, solvents, and asphalts. The Cleveland Open Cup method (ASTM D92 or ISO 2592) is used for petroleum fractions with flash points above 80 °C (175 °F), excluding fuel oil. This method usually gives flash points 3–6 °C higher than the above two methods [9]. Flash point should not be mistaken with *fire point*, which is defined as the minimum temperature at which the hydrocarbon will continue to burn for at least 5 s after being ignited by a flame. There are several correlations to estimate flash point of hydrocarbons and petroleum fractions that are discussed in ASTM Manual 50 [2].

4.8 VISCOSITY AND KINEMATIC VISCOSITY

Viscosity, commonly shown by μ, is a molecular property of a fluid and is defined from Newton's law of viscosity. Viscosity is a property that is related to fluidity of a liquid, and a liquid with higher viscosity has less tendency to flow whereas low-viscosity fluids can easily flow. Viscosity is needed in calculations related to the power requirement to transport a fluid and is a function of temperature. Viscosity of gases is less than those of liquids. Viscosity of liquids decreases with increase in temperature while for gases viscosity increases with temperature. Viscosity is also an important characteristic of lubricating engine oils. Viscosity of liquids usually is measured in terms of kinematic viscosity, which is defined as the ratio of absolute (dynamic) viscosity to absolute density ($\nu = \mu/\rho$). Kinematic viscosity is expressed in centistokes (cSt), Saybolt Universal seconds (SUS), and Saybolt Furol seconds (SFS). Values of kinematic viscosity for pure liquid hydrocarbons are usually measured and reported at two reference temperatures of 38 °C (100 °F) and 99 °C (210 °F) in cSt. However, other reference temperatures of 40 °C (104 °F), 50 °C (122 °F), and 60 °C (140 °F) are also used to report kinematic viscosities of petroleum fractions. Viscosity is one of the most important properties of lubricating oils and heavy oils.

When viscosity at two temperatures is known, one can obtain the viscosity at other temperatures. Measurement of viscosity is easy, but the method and the instrument depend on the type of sample. For Newtonian and high-shear fluids such as engine oils, viscosity can be measured by a capillary U-type viscometer. An example of such a viscometer is the Cannon–Fenske viscometer. The test method is described in ASTM D445, which is equivalent to the ISO 3104 method, and kinematic viscosity is measured at temperatures from 15 to 100 °C (~60–210 °F). In this method, repeatability and reproducibility are 0.35 and 0.7 %, respectively [2]. Another type of viscometer is a rotary viscometer, which is used for a wide range of shear rates, especially for low shear rate and viscous fluids such as lubricants and heavy petroleum fractions. In these viscometers, fluid is placed between two surfaces—one is fixed, and the other one is rotating. In these viscometers absolute viscosity can be measured, and an example of such a viscometer is the Brookfield viscometer.

4.9 FREEZING AND MELTING POINTS

Petroleum and most petroleum products are in the form of a liquid or gas at ambient temperatures. However, for oils containing heavy compounds such as waxes or asphaltenic oils, problems may arise from solidification, which causes the oil to lose its fluidity characteristics. For this reason, knowledge of the freezing point is important and it is one of the major specifications of jet fuels and kerosenes. For a pure compound, the *freezing point* is the temperature at which liquid solidifies at a pressure of 1 atm. Similarly, the *melting point* is the temperature that a solid substance liquefies at 1 atm. A pure substance has the same freezing and melting points; however, for petroleum mixtures, there are ranges of melting and freezing points versus percent of the mixture melted or frozen. For a mixture the initial melting point is close to the melting point of the lightest compound in the mixture whereas the initial freezing point is close to the freezing point (or melting point) of the heaviest compound in the mixture. Because the melting point increases with molecular weight, for petroleum mixtures the initial freezing point is greater than the initial melting point. Melting point is an important characteristic parameter for petroleum and paraffinic waxes.

Freezing point is one of the important characteristics of aviation fuels, in which it is determined by the procedures described in the ASTM D2386 (United States), IP 16 (United Kingdom), and NF M 07-048 (France) test methods. The maximum freezing point of jet fuels is an international specification that is required to be at –47 °C (–53 °F) as specified in the "Aviation Fuel Quantity Requirements for Jointly Operated Systems" [8]. This maximum freezing point indicates the lowest temperature that the fuel can be used without risk of separation of solidified hydrocarbons (wax). Such separation can result in the blockage in fuel tank, pipelines, nozzles, and filters [9]. Methods of calculation of freezing points of petroleum fractions are discussed in ASTM Manual 50 [2].

4.10 POUR POINT

The pour point of a petroleum fraction is the lowest temperature at which the oil will pour or flow when it is cooled without stirring under standard cooling conditions. Pour point represents the lowest temperature at which an oil can be stored and still be capable of flowing under gravity and is one of the low-temperature characteristics of heavy fractions. When the temperature is less than the pour point of a petroleum product it cannot be stored or transferred through a pipeline. Test procedures for measuring pour points of petroleum fractions are given under the ASTM D97 (ISO 3016 or IP 15) and ASTM D5985 methods. For commercial formulation of engine oils, the pour point can be lowered to the limit of –25 and –40 °C. This is achieved by using pour point depressant additives, which inhibit the growth of wax crystals in the oil [10]. The presence of wax and heavy compounds causes an increase in the pour point of petroleum fractions.

4.11 CLOUD POINT

The cloud point is the lowest temperature at which wax crystals begin to form by a gradual cooling under standard conditions. At this temperature, the oil becomes cloudy and the first particles of wax crystals are observed. The standard procedure to measure the cloud point is described under the ASTM D2500, IP 219, and ISO 3015 test methods. Cloud point is another cold characteristic of petroleum oils under low-temperature conditions and increases as the molecular weight of an oil increases. Cloud points are measured for oils that contain paraffins in the form of wax; therefore, for light fractions such as naphtha or gasoline, no cloud point data are reported. Cloud points usually occur at 4–5 °C (7–9 °F) above the pour point, although the temperature differential could be in the range of 0–10 °C (0–18 °F). The difference between cloud and pour point depends on the nature of oil, and there is no simplified method to predict this difference. Cloud point is one of important characteristics of crude oils under low-temperature conditions. As temperature decreases below the cloud point, the formation of wax crystals is accelerated. Therefore, low cloud point products are desirable under low-temperature conditions. Wax crystals can plug the fuel system lines and filters, which could lead to stalling aircraft and diesel engines under cold conditions. Because cloud point is higher than pour point, it can be considered that the knowledge of cloud point is more important than the pour point in establishing distillate fuel oil specifications for cold-weather usage [10]. Table 4.1 shows the difference between cloud and pour points for some petroleum products. The amount of n-paraffins in petroleum oil has a direct effect on the cloud point of a fraction. The presence of gases dissolved in oil reduces the cloud point, which is desirable. The exact calculation of cloud point requires solid-liquid equilibrium calculations, which are discussed in reference 2.

4.12 FLAMMABILITY RANGE

Three elements are required for combustion: fuel (hydrocarbon vapor), oxygen (i.e., air), and a spark to initiate the combustion. One important parameter for good combustion is the ratio of air to hydrocarbon fuel. The combustion does not occur if there is too much air (little fuel) or too little air (too much fuel). This suggests that combustion occurs when the hydrocarbon concentration in the air is within a certain range. This range is called the *flammability range* and usually is expressed in terms of lower and upper volume percent in the mixture of hydrocarbon vapor and air. The actual volume percent of hydrocarbon vapor in the air may be calculated from the vapor pressure of the hydrocarbon. When a liquid is open to the atmosphere at a temperature of T, in which the vapor pressure of liquid is P^{vap}, the volume percent of the compound vapor in the air at atmospheric pressure is $100\ P^{vap}$, where P^{vap} is the vapor pressure in atmosphere. When the calculated volume percent of a hydrocarbon in the air is within the flammability range, then the mixture is flammable by a spark or flame. The flammability ranges for some pure hydrocarbons are as follows: propane, 2.1–9.5; butane, 1.8–8.4; benzene, 1.4–7.1; hydrogen, 4.3–45.5; and methanol, 2.3–36.0 vol % [2].

4.13 OCTANE NUMBER

Octane number is a parameter defined to characterize the antiknock characteristic of a fuel (gasoline) for spark-ignition engines. Octane number is a measure of a fuel's ability to resist autoignition during compression and before ignition by a spark. Higher octane number fuels have better engine performance. The octane number of a fuel is measured based on two reference hydrocarbons of *n*-heptane, with an assigned octane number of zero, and a specific isooctane (2,2,4-trimethylpentane), with an assigned octane number of 100. A mixture of 70 vol % 2,2,4-trimethylpentane and 30 vol % *n*-heptane has an octane number of 70. There are two methods of measuring the octane number of a fuel in the laboratory: *motor octane number* (MON) and *research octane number* (RON). MON is indicative of high-speed performance (900 rpm) and is measured under heavy road conditions (ASTM D357). RON is indicative of normal road performance under low engine speed (600 rpm) city driving conditions (ASTM D908). A third type of octane number is defined as the *posted octane number* (PON), which is the arithmetic average of MON and RON [$PON = (MON + RON)/2$]. Isoparaffins generally have a higher octane number than normal paraffins. Naphthenes have a relatively higher octane number than their corresponding paraffins, and aromatics have very high octane numbers. The octane number of a fuel can be improved by adding tetraethyl lead (TEL) or methyl tertiary butyl ether (MTBE). Use of lead (Pb) to improve the octane number of fuels is limited

TABLE 4.1—Cloud (T_{CL}) and Pour (T_P) Points and Their Differences for Some Petroleum Products

Fraction	API Gravity	T_P (°C)	T_{CL} (°C)	T_P–T_{CL} (°C)
Indonesian distillate	33.0	–43.3	–53.9	10.6
Australian GO	24.7	–26.0	–30.0	4.0
Australian HGO	22.0	–8.0	–9.0	1.0
Abu Dhabi LGO	37.6	–19.0	–27.0	8.0
Abu Dhabi HGO	30.3	7.0	2.0	5.0
Abu Dhabi distillate	21.4	28.0	26.0	2.0
Abu Dhabi diesel	37.4	–12.0	–12.0	0.0
Kuwaiti kerosene	44.5	–45.0	–45.0	0.0
Iranian kerosene	44.3	–46.7	–46.7	0.0
Iranian kerosene	42.5	–40.6	–48.3	7.8
Iranian GO	33.0	–11.7	–14.4	2.8
North Sea GO	35.0	6.0	6.0	0.0
Nigerian GO	27.7	–32.0	–33.0	1.0
Middle East kerosene	47.2	–63.3	–65.0	1.7
Middle East kerosene	45.3	–54.4	–56.7	2.2
Middle East kerosene	39.7	–31.1	–34.4	3.3
Middle East distillate	38.9	–17.8	–20.6	2.8

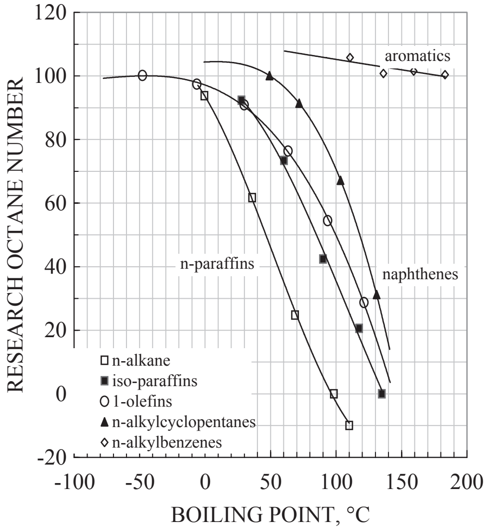


Figure 4.2—RON of different families of hydrocarbons.

in many industrial countries. In these countries MTBE is used for octane number improvement; MTBE has MON and RON values of 99 and 115, respectively [2]. Lead generally improves octane number of fuels better than MTBE. The addition of 0.15 g Pb/L to a fuel with a RON of approximately 92 can improve its octane number by 2–3 points. With 0.6 g Pb/L one may improve the octane number by 10 points. However, as mentioned above, because of environmental hazards, use of lead is restricted in many North American and Western European countries, and unleaded fuels are used all over the world. Values of the octane number measured without any additives are called “clear octane number.” However, recently it was found that use of MTBE could cause pollution of groundwater, and as a result dimethyl carbonate is being considered as an alternative additive to improve octane number. For pure hydrocarbons, aromatics have the higher octane number, whereas n-paraffins have the lowest octane number values when compared with other groups, as shown in Figure 4.2. Values of RON and MON of some oxygenates that may be used as additives to improve the octane number of fuels are given in Table 4.2 [2].

4.14 ANILINE POINT

The aniline point for a hydrocarbon or petroleum fraction is defined as the minimum temperature at which equal volumes of liquid hydrocarbon and aniline are miscible. Aniline is an aromatic compound with a structure of a benzene molecule in which one atom of hydrogen is replaced by an amino (–NH_2) group (C_6H_5—NH_2). The aniline point is important in the characterization of petroleum fractions and analysis of molecular type. The aniline point is also used as a characterization parameter for the ignition quality of diesel fuels. It is measured by the ASTM D611 test method. Within a hydrocarbon group, aniline point decreases with molecular weight or carbon number (i.e., 536.9 ºC for methane to 201.9 for *n*-C_{20}), but for the same carbon number it increases from aromatics to paraffinic hydrocarbons. Generally, oils with lower aniline points have higher aromatic content.

TABLE 4.2—Octane Numbers of Some Alcohols and Ethers (Oxygenates)

Compound	RON	MON
Methanol	125–135	100–105
MTBE	113–117	95–101
Ethanol	120–130	98–103
ETBE	118–122	100–102
TBA	105–110	95–100
TAME	110–114	96–100

ETBE, ethyl-tertiary-butyl ether; TBA, tert-butyl alcohol; TAME, tertiary-amyl-methyl ether.

4.15 CETANE NUMBER AND DIESEL INDEX

For diesel engines, the fuel must have a characteristic that favors autoignition. The ignition delay period can be evaluated by the fuel characterization factor called *cetane number* (CN). The behavior of a diesel fuel is measured by comparing its performance with two pure hydrocarbons: *n*-cetane or *n*-hexadecane (n-$C_{16}H_{34}$), which are given the CN of 100, and α-methylnaphthalene, which is given the CN of 0. A diesel fuel has a CN of 60 if it behaves like a binary mixture of 60 vol % cetane and 40 vol % α-methylnaphthalene. In practice, heptamethylnonane (HMN), a branched isomer of *n*-cetane with a CN of 15, is used instead of α-methylnaphthalene [8]. Therefore, in practice, the CN is defined as

$$CN = vol\ \%\ (n\text{-}cetane) + 0.15(vol\ \%\ HMN) \tag{4.6}$$

The CN of a diesel fuel can be measured by the ASTM D613 test method. The shorter the ignition delay period, the higher the CN value. Higher CN fuels reduce combustion noise and permit improved control of combustion, resulting in increased engine efficiency and power output. Higher CN fuels tend to result in easier starting and faster warm-up in cold weather. CN requirements of fuels vary with their uses. For high-speed city buses in which kerosene is used as fuel the required CN is 50. For premium diesel fuel for use in high-speed buses and light marine engines, the required number is 47, whereas for marine distillate diesel for low-speed buses and heavy marine engines the required CN is lower. In France the minimum required CN of fuels by automotive manufacturers is 50. The products distributed in France and Europe have CNs in the range of 48–55. Higher CN fuels and better starting conditions can reduce air pollution [8].

Because determination of CN is difficult and costly, ASTM D976 (IP 218) proposes a method of calculation. The calculated number is called the “calculated cetane index” (CCI) and can be determined from SG and distillation data [2]. Another characteristic of diesel fuels is called the “diesel index” (DI), which is defined in terms of API gravity and aniline point.

The CN of diesel fuels can be improved by adding compounds such as 2-ethyl-hexyl nitrate or other types of alkyl nitrates. CN is usually improved by 3–5 points when 300–1000 ppmw of such compounds is added. Generally, CCI is less than the measured CN, and for this reason in France automobile manufacturers have established minimum CN for the CCI (49) and the measured CN (50) for the quality requirement of the fuels [8].

4.16 CARBON RESIDUE

When a petroleum fraction is vaporized in the absence of air at atmospheric pressure, the nonvolatile compounds have a carbonaceous residue known as *carbon residue* (CR). Therefore, heavier fractions with more aromatic contents have higher CRs, whereas volatile and light fractions such as naphthas and gasolines have no CRs. CR is a particularly important characteristic of crude oils and petroleum residues. Higher CR values indicate low-quality fuel and less hydrogen content. There are two older different test methods to measure CRs: Ramsbottom (ASTM D524) and Conradson (ASTM D189). The relationship between these methods is also given by the ASTM D189 method. Oils that have ash-forming compounds give erroneously high CRs by both methods. For such oils, ash should be removed before the measurement. There is a more recent test method (ASTM D4530) that requires smaller sample amounts and is often referred to as *microcarbon residue* (MCR), and, as a result, it is a less precise but it is a practical technique [6]. In most cases CRs are reported in weight percent by the Conradson method, which is designated by % CCR.

CR can be correlated to several other properties. It increases with an increase in carbon-to-hydrogen ratio (CH); sulfur, nitrogen, and asphaltene content; or viscosity of the oil. The most precise relation is between CR and the hydrogen content: as hydrogen content increases, the CR decreases [6]. CR is nearly a direct function of high-boiling-point asphaltic materials, and Nelson has reported a linear relation between CR and asphalt yield. One of the main characteristics of residuum is its asphaltene content. Asphaltenes are insoluble in low-molecular-weight n-alkanes, including *n*-pentane. Knowledge of *n*-pentane insolubles in residual oils is quite important in determining yields and product quality for deasphalting, thermal visbreaking, and hydrodesulfurization processing.

4.17 SMOKE POINT

Smoke point is a characteristic of aviation turbine fuels and kerosene and indicates the tendency of a fuel to burn with a smoky flame. A higher amount of aromatics in a fuel causes a smoky characteristic for the flame and energy loss due to thermal radiation. The smoke point (SP) is the maximum flame height at which a fuel can be burned in a standard wick-fed lamp without smoking. It is expressed in millimeters, and a high SP indicates a fuel with low smoke-producing tendency [6]. Measurement of SP is described under the ASTM D1322 (United States) or IP 57 (United Kingdom) and ISO 3014 test methods. For the same fuel, the measured SP by the IP test method is higher than that measured by the ASTM method by 0.5–1 mm for SP values in the range of 20–30 mm [9]. SP can be best estimated through PNA composition and various methods of estimation of SP are given in ASTM Manual 50 [2].

4.18 DEFINED CHARACTERIZATION PARAMETERS

There are several properties and characteristics that are not directly measurable but are defined based on measured properties and are in some cases useful parameters to determine the quality and properties of petroleum fluids.

4.18.1 Watson (UOP) Characterization Factor, K_W

Since the early years of the petroleum industry, a characterization parameter to classify petroleum and identify hydrocarbon molecular types was desired that was defined based on measurable parameters. The Watson characterization factor, denoted by K_W, is one of the oldest characterization factors originally defined by Watson et al. of Universal Oil Products (UOP) in the mid-1930s. For this reason, the parameter is sometimes called the UOP characterization factor and is defined as

$$K_W = \frac{(1.8T_b)^{1/3}}{SG} \tag{4.7}$$

where:

T_b = mean average normal boiling point in K

SG = specific gravity at 15.5 °C.

The purpose of definition of this factor was to classify the type of hydrocarbons in petroleum mixtures. The naphthenic hydrocarbons have K_W values between paraffinic and aromatic compounds. In general, aromatics have low K_W values whereas paraffins have high values. Further information on limitations and uses of this parameter is given in ASTM Manual 50 [2]. Because for very heavy fractions the normal boiling point cannot be measured, this parameter is not useful for heavy oils.

4.18.2 Refractivity Intercept

A plot of refractive index of n-paraffins versus density (d_{20}) in the carbon number range of C_5–C_{45} is a straight line represented by the equation $n = 1.0335 + 0.516d_{20}$, with an R^2 value of 0.9998 ($R^2 = 1$ for an exact linear relation). Other hydrocarbon groups show similar performance with an exact linear relation between n and d. On the basis of this observation, a characterization parameter called the *refractivity intercept*, R_i, was defined as $R_i = n - \frac{d}{2}$, where n and d are the refractive index and density of the liquid hydrocarbon, respectively, at the reference state of 20 °C and 1 atm and where density must be in grams per cubic centimetre. R_i is high for aromatics and low for naphthenic compounds, whereas paraffins have intermediate R_i values. R_i is a useful parameter for estimation of the composition and sulfur content of petroleum fractions [2].

4.18.3 Viscosity Gravity Constant

Another parameter defined in the early years of petroleum characterization is the *viscosity gravity constant* (VGC). This parameter is defined based on an empirical relation developed between SUS viscosity and SG through a constant. VGC is defined at two reference temperatures of 38 °C (100 °F) and 99 °C (210 °F) as [5]

$$VGC = \frac{10SG - 1.0752\log_{10}(V_{38} - 38)}{10 - \log_{10}(V_{38} - 38)} \tag{4.8}$$

$$VGC = \frac{SG - 0.24 - 0.022\log_{10}(V_{99} - 35.5)}{0.755} \tag{4.9}$$

where:

V_{38} = viscosity at 38 °C (100 °F) in SUS

V_{99} = SUS at 99 °C (210 °F).

Conversion factors between cSt and SUS are given in ASTM Manual 50 [2]. VGC varies for paraffinic hydrocarbons from 0.74 to 0.75, for naphthenic hydrocarbons from

0.89 to 0.94, and for aromatic hydrocarbons from 0.95 to 1.13. The main limitation in use of VGC is that it cannot be defined for compounds or fractions with viscosities less than 38 SUS (~3.6 cSt) at 38 °C. ASTM D2501 suggests calculation of VGC using SG and viscosity in mm^2/s (cSt) at 40 °C.

4.18.4 Viscosity Index

Another useful parameter, especially for lubricating oils, is the viscosity index (VI), which shows the variation of viscosity with temperature as an indication of the composition of viscous fractions. VI is an empirical number indicating variation of the viscosity of oil with temperature. A low VI value indicates a large variation of viscosity with temperature, which is a characteristic of aromatic oils. Similarly, paraffinic hydrocarbons have high VI values. The method is described under ASTM D2270 and ISO 2909. In English unit systems, VI is defined in terms of viscosity at temperatures 37.8 and 98.9 °C (100 and 210 °F). However, in SI units, viscosities at reference temperatures of 40 and 100 °C have been used to define the VI. Details of calculation of VI are given in ASTM Manual 50 [2].

4.18.5 CH Weight Ratio

CH is defined as the ratio of the total weight of carbon atoms to the total weight of hydrogen in a compound or a mixture and is used to characterize a hydrocarbon compound. At the same carbon number, the atomic ratio of the number of carbon (C) atoms to the number of hydrogen (H) atoms increases from paraffins to naphthenes and aromatics. For example, *n*-hexane (C_6H_{14}), cyclohexane (C_6H_{12}), and benzene (C_6H_6) from three different hydrocarbon groups all have six carbon atoms but have different CH atomic ratios of 6/14, 6/12, and 6/6, respectively. If the atomic CH ratio is multiplied by the ratio of the atomic weights of carbon (12.011) to hydrogen (1.008), then the CH weight ratio is obtained. For example, for *n*-hexane, the CH value is calculated as (6/14) × (12.011/1.008) = 5.107. This number for benzene is 11.92. Therefore, the CH weight ratio is a parameter that is capable of characterizing the hydrocarbon type. In addition, within the same hydrocarbon group, the CH value changes from low to high carbon number. For example, methane has a CH value of 2.98 whereas pentane has a CH value of 4.96. For extremely large molecules ($M \to \infty$), the CH value of all hydrocarbons regardless of their molecular type approaches the limiting value of 5.96. This parameter can be used to estimate the hydrocarbon properties or the composition of petroleum fractions. In some references, the hydrogen-to-carbon (HC) atomic ratio is used as the characterizing parameter. According to the definition, the CH weight ratio and the atomic HC ratio are inversely proportional. The limiting value of the HC atomic ratio for all hydrocarbon types is 2 [2].

Another use of the CH weight ratio is to determine the quality of a fossil-type fuel. Quality and the value of a fuel are determined from its heat of combustion and heating value. The heating value of a fuel is the amount of heat generated by complete combustion of one unit mass of the fuel. For example, *n*-hexane has the heating value of 44,734 kJ/kg (19,232 Btu/lb) and benzene has the heating value of 40,142 kJ/kg (17,258 Btu/lb). This is also known as the net heat of combustion. Calculation of heating values is discussed in ASTM Manual 50. From this analysis it is clear that as the CH value increases the heating value decreases. Hydrogen (H_2), which has a CH value of zero, has a heating value more than methane (CH_4), and methane has a heating value more than any other hydrocarbon. Heavy aromatic hydrocarbons that have high CH values have lower heating values. In general, by moving toward lower CH value fuel, not only do we have better heating value but also better and cleaner combustion of the fuel. It is for this reason that the use of natural gas is preferable to any other type of fuel, and hydrogen is an example of a perfect fuel with zero CH value (CH = 0) whereas black carbon is an example of the worst fuel with a CH value of infinity [2]. Accurate values of CH can be determined from the elemental analysis of a fuel.

4.18.6 Correlation Index

The correlation index (CI), defined by the U.S. Bureau of Mines, is expressed by the following equation [6]:

$$CI = \frac{48{,}640}{T_\mathrm{b}} + 473.7\mathrm{SG} - 456.8 \tag{4.10}$$

where T_b is the volume average boiling point (VABP) in K. Values of CI between 0 and 15 indicate a predominantly paraffinic oil. A value of CI greater than 50 indicates a predominance of aromatic compounds. CI has a tendency to increase with increasing boiling point in a given crude oil [6].

4.19 STANDARD METHODS

There are several international organizations that are known as standard organizations and they recommend specific characteristics or standard measuring techniques for various petroleum products through their regular publications. Some of these organizations in different countries that are known by their abbreviations are as follows [2]:

- ASTM (American Society for Testing and Materials) in the United States. This is now known as ASTM International (http://www.astm.org) and is based in West Conshohocken, PA.
- ISO (International Organization for Standardization) (http://www.iso.org) is based in Geneva, Switzerland.
- Energy Institute (formerly IP) (http://uk.ihs.com/collections/ipbs/index.htm) is based in London, United Kingdom.
- API (American Petroleum Institute) (http://www.api.org) is based in Washington, DC, in the United States.
- AFNOR (Association Francaise de Normalisation) (http://www.afnor.org/) is an official standard organization in France.

ASTM is composed of several committees, in which a *D committee* is responsible for petroleum products and for this reason its test methods for petroleum materials are designated by the prefix D. For example, the test method ASTM D2267 provides a standard procedure to determine the benzene content of gasoline. In France this test method is designated by EN 238, which is described in AFNOR information document M 15-023. Most standard test methods in different countries are very similar in practice but they are designated by different codes. For example, the international standard ISO 6743/0, accepted as the French standard NF T 60-162, treats all of the petroleum lubricants, industrial oils, and related products. The abbreviation NF is used for the French standard whereas EN is used for European standard methods. Most ISO test methods are adopted from ASTM but are given a different code.

TABLE 4.3—Standard Test Methods for Measurement of Some Properties of Liquid Petroleum Products [2]

Property	ASTM D	IP	ISO	Property	ASTM D	IP	ISO
Aniline point	611	2/98	2977	Flash point	93	34/97	2719
CR (Ramsbottom)	524	14/94	4262	Freezing point	2386	16/98	3013
CR (Conradson)	189	13/94	6615	Hydrocarbon types	1319	156/95	3837
CN	4737	380/98	4264	Heating value	240		
Cloud point	2500	219/94	3016	Kinematic viscosity	445	71/97	3104
Color	1500	196/97	2049	Octane number (MON)	2700	236/09	5163
Density/SG	4052	365/97	2185	Refractive index	1218		
Distillation at atmospheric pressure	86	123/99[a]	3405	Pour point	97	15/95	3015
Distillation at reduced pressures	1160		6616[a]	Sulfur content	1266	107/86	2192
Distillation by GC	2887	406/99[a]		SP	1322	–	–
Distillation of crude oils	2892		8708[a]	Vapor pressure (RVP)	323	69/94	3007
Autoignition	2155		3988	Viscosity (viscous oils)	2983	370/85[a]	

[a] Methods are similar but not identical to other standard methods.
Most IP methods are also used as British Standard under BS2000 methods.
The number after the IP number indicates the year of last approval.

Government regulations to protect the environment or to save energy, in many cases, rely on the recommendation by official standard organizations. For example, in France, AFNOR gives specifications and requirements for various petroleum products. For diesel fuels, it recommends (after 1996) that the sulfur content should not exceed 0.05 wt % and the flash point should be greater than 55 °C [6]. Some test methods (ASTM, ISO, and IP) for quality-related properties are given in Table 4.3 [2].

4.20 CRUDE OIL ASSAYS

Composition of a crude may be expressed similar to a reservoir fluid in terms of C_1 through n-C_5 as pure components, C_6 (hexanes), and C_{7+} (heptane-plus). A crude is produced through reducing the pressure of a reservoir fluid to atmospheric pressure and separating light gases. Therefore, a crude oil is usually free of methane gas and has a higher amount of C_{7+} than the original reservoir fluid. However, in many cases information on characteristics of crude oils are given through crude assay. Complete data on crude assay contain information on specification of the whole crude oil as well as its products from atmospheric or vacuum distillation columns. The *Oil & Gas Journal Data Book* has published a comprehensive set of data on various crude oils from around the world [11]. Characteristics of two crude oils from two different countries and their products are given in Table 4.4. A crude assay data set contains information on API gravity, sulfur and metal contents, kinematic viscosity, pour point, and RVP. In addition to boiling point range, API gravity, viscosity, sulfur content, PNA composition, and other characteristics of various products obtained from each crude are given. From information given for various fractions, boiling point curve for the whole crude can be obtained.

Quality of crude oils are mainly evaluated based on a higher value for the API gravity (lower SG); lower aromatic, sulfur, nitrogen, and metal contents; and lower pour point, CH, viscosity, CR, and salt and water contents. Higher API crudes usually contain higher amounts of paraffins, a lower CH ratio, less sulfur and metals, and have lower CR and viscosity. For this reason, API gravity is used as the primary parameter to quantify quality of a crude. API gravity of crudes varies from 10 to 50; however, most crudes have an API gravity between 20 and 45 [7]. A crude oil having an API gravity greater than 40 (SG < 0.825) is considered as a *light* crude whereas a crude with an API gravity less than 20 (SG > 0.934) is considered as a *heavy* oil. Crudes with API gravity between 20 and 40 are called *intermediate* crudes. However, this division may vary from one source to another and usually there is no sharp division between light and heavy crude oils. Crude oils having an API gravity of 10 or lower (SG > 1) are referred as *very heavy* crudes and often have more than 50 wt % residues. Some Venezuelan crude oils are from this category. Another parameter that characterizes the quality of a crude oil is the total sulfur content. The total sulfur content is expressed in weight percent and it varies from less than 0.1 % to more than 5 %. Crude oils with a total sulfur content of more than 0.5 % are termed as *sour* crudes, and when the sulfur content is less than 0.5 % they are referred to as *sweet* crudes [7]. After sulfur content, lower nitrogen and metal contents signify the quality of a crude oil.

4.21 QUALITY OF PETROLEUM PRODUCTS

Methods presented in this chapter can be used to evaluate the quality of petroleum products from available parameters. The quality of a petroleum product depends on certain specifications or properties of the fuel to satisfy required criteria set by the market demand. These characteristics are specified for the best use of a fuel (i.e., highest engine performance) or for a cleaner environment while the fuel is in use. These specifications vary from one product to another and from one country to another. For example, for gasoline the quality is determined by a series of properties such as sulfur and aromatic contents, octane number, vapor pressure, hydrogen content, and boiling range. Engine warm-up time is affected by the percent distilled at 70 °C and ASTM 90 % temperature. For the ambient temperature

TABLE 4.4—Crude Assay Data for Two Oils [11]

Crude 1			Crude 2		
Kuwaiti Crude Oil for Export			**Boscan, Venezuela**		
Mina Al Ahmadi **Crude** Gravity, °API: 31.4 Viscosity, SUS at 100 °F: 58.1 Pour point, °F: +5 Sulfur, wt %: 2.52 Ni/V (calcined), ppm: 8/30 RVP, psi: 6.7 H_2S, wt %: <0.001 C_1–C_4 (GC analysis), vol %: 3.03 **Naphtha** Range, °F: Over point to 140 Yield, vol %: 3.80 Gravity, °API: 89.7 Sulfur, wt %: 0.04 RON (micro), clear: 71.8 RON + 3 mL TEL: 89.3 **Naphtha** Range, °F: 140–170 Yield, vol %: 2.26 Gravity, °API: 78.6 Sulfur, wt %: 0.02 Aniline point, °F: 147.7 RON, clear/+3 mL TEL: 58.2/80.40 Paraffins, vol %: 88.5 Monocycloparaffins, vol %: 9.9 Total aromatics, vol %: 1.6	**Heavy Naphtha** Range, °F: 170–310 Yield, vol %: 11.91 Gravity, °API: 62.1 Sulfur, wt %: 0.03 Aniline point, °F: 136.2 Paraffins vol %: 70.1 Monocycloparaffins, vol %: 20.4 Dicycloparaffins, vol %: 0.4 Total aromatics, vol %: 9.1 **Kerosene** Range, °F: 310–520 Yield, vol %: 18.43 Gravity, °API: 45.9 Pour point, °F: –45 Sulfur, wt %: 0.39 Aniline point, °F: 142.9 Cetane index: 53.8 SP, mm: 26 **Heating Oil** Range, °F: 520–680 Yield, vol %: 14.89 Gravity, °API: 32.9 Viscosity, SUS at 100 °F: 43.3 Pour point, °F: +20 Total nitrogen, ppm: 100 Sulfur, wt %: 1.98 Aniline point, °F: 160.2 Cetane index: 54.3	**Gas Oil** Range, °F: 680–1000 Yield, vol %: 24.09 Gravity, °API: 21.4 Pour point, °F: +100 Sulfur, wt %: 3.12 Total nitrogen, ppm: 900 Ni/V, ppm: <0.1/<0.1 Vis, SUS at 130 °F: 175.2 Ramsbottom CR, wt %: 0.47 **Residuum** Range (VEFV), °F: 1,000+ Yield, vol %: 21.78 Gravity, °API: 5.8 Sulfur, wt %: 5.11 V/Ni, ppm: 116/34 Vis., SUV, sec@250 °F: 3,394 Ramsbottom CR, wt %: 21.9	Bajo Grande Lake Maracaibo **Crude** Gravity, °API: 10.10 Sulfur, wt %: 5.5 Viscosity, SUS at 100 °F: 90,000 Pour point, °F: +50 **Light Naphtha** Range, °F: 82–200 Yield, vol %: 0.55 **Heavy Naphtha** Range, °F: 200–300 Yield, vol %: 1.32 Sulfur, wt %: 0.68 Paraffins, %: 53.28 **Naphtha** Range, °F: 300–350 Yield, vol %: 0.88 Sulfur, wt %: 1.28 Paraffins, %: 34.9 **Kerosene** Range, °F: 350–400	Yield, vol %: 1.28 Sulfur wt %: 1.88 Aromatics, %: 24.04 Pour point, °F: –141.0 SP, mm: 16.0 Aniline point, °F: 112.69 **Gas Oil** Range, °F: 400–500 Yield, vol %: 3.96 Gravity, °API: 34.0 Sulfur, wt %: 3.14 Kinematic viscosity at 122 °F: 1.81 Pour point, °F: –77.53 SP, °F: 16.11 Aniline point, °F: 113.83 Cetane index: 37.24 **Gas Oil** Range, °F: 500–550 Yield, vol %: 2.66 Gravity, °API: 28.62 Sulfur, wt %: 4.02 **Gas Oil** Range, °F: 550–650 Yield, vol %: 6.46 Gravity, °API: 25.54 Sulfur, wt %: 4.47 Pour point, °F: –10.9 CN: 38.0	Aniline point, °F: 117.3 Cetane index: 42.27 **Residue** Range, °F: 650+ Yield, vol %: 82.9 Sulfur, wt %: 5.86 Gravity, °API: 6.10 Sulfur, wt %: 5.86 Ni/V, ppm: 175/1407 Kinematic viscosity at 122 °F: 22,502

of 26.7 °C (80 °F), a gasoline must have ASTM distillation of 90 % distilled at 188 °C and 3 % distilled at 70 °C to give an acceptable warm-up time [7]. Standard organizations such as ASTM give such specifications for various products. The amount of particulate emissions is directly related to the aromatic and sulfur content of a fuel. Figure 4.3 shows the influence of sulfur reduction in gasoline from 500 to 50 ppm in the reduction of pollutant emissions [8].

The vapor pressure of gasoline or jet fuel determines their ignition characteristics. Freezing point is important for jet fuels and gas oils. For lubricating oil, properties such as viscosity and VI are important in addition to sulfur and PAH composition. Aniline point is a useful characteristic to indicate the power of solubility of solvents as well as aromatic contents of certain fuels. For heavy petroleum products, knowledge of properties such as CR, pour point, and cloud point are of interest.

One of the techniques used in refining technology to produce a petroleum product with a certain characteristic is the blending method. Once a certain value for a property (i.e., viscosity, octane number, pour point, etc.) of a petroleum product is required, the mixture may be blended with a certain component, additive, or another petroleum fraction to produce the required final product. For example, to increase the vapor pressure of gasoline, *n*-butane may be added during the winter season to improve the

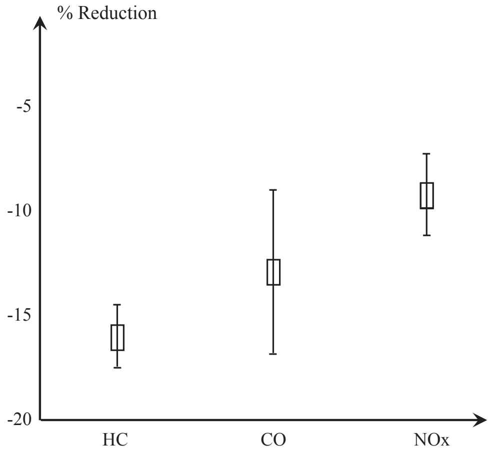


Figure 4.3—Influence of sulfur content in gasoline (from 500 to 50 ppm) in the reduction of pollutant gases [2,8]. HC, hydrocarbon; CO, carbon monoxide; NOx, nitrogen oxide.

engine-starting characteristics of the fuel [7]. The amount of required butane to reach a certain vapor pressure value can be determined through calculation of the vapor pressure blending index for the components, which is discussed in reference 2.

4.22 SPECIFICATIONS OF VARIOUS FUELS

Generally fuels are formulated specifically for different cars, different parts of the world, and different markets. Some general specifications for fuels are providing higher energy for power, forming a combustible mixture, easy ignition, minimizing harmful emissions, burning smoothly, and protecting the fuel delivery system. In this section, we present specifications recommended by international standard organizations and manufacturers for several fuels such as LPG, gasoline, jet fuel, diesel, marine fuel and middle distillates, biodiesel, fuel oil, and petroleum coke. Tables 4.5–4.20 list the current specifications for petroleum products that rely on the designated properties and standard methods that were introduced earlier in this chapter.

4.22.1 LPG Specifications

Liquefied petroleum gas (LPG) is a general term that refers to propane (C_3), butane (C_4), or a mixture of the two with impurities such as ethane, pentane, hydrogen sulfide (H_2S), and water. Propane, butane, and their mixtures are ideal fuels that can be stored and transported as liquids at ambient temperatures and moderate pressures. LPG has numerous applications because of its stability, high-energy content, relatively low sulfur content, and clean-burning properties [12]. The U.S. Gas Processors Association (GPA) specifies the properties for commercial LPG for propane, butane, and their mixtures [13]. Table 4.5 lists the GPA specifications for propane, butane, and propane-butane mixtures, including specifications for propane used as automotive fuel (HD-5) [13].

The use of LPG as automotive fuel has increased over the years, prompting more strict specifications, for example, propane HD-5, as given in Table 4.5. Table 4.6 compares the specifications of automotive LPG and domestic LPG. The composition and specifications of LPG vary depending on the country, and different suppliers have come up with their own specifications of "autogas." For example, Italy uses butane, the United Kingdom uses propane, and France uses a mixture of propane and butane as autogas. When used as a mixture, the fuel usually consists of 50 % propane and 50 % butane. Table 4.7 shows the autogas specifications reported by Shell [14].

4.22.2 Gasoline Specifications

Gasoline is used as fuel in spark-ignition engines. The term "petrol" is still used in several countries to denote gasoline. Gasoline specifications have evolved considerably in the last 25 years and show significant variations among countries in key properties such as octane number, vapor pressure, benzene, total aromatic sulfur content, and oxygenated compounds [15]. More changes are on the way to increase fuel efficiency and to reduce pollutant emissions.

In the United States, regulatory gasoline specifications enforced by the state governments and the U.S. Environmental Protection Agency (EPA) are guided by standard methods given by ASTM D4814. Some general specifications are as follows:

- Maximum sulfur content = 0.03 wt %
- Maximum lead content = 0.05 g Pb/gal
- Oxidation stability = 240 min
- Maximum benzene content = 1.0 wt %
- Oxygen content = 1.5–4.0 wt %
- VOC reduction of 21.4–23.4 %
- Maximum RVP = 6.4–15.0 psi
- Maximum distillation temperature for 10 % volume = 122–158 °F, for 50 % volume = 230–250 °F, and for 90 % volume = 365–374 °F

TABLE 4.5—Specifications for Commercial Propane, Butane, and Propane-Butane Mixture [13]

Property	Propane	Butane	Propane-Butane Mixture	Propane, HD-5 Automotive Fuel
Main components	Propane and propene	Butane and butene	Propane, propene, butane, butene	>90 % propane, <5 % propene
Maximum vapor pressure at 37.8 °C, kPa	1434	483	1434	1434
95 % boiling point at 100 kPa, T95, °C	–38	2	2	–38
Butane and heavier, vol %	2.5	–	–	2.5
Pentane and heavier, vol %	–	2	2	–
Oil stain observation (ASTM D2158)	Pass	–	–	Pass
Residue on evaporation of 100 mL (max), mL	0.05	–	–	0.05
Corrosion, copper strip (max)	No. 1	No. 1	No. 1	No. 1
Volatile sulfur, mg/m^3 (max)	34	34	34	23
Moisture content (ASTM D2713-70	Pass	–	–	Pass
Free water content	–	None	None	–

TABLE 4.6—Shell Autogas Specifications (date revised June 9, 2009) [14]

Property	Method	Typical Value
Vapor pressure at 40 °C, kPa	ISO 4256:1996 ISO 8973:1997	800 min 1530 max
Volatile residue C_5 and higher hydrocarbons, mol %	ISO 7941:1998	2.0 max
Residue on evaporation, mg/kg	JLPGA-S-05T/86 (105 °C)	20 max
Corrosion, copper strip	ISO 6251:1996	Class 1
Sulfur, mg/kg	ASTM D2784-98	100 max
Dienes, mol %	ISO 7941:1998	0.3 max
Moisture content	ISO 13758:1996	Pass
Free water	Visual inspection	Pass
MON	ASTM D2699	90.5

TABLE 4.7—The CaRFG Phase Standards [15]

Property	Flat Limits	Averaging Limits	Cap Limits	Methods
RVP,[a] psi max	7.00 or 6.90[b]	Not Applicable	6.40–7.20	ASTM D323-58 or 13 C.C.R. Section 2297
Sulfur, ppmw max	20	15	60[c]	ASTM D2622-94 or ASTM D5453-93
			30[c]	
			20[c]	
Benzene, vol % max	0.80	0.70	1.10	ASTM D5580-00
Aromatics, vol % max	25.0	22.0	35.0	ASTM D5580-00
Olefins, vol % max	6.0	4.0	10.0	ASTM D6550-00
T50, °F	213	203	220	ASTM D86-99
T90, °F	305	295	330	ASTM D86–99
Oxygen, wt %	1.8–2.2	Not Applicable	1.8[d]–3.5[e]	ASTM D4815-04
			0[d]–3.5[e]	

[a] The RVP standards apply only during the warmer weather months.

[b] The 6.90-psi flat limit applies when a producer or importer is using the CaRFG Phase 3 Predictive Model to certify a final blend not containing ethanol; otherwise, the 7.0-psi limit applies.

[c] The CaRFG Phase 3 sulfur content cap limits of 60, 30, and 20 ppm are phased in starting December 31, 2003, December 31, 2005, and December 31, 2011, respectively.

[d] The 1.8 wt % min oxygen content cap only applies during specified winter months in the areas identified in Section 2262.5(a).

[e] If the gasoline contains more than 3.5 wt % oxygen from ethanol but no more than 10.0 vol % ethanol, the maximum oxygen content cap is 3.7 wt %.

- Maximum EP = 437 °F
- Volatility temperature (V/L = 20) minimum = 105–124 °F

Fuel manufacturers report their own specifications in compliance with federal and state government regulations. They usually provide Material Safety Data Sheets for safe and efficient use of fuels, especially on the main hazards such as fire. Fuels are also harmful or fatal if swallowed.

The three grades of gasoline usually sold in the United States are regular grade with a posted octane $[(R + M)/2]$ level of 87, an intermediate grade with an octane level of 89, and a super grade with an octane number between 93 and 94. Ethanol is used as an octane booster or for environmental purposes in more than half of the gasoline sold in the United States.

Table 4.7 lists the California Reformulated Gasoline specifications known as CaRFG Phase 3 standards as mandated by the state law as of August 29, 2008 [15,16]. These standards are the most restrictive specifications in the United States. Reformulated gasoline (RFG) was introduced in the 1990s in the United States to be used in carbon monoxide and ozone nonattainment areas during certain times of the year. RFGs have lower vapor pressure and lower benzene, aromatic, and olefin contents. RFG specifications are mandated by federal law and implemented by EPA.

In Europe, the European Commission sponsored the Auto Oil Programme starting in the 1990s with the collaboration of Europia (the Association of European Oil Companies) and ACEA (the Association of European Motor Manufacturers). This has culminated in the introduction of new gasoline specifications that were implemented in two stages starting in 2000 and 2005, respectively. The changes in the specifications included lowering the limits for benzene, sulfur, olefin, and total aromatic concentrations and reducing the vapor pressure. Table 4.8 lists the current specifications for European Union Norm EN 228 [15,17] and ACEA Worldwide Fuel Charter Category 4 gasoline [15,18]. The standard methods used in measuring the listed properties are also included in references 17 and 18.

Table 4.9 gives the specifications for unleaded gasoline use in the major cities in India [15,19]. There are plans

TABLE 4.8—Specifications for European Union Norm EN 228 Gasoline [17] and ACEA Worldwide Fuel Charter Category 4 Gasoline [18]

Property	European Union Norm EN 228	ACEA Worldwide Fuel Charter Category 4 Gasoline
Octane rating, (*RON* + *MON*)/2	90	87–93
Vapor pressure, kPa	45–90[a]	45–60[b]
Sulfur concentration, ppmw max	10	10
Benzene concentration, vol %	1.0	1.0
Aromatic concentration, vol %	35.0	35.0
Olefin concentration, vol %	18.0	10.0
T50, °C	–	77–100
T90, °C	–	130–175
Percent evaporated at, vol %		
70 °C (E70 summer)	20–48	–
70 °C (E70 winter)	22–50	–
70 °C (E70)	–	20–45[b]
100 °C (E100)	–	50–65[b]
150 °C (E150)	75	–
180 °C (E180)	–	90
FBP, °C	210	195
Oxygen concentration, wt %	2.7[c]	2.7[d]

[a] Range is from summer minimum (45 kPa) to winter maximum (90 kPa).

[b] Absolute vapor pressures and distillation temperature points are for gasoline markets with ambient temperatures above 15 °C. Other limits apply for markets with lower ambient temperatures.

[c] Permitted max vol % oxygenates: methanol = 3 %, ethanol = 5 %, isopropanol = 10 %, isobutanol = 10 %, ethers (≥5 carbon atoms) = 15 %.

[d] Where oxygenates are used, ethers are preferred. Where up to 10 vol % of ethanol is permitted by existing regulations, the gasoline must meet all of the other limits above. Methanol is prohibited. Propanol and higher alcohols are limited to ≤0.1 vol %.

TABLE 4.9—Unleaded Gasoline Specifications for Urban Areas in India [19]

Property	Regular Gasoline Limit	Premium Gasoline Limit
Octane rating, (RON + MON)/2	86	90
Vapor lock index,[a] kPa	750–950	750–950
Sulfur concentration, ppmw max	150	150
Benzene concentration, vol %	1.0	1.0
Aromatic concentration, vol %	42.0	42.0
Olefin concentration, vol %	21.0	18.0
T90, °C	150	150
FBP, °C	210	210
Oxygen concentration, % wt	3.9	–
MTBE, vol %	15	15

[a] Vapor pressures are expressed as vapor lock index (VLI), which is 10(RVP) + E70, where E70 is the vol % evaporated at 70 °C.

for lowering the maximum sulfur content from 150 to 50 ppmw in the near future. The standards for the rural areas are more flexible.

Table 4.10 gives the gasoline specifications developed by the national governments in Australia [15,20] and New Zealand [15,21]. The individual states in Australia and the regional councils may enforce their own standards.

In Canada, gasoline quality has been monitored by provincial governments since 2008, except for some national standards over sulfur, benzene, and lead and the ability to require certain amounts of renewable fuels such as ethanol. The voluntary national standard CGSB 3.5 for automotive gasoline was developed by the Canadian General Standards Board (CGSB) to mandate the sulfur, benzene, and lead limits as follows [15,22]:

- Sulfur = 30 ppmw maximum
- Benzene = 1 vol % maximum
- Lead banned completely

TABLE 4.10—Unleaded Gasoline Specifications for Australia [20] and New Zealand [21]

Property	Australia National Standard [20]	New Zealand National Standard [21]
Octane rating, (*RON* + *MON*)/2	88	90
Vapor pressure, kPa	–	45–95[a]
Flexible volatility index,[b] kPa	–	115 max
Sulfur concentration, ppmw max	50	150[c]
Benzene concentration, vol %	1.0	1.0
Aromatic concentration, vol %	42.0	42.0
Olefin concentration, vol %	18.0	18.0
Percent evaporated at, vol %		
• 70 °C (E70)	–	22–48
• 100 °C (E100)	–	45–70
• 150 °C (E150)	–	75
FBP, °C	210	210
Oxygen concentration, wt %	3.9	–
Ethanol, vol %	10[d]	10[e]

[a] Range is from summer minimum (45 kPa) to winter maximum (95 kPa).
[b] Flexible volatility index is vapor pressure in kPa + 0.7(E70).
[c] The New Zealand sulfur standard is 150 ppmw as of January 2008. However, it includes a statement that there is an "ultimate requirement of 10–15 ppmw."
[d] Permitted maximum vol % of oxygenates other than ethanol: ethers = 1 %, and *tert*-butanol = 0.5 %.
[e] Permitted maximum vol % of oxygenates other than ethanol: total other oxygenates = 1 %.

TABLE 4.11—ASTM D1655-07 (July 1, 2007) Requirements for Jet A and Jet A-1

Specification	ASTM Test Method	Recommended Value
Appearance	Visual	Clear and bright
Aromatics, vol % (max)	D1319	25
Total sulfur, wt % (max)	D1266, D1552, D2622, D4244, D5453	0.3
Sulfur, mercaptan, wt % (max)	D3227	0.003 (30 ppmw)
Distillation, 10 % recovery, °C (max)	D86	205
Flash point, °C (min)	D58, D3828	38
Density at 15 °C (kg/m^3)	D1298, D4052	775–840
Vapor pressure (at 100 °F), max, kPa	D323, D5191	14–21
Freezing point, °C (max)	D2386, D7153, D7154	–40 (Jet A), –47 (Jet A-1)
Viscosity, cSt at –20 °C (max)	D445	8
SP, mm	D1322	25
Naphthalene, vol % (max)	D1840	3.0
Net heat of combustion, MJ/kg	D3338, D4529	42.8

4.22.3 *Jet Fuel Specifications*

Jet fuel is used in jet and turboprop aviation engines; it is a kerosene-based fuel different from aviation gasoline (avgas—a high-octane gasoline) that is used in smaller piston-powered aircraft. Among the most important properties of jet fuel are the freezing point, density, sulfur content, and SP. Jet A is a designation for commercial jet fuel used in the United States similar to Jet A-1 fuel, which is used outside of the United States. Table 4.11 gives ASTM D1655-07 (July 1, 2007) requirements for Jet A/A-1 fuel.

ExxonMobil gives a good summary of specifications for various jet fuels around the world [23]. An engine manufacturer's requirements for aviation fuel are given in Table 4.12 [23]. Icing inhibitors used for jet fuels are based on ethylene glycol ethyl ether (EGEE) or ethylene glycol monomethyl ether (EGME), which are blended with methanol and usually have a boiling range of 127–140 °C with a maximum water content of 0.2 %.

4.22.4 *Diesel Fuel Grades and Specifications*

Diesel fuel is used in compression-ignition engines; it is derived from the gas oil fraction of crude oil. Important properties include autoignition characteristics (CN or cetane index), low-temperature performance (e.g., cloud point and pour point), and sulfur content. ASTM D975-09a covers seven grades of diesel fuel oils suitable for various types of diesel engines. These grades are described in Table 4.13. The sulfur grade Sxxx designation has been

TABLE 4.12—Engine Manufacturer's Requirement for Aviation Fuel Wide-Cut Kerosene (Pratt & Whitney, February 23, 2007)

Specification	ASTM Test Method	Recommended Value
Appearance	–	Clear and Bright
Aromatics, vol % (max)	D1319	25
Total sulfur, wt % (max)	D1266, D1552, D2622, D4244, D5453	0.3
Sulfur, mercaptan, wt % (max)	D3227	0.005 (50 ppmw)
Distillation, 10 % recovery, °C (max)	D86	205
FBP (EP), °C (max)	D86	300
API gravity	D287, D1298, D4052	37–57
Vapor pressure (at 100 °F), max, psi	D323	3
Freezing point, °C (max)	D2386, D5972	–40
Viscosity, cSt at –20 °C (max)	D445	8.5
Net heat of combustion, MJ/kg	D240, D1405, D2382, D3338, D1322	25

TABLE 4.13—U.S. Diesel Fuel Grades According to ASTM D975-09a

Fuel Grades	Description	Max Sulfur (ppm)
No. 1-D S15	A special-purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 15-, 500-, or 5000-ppm sulfur (max), as indicated, and higher volatility than those provided by No. 2-D fuels.	15
No. 1-D S500		500
No. 1-D S5000		5000
No. 2-D S15	A general-purpose, middle distillate fuel for use in diesel engines requiring a fuel with 15-, 500-, or 5000-ppm sulfur (max), as indicated, especially suitable for use in applications with conditions of varying speed and load.	15
No. 2-D S500		500
No. 2-D S5000		5000
No. 4-D	A heavy distillate fuel, or a blend of distillate and residual oil, for low- and medium-speed diesel engines in applications involving predominantly constant speed and load.	

adopted to distinguish grades by sulfur. S5000 grades correspond to the previous "regular" sulfur grades No. 1-D and No. 2-D. S500 grades correspond to the previous "low-sulfur" grades. S15 grades were not included in the previous grade system and are commonly referred to as "ultralow sulfur" grades.

Table 4.14 compares specifications of No. 2 diesel fuel in the United States (according to ASTM D975) and Europe (EN 590–2005).

The European Commission's latest "Auto-Oil II" discussion paper proposed that a 10-ppm sulfur ultralow sulfur diesel (ULSD) be gradually phased in, starting with a 10 % supply requirement on January 1, 2007. This 10-ppm fuel was a phase-in alongside a 50-ppm sulfur ULSD that became mandatory throughout Europe in 2005. It was suggested that the 10-ppm sulfur ULSD supply mandate would jump to a minimum of 25 % in 2011, although individual countries could petition for 3-year derogation of the 25 % mandate if they could prove no benefits in greenhouse gas reductions [24].

European governments earlier agreed that highway diesel sulfur be cut to 50 ppm starting in 2005, but they left it to the Auto-Oil II program to recommend other specifications for cetane, distillation, density, and polyaromatic limits. The European Commission had also agreed to consider whether all ULSD should drop from 50- to 10-ppm sulfur in 2008, as was recommended by Germany. However, the European Commission's Auto-Oil II draft proposal fell short of recommendations by most of the Northern European member states (Scandinavia) to require 100 % 10-ppm ULSD by 2007/2008. The situation in the United States is somewhat different. The U.S. Department of Energy said it would be unwise to set a 15-ppm sulfur cap until catalyst developers determine maximum sulfur tolerance for nitrogen oxide (NO_x) traps combined with particulate matter (PM) traps, the technology of choice in EPA's diesel emissions regulatory scheme.

One report shows that in Europe in 1998, approximately one third of countries were using diesel fuel with a sulfur content of 0.05 % (500 ppm); within 3 years this number had reduced to less than one quarter. Use of ULSD is spreading; for example, one of the South African diesel fuel samples found in the survey also was a near-zero-sulfur ULSD, although South Africa does not require such fuel. The same report shows that Korea and Singapore have sharply cut diesel sulfur limits, and similar trends are expected throughout the Asia Pacific region. Specifications are tightening in an effort to reduce smoke production, particularly in China, Malaysia, and India. Despite these new density/distillation limits, cold flow performance remains essentially unchanged across all regions. However, one problem associated with sulfur reduction is a drop in fuel lubricity, which refineries should address by adding

TABLE 4.14—Specifications for U.S. Diesel Fuel No. 2-D S15 and Europe EN 590 (2005) [25]

	United States, ASTM D975 –09a		Europe, EN 590 (2005)	
Specification	**ASTM Test Method**	**Recommended Value**	**IP Test Method**	**Recommended Value**
Flash point, °C (min)	D93	52	IP 404	55
Water and sediment, vol % (max)	D2709	0.05	ISO 12937	0.02
Distillation temperature, °C, at vol % vaporized	D86	T90, 282/338 (min/max)	ISO 3405	T85, 350 (max) T95, 360 (max)
Kinematic viscosity, (mm^2/s) at 40 °C (min/max)	D445	1.9/4.1	IP 71	2.0/4.5
Ash, wt % (max)	D482	0.01	IP 4	0.01
Sulfur, ppmw (max)	D2622	15	IP 336	50
CN, min	D613	40	ASTM D613	51

TABLE 4.15—Requirements for Three Types of Marine Distillate Fuels in Europe [27]

Property	Test Method	Category A	Category B	Category C
Density at 15 °C, kg/m^3	ISO 3675	890	900	920
Viscosity at 40 °C, mm^2/s	ISO 3140	6.0	11.0	14.0
Flash point, °C (min)	ISO 2719	60	60	60
Pour point, °C (max)				
Winter quality	ISO 3016	–6	0	0
Summer quality		0	0	6
Sulfur, %	ISO 8754/ISO 14596	1.5	2	2
Cetane index (min)	ISO 4264	40	35	–
CR (max)	ISO 10370	0.3	0.3	2.5
Ash, wt % (max)	ISO 6245	0.01	0.01	0.03
Appearance	Visual	Clear and bright		
Water, % (vol/vol)	ISO 3733	–	0.3	0.3
Vanadium, ppmw (mg/kg)	ISO 14597 (IP 501)	–	–	100
Aluminum plus silicon	ISO 10478 (IP 501)	–	–	25

lubricity additives. Between 1998 and 2001, the average CN of diesel fuels jumped from 50.6 to 54.6 according to the EN 590 specifications [26].

An ASTM standard (D2069) was used to cover different marine diesel fuels, but it has been withdrawn. Technically, it was equivalent to ISO 8217. Table 4.15 gives some requirements for three types of marine fuels in Europe [27]. The user's requirement will always be that the burner fuel should be safe to handle and easy to transfer; be capable of being adequately cleaned of catalyst fines, dirt, and water; and should be noncorrosive. ISO 8217 standard does cover these properties for marine distillate fuels.

4.22.5 Specification of Biodiesels

Technically, biodiesel is a fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fat that meets prevailing standard specifications [28]. Various countries have their own biodiesel standards, and Table 4.16 shows Indian (IS 15670), U.S. (ASTM D6751), and European (EN 14214) biodiesel standards.

4.22.6 Fuel Oil (Heating Oil) Grades and Specifications

Fuel oil is burned to generate heat for different applications ranging from space heating to electricity generation. Different types of burners used in these applications require different grades of fuel oils. ASTM D396 divides fuel oils into five different grades designated as No. 1, 2, 4, 5, and 6. Table 4.17 lists these grades along with their common uses and significant properties [29]. In general, all grades of fuel oils should be homogeneous hydrocarbon liquids free from inorganic acid and excessive foreign solid matter.

Table 4.18 lists some specifications for the different grades of fuel oils. The viscosity values given in parentheses are for information only, not necessarily limiting.

TABLE 4.16—Common Uses and Some Significant Properties of Different Grades of Fuel Oils [28]

Grade	Classification	Application	Significant Properties
No. 1	Distillate	Domestic and small industrial burners of the vaporizing type	Volatility and pour point
No. 2	Distillate	Atomizing-type domestic and small industrial burners	Volatility and viscosity
No. 4 (light)	Heavy distillate	Pressure-atomizing-type commercial/industrial burners	Viscosity and pour point
No. 4	Heavy distillate, distillate/residual blends	Pressure-atomizing-type commercial/industrial burners; preheating not required for handling or burning	Viscosity, flash point, and sulfur content
No. 5 (light) and No. 5 (heavy)	Residual	Industrial burners; preheating may be required for handling and burning	Viscosity, flash point, and sulfur content
No. 6 or Bunker C	Residual	Industrial burners; preheating required for handling and burning	Viscosity, flash point, and sulfur content

TABLE 4.17—Some Specifications for Fuel Oils (ASTM D396)

Properties	No. 1	No. 2	No. 4	No. 5	No. 6
SG, 60/60 °F	0.8499	0.8762	–	–	–
°API	35 min	30 min			
Flash point, °C min	38	38	55	55	60
Pour point, °C max	–18	–6	–6	–	–
Kinematic viscosity, mm^2/s (cSt)					
At 40 °C (104 °F) min	1.3	1.9	5.5	–	
max	2.0	3.4	24.0	–	–
At 50 °C (100 °F) min	–	–	–	5.0	15.0
max	–	–	–	5.0	50.0
Distillation temperature, °C					
10 % point max	215	–			
90 % point min	–	282			
max	288	338			
Sulfur content, mass, max	0.5	0.5			
Corrosion copper strip, max	3	3			
Sulfated ash, % mass, max			0.10	0.15	
Water and sediment, vol %, max	0.05	0.05	(0.50)	(1.00)	(2.00)

4.22.7 Classification and Properties of Petroleum Coke

Petroleum coke is generally defined as a solid carbonization product from delayed coking or fluid coking of vacuum distillation residua to produce sponge coke (or fluid coke), or from delayed coking of fluid catalytic cracking (FCC) decant oil to produce needle coke. Table 4.19 shows an overall classification of green petroleum cokes (sponge, fuel, shot, needle, and fluid coke) and their industrial applications [29].

TABLE 4.18—Various Biodiesel Standards Applicable in India, United States, and Europe [28]

Property	BIS (IS 15670)	ASTM D6751	EN 14214
Density at 15 °C, kg/m^3	860–900	–	860–900
Kinematic viscosity at 40 °C, cSt	2.5–6.0	1.9–6.0	3.5–5.0
Flash point (PMCC) °C, min	120	93 (Closed Cup)	>101
Sulfur, ppm (max)	50	15	10
CR, % by mass	0.05	0.05 (max)	0.3
Water content and sediment	500 mg/kg	0.05 vol % (max)	500 mg/kg
Total contamination, ppm (max)	24	24	24
Sulfated ash content, % (m/m)	0.02	200 ppm (max)	0.02
Copper strip corrosion (3 h at 50 °C)	Class 1 (max)	Class 3	Class 1 (max)
CN, min	51	47	51
Acid value, mg KOH/g	0.5	0.50	0.5
Iodine value	NA	NA	120
Free glycerol, % mass (max)	0.02	0.020	0.02
Total glycerol, % mass (max)	0.25	0.240	0.25
Oxidation stability at 110 °C (h) (max)	6	3	6
Phosphorous, mg/kg	10	10 ppm (max)	10
Alkaline metals	NA	<5 ppm Group I (Na, K) <5 ppm Group II (Ca, Mg)	<5 mg/kg Group I (Na, K) <5 mg/kg Group II (Ca, Mg)

NA, not applicable.

TABLE 4.19—Coking Processes, Feedstocks, and Commercial Uses of Petroleum Coke [29]

Process	Product	Commercial Uses of Coke
Delayed coking	Sponge coke	Carbon anodes for aluminum industry
	Fuel coke	Fuel for cement kilns, industrial heat and steam raising, fuel for utility industry
	Shot coke	No significant commercial use, some niche applications (e.g., TiO_2 production), packing material
	Needle coke	Graphite electrodes for electric-arc furnaces for iron and steel industry
Fluid coking	Fluid coke	Industrial heat and steam raising
Flexi-coking	Fluid coke, or fuel gas	Industrial heat and steam raising

Petroleum cokes produced by delayed or fluid coking are generically called *green cokes* because of their relatively high volatile matter content (5–15 %). Fluid cokes generally have lower volatile matter content than delayed cokes (typically ~5 %) because of the relatively high temperatures used in fluid coking. The flexi-coking process is a variation of fluid coking in which part or the entire coke product can be gasified to produce fuel gas. This is particularly useful for high-sulfur- and high-metal-content cokes that are not suitable for combustion. Green cokes with relatively low sulfur, metal, and ash contents are calcined (i.e., heat treated to ~1300 °C) to remove volatile matter. Calcined coke has a mass fraction of hydrogen less than 0.1 %. Calcined cokes are used as fillers for carbon anodes, graphite electrodes, or specialty carbons. Table 4.20 lists the specifications of calcinable green cokes and calcined cokes used in carbon anode and graphite manufacture [29]. Not all green cokes produced by delayed coking of vacuum distillation residua are suitable for calcination. Depending on their sulfur and metal contents, noncalcinable delayed cokes or fluid cokes are used as fuel in industrial furnaces.

4.23 MINIMUM LABORATORY DATA

As discussed earlier, measurement of all properties of various petroleum fractions and products in the laboratory is an impossible task because of the required cost and time. However, there are several basic parameters that must be known for a fraction to determine various other properties needed for design, operation, and quality of a fuel. For example, to estimate sulfur content of a fraction, the input parameters of SG, molecular weight, density, and refractive index at 20 °C are needed [2]. If experimental values of

TABLE 4.20—Typical Green and Calcined Coke Specifications [29]

Property	Green Coke	Calcined Coke
Ash	0.1–1.0 %	0.2–1.5 %
Calcium	25–500 ppm	25–500 ppm
Fixed carbon	87–97 %	97–99 %
Hydrogen	3.0–4.5 %	<0.1 %
Iron	50–2000 ppm	50–2000 ppm
Manganese	2–100 ppm	2–100 ppm
Magnesium	10–250 ppm	10–250 ppm
Moisture	0.5–2.0 %	Negligible
Nickel	10–100 ppm	10–100 ppm
Nitrogen	0.1–0.5 %	<0.1 %
Real density	1.6–1.8 g/cm^3	2.08–2.13 g/cm^3
Silicon	50–300 ppm	50–300 ppm
Sulfur	0.2–2.5 %	0.2–2.5 %
Titanium	2–60 ppm	2–60 ppm
Vanadium	5–500 ppm	5–500 ppm
Volatile matter	5–15 %	<0.5 %

all of these parameters are available, then a good estimate of sulfur content can be obtained. However, because all of these data are not normally available, M, n, and d_{20} should be estimated from SG and T_b. Therefore, a minimum of two parameters (i.e., boiling point and SG) are needed to estimate the sulfur content. However, for heavy fractions in which distillation data are not reported, M should be estimated from kinematic viscosity at 38 and 99 °C (ν_{38} and ν_{99}) and SG. Once M is estimated, n can be estimated from M and SG and density at 20 °C is estimated directly from SG. With the knowledge of M and SG, all other parameters can be estimated from methods presented in ASTM Manual 50 [2]. Therefore, at least three parameters (i.e., ν_{38}, ν_{99}, and SG) must be known to determine sulfur content or other characteristics. In the case that only one viscosity value is known (i.e., ν_{38}), the ν_{99} may be estimated from SG. In this way, the estimated value of M is less accurate than when the values of ν_{38}, ν_{99}, and SG are known from experimental measurements. We see that again for heavy fractions with knowledge of only two parameters (i.e., ν_{38} and SG or ν_{99} and SG) all basic properties of the fraction can be estimated. Therefore, to obtain the basic characterization parameters of a petroleum fraction, a minimum of two parameters are needed.

With the knowledge of PNA composition a better characterization of a fraction is possible through available techniques. Therefore, if the composition along boiling point is available, nearly all other parameters can be determined through mid-boiling point and PNA composition with better accuracy than using only boiling point and SG. For heavy fractions in which T_b may not be available, the best alternative parameter is to measure M and PNA composition. Because there are many scenarios to estimate the basic properties of petroleum fractions, use of available data to predict the most accurate characterization parameters is an engineering art that has a direct effect on the subsequent prediction of physical properties and eventually on design calculations. The basic laboratory data that are useful in characterization methods on the basis of their significance and simplicity are as follows:

- Distillation data, boiling point
- SG
- Composition (i.e., PNA content)
- Molecular weight
- Refractive index
- Elemental analysis (i.e., C, H, and S composition, metal composition, etc.)
- Kinematic viscosity at 37.8 and 98.9 °C (100 and 210 °F)

Using these properties, various physical properties can be estimated with a good degree of accuracy. However, specific properties that are characteristic of each quality product should be measured in addition to the above properties. For example, for diesel fuel, cetane index should be measured, whereas for motor and aviation gasoline, octane number needs to be known. Freezing point must be known for jet fuels, whereas pour point is needed for heavy products as discussed above for each specific property.

REFERENCES

[1] ASTM, *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 2005.

[2] Riazi, M.R., "Characterization and Properties of Petroleum Fractions," MNL5, ASTM International, West Conshohocken, PA, 2005.

[3] Private communication with James F. McGehee of UOP, Des Plaines, IL, May 21, 2009.

[4] ASTM Standard D6352: Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700 °C by Gas Chromatography, *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 2004.

[5] *API Technical Data Book—Petroleum Refining*, 6th ed., T.E. Daubert, R.P. Danner, Eds., American Petroleum Institute (API), Washington, D.C., 1997.

[6] Speight , J.G., *The Chemistry and Technology of Petroleum*, 3rd ed., Marcel Dekker, Inc., New York, 1998.

[7] Gary, J.H., Handwerk, G.E., and Kaiser, M.J., *Petroleum Refining, Technology and Economics,* 5th ed., Marcel Dekker, Inc., New York, 2007.

[8] Wauquier, J.-P., *Petroleum Refining, Vol. 1 Crude Oil, Petroleum Products, Process Flowsheets*, Editions Technip, Paris, 1995.

[9] Baird, C.T., *Crude Oil Yields and Product Properties,* Geneva, Switzerland, 1981.

[10] Denis, J., Briant, J., and Hipeaux, J.C., *Lubricant Properties Analysis & Testing,* G. Dobson, trans., Editions Technip, Paris, France, 1997.

[11] *Oil and Gas Journal Data Book,* 2000 edition, PennWell, Tulsa, OK, 2000, pp. 295–365.

[12] Falkiner, R.J., "Liquified Petroleum Gas," *Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing*, MNL37, ASTM International, West Conshohocken, PA, 2003, pp. 31–53.

[13] *Liquified Petroleum Gas Specifications and Test Methods*, Publication 2140, Gas Processors Association, Tulsa, OK, 1997.

[14] "Shell Autogas Properties," http://www.shell.com/home/content/au-en/shell_for_motorists/fuels/autogas/autogas_properties_0821.html.

[15] "Gasoline," http://en.citizendium.org/wiki/Gasoline.

[16] "California Reformulated Gasoline Phase 3 Specifications," http://www.arb.ca.gov/fuels/gasoline/gasoline.htm.

[17] "European Union Norm EN 228 for Gasoline," http://www.biofuels-platform.ch/en/infos/en228.php.

[18] "ACEA Worldwide Fuel Chapter," http://www.acea.be/images/uploads/pub/Final WWFC 4 Sep 2006.pdf.

[19] "India Gasoline Specifications," http://www.apecconsulting.com/PDF/WebProductQualitySample.pdf.

[20] "Gasoline Specifications for Australia," http://www.environment.gov.au/atmosphere/fuelquality/standards/petrol/index.html.

[21] "New Zealand Gasoline Specifications," http://www.med.govt.nz/templates/MultipageDocumentPage____ 10182.aspx#P437_17784.

[22] "Gasoline Specifications for Canada," http://www.visiondurable.com/media/pdf/ressources/etudes/Fuel_Quality_ in_Canada_-_Final_Report.pdf.

[23] Warren, K.A., *World Jet Fuel Specifications*, ExxonMobil Publication, Fairfax, VA, 2008, http://www.exxonmobil.com/AviationGlobal/Files/WorldJetFuelSpecifications2005.pdf.

[24] Peckham, J., "European Commission Proposes 10 ppm ULSD Phase-In from 2007," http://findarticles.com/p/articles/mi_m0CYH/is_5_5/ai_71836375/.

[25] "Diesel Fuel," http://www.adb.org/Documents/Guidelines/Vehicle.../cf_ch04.pdf.

[26] Peckham, J., "2/3 of World's Diesel Fuel Now Low-Sulfur: Infineum Survey," March 5, 2001, http://findarticles .com/p/articles/mi_m0CYH/is_5_5/ai_718363363/.

[27] Fabrick, W., "Updating ISO 8217," International Fuel Executive Testing Services, World Bunkering, United Kingdom, 2005.

[28] Agrawal, A.K., Bajaj, T.P., "Process Optimisation of Base Catalysed Transesterification of Karanja Oil for Biodiesel Production," *Int. J. Oil, Gas Coal Technol.*, Vol. 2, 2009, pp. 297–310.

[29] Eser, S., and Andrésen, J., "Properties of Fuels, Petroleum Pitch, Petroleum Coke, and Carbon Materials," *Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing*, MNL37, ASTM International, West Conshohocken, PA, 2003, pp.757–786.

5

Crude Oil Refining Processes

Semih Eser[1] and M.R. Riazi[2]

5.1 A BRIEF HISTORICAL PERSPECTIVE OF CRUDE OIL REFINING

Petroleum in the past century and present time has been the major fossil fuel that provides most of the energy consumed by humans. For this reason, the last 100–150 years are referred to as the "Oil Century," or "Petroleum Era" [1]. It seems that at least for the present century, petroleum either in the form of liquid crude oil or natural gas will remain as a major source to meet the world energy demand. The use of petroleum and its derivatives has a long history. Sumerians, Assyrians, and Babylonians used crude oil and asphalt found in natural seeps more than 5000 years ago. Around 500 BC, Egyptians used asphalt for mummification of their dead rulers. Some 2000 years ago, Arab scientists developed methods for the distillation of petroleum, and these methods were introduced to Europe by way of Spain. Discovery of distillation led to fractionation of petroleum into various products such as naphtha (or naft), and it was used as an illuminant [1]. Greeks also used petroleum products known as Greek fire in warfare. Marco Polo (13th century) reported on the petroleum industry in the Baku region of northern Persia (now part of Azerbaijan). Although petroleum has been known for many centuries, the strong demand for kerosene to substitute for whale oil as an illuminant led to the birth of the modern petroleum technology and refining. In an effort to secure a reliable supply of kerosene, a group of investors in Pennsylvania charged E.L. Drake to drill for petroleum, and he completed the first commercial oil well in 1859 in Titusville, PA, in the United States [1].

The first refinery in the United States was built near Oil Creek, PA, in 1860 by William Barnsdall and William H. Abbott. By 1870, a basic operating pattern had been developed to produce more kerosene for lamps and more lubricant for steam engines from the remainder of the crude. In 1876, Chevron built a simple refinery in California. Stills were used to heat 25–40 bbl/day of crude to produce kerosene, lubricants, waxes, and gasoline, which was considered a useless byproduct at the time. In the early 1900s, the demand for kerosene decreased with the advent of electric light, but the introduction of the internal combustion engine and mass production of automobiles created a large demand for gasoline. In the early days of the petroleum industry in the United States, oil was processed in simple batch distillation units [1]. For each distillation run, 200 bbl of oil were charged into stills, and the oil temperature was raised to 750°F. The produced vapors were condensed in two-stage condensers: one with reflux and the second without reflux cooled by water. Gases in the product were separated to produce approximately 3 bbl of gasoline from 200 bbl of charge. The remaining crude in the still was removed as tar and heavy fuel. The process took 24 h, and after each run the still had to be cleaned. Coal was used as fuel to heat the oil. Today's refineries can produce more than 50 bbl of gasoline from each 100 bbl of crude through chemical changes in the crude composition. This development indicates how the refining industry has advanced over the last century, particularly with the introduction of thermal and catalytic conversion processes.

Until the early 1940s, most petroleum refineries in the United States comprised just atmospheric crude oil distillation units. More advanced refineries also had vacuum distillation units and simple thermal cracking units such as visbreakers. World War II and the burgeoning air transportation industry created demand for a higher quantity and a higher quality of motor and aviation gasoline. Many of the refining processes that constitute today's complex refineries were often developed through collaboration between the oil companies in the 1940s. These processes became commercially available within 5–10 years after the end of the war and caused a rapid growth of the worldwide petroleum industry with the increasing demand for distillate fuels, gasoline, jet fuel, and diesel. Up until the 1970s, a principal focus in refining was to improve the performance characteristics of the fuels, such as the octane number for gasoline. Environmental regulations on petroleum fuels introduced mostly through the environmental legislation in the 1970s have focused on reducing the heteroatom content of fuels, particularly that of sulfur species, placing limits on the air emissions of designated pollutants from combustion [2]. Recent trends in refinery configurations include adding capacity and processes to convert heavier (lower API gravity) and dirtier (higher heteroatom content) crude oils into increasingly cleaner fuels as designated by environmental regulations. This has increased the significance of catalytic processes and catalyst development as well as the demand for hydrogen, which is used in hydrotreating and hydrocracking processes, as described in the following sections.

5.2 OBJECTIVES OF CRUDE OIL REFINING

An overall objective of a petroleum refinery is to add value to a crude oil feed through production of marketable fuels and materials at the lowest possible cost in accordance with product specifications and environmental regulations. In technical terms, achieving this objective generally depends on the composition and properties of the selected crude as well as the configuration of refinery processes.

---

[1] The Pennsylvania State University, University Park, PA, USA

[2] Kuwait University, Kuwait

Considering that the products that are in high demand are light and middle distillates such as gasoline, jet fuel, and diesel, and these fuels have higher H/C ratios than crude oils, the two processing pathways for crude oil refining include carbon rejection and hydrogen addition.

A refinery configuration should incorporate an optimal combination of the two pathways in separation and conversion processes to achieve the overall refinery objective. A multitude of economic factors that may be unique to a given refinery (e.g., crude oil market, product markets, capital cost, etc.) must be considered in setting up specific refinery objectives. Any discussion of refinery economics is beyond the scope of this chapter. However, it may be pointed out that because of the volatility of crude oil prices and fluctuations in product demands, operational flexibility in terms of a refinery's capability to process a wide range of crudes and to adjust the product slate according to the prevailing product markets has become a critical factor to realize the refinery objectives. This requires the optimization of each refinery process within an optimal integration of all of the processes to achieve the desirable product slate at the lowest cost. A general description of overall refinery flow and the introduction of major refinery processes follow in Section 5.3.

5.3 OVERALL REFINERY FLOW

In a refinery, crude oil is transformed into commercial fuels and materials using an integrated sequence of different processes that can be classified into four categories: separation, conversion, finishing, and supporting. Figure 5.1 shows an overall refinery flow diagram starting with the crude oil entering a refinery at the top left and its generic progression through different types of processes that eventually lead to commercial fuels and materials, including liquefied petroleum gas (LPG), motor gasoline, jet fuel, diesel fuel, fuel oil, solvents, lubrication oils, asphalt, and coke. The key properties and specifications of these fuels and materials are discussed in Chapter 2. The four groups of processes that are shown in Figure 5.1 are introduced and discussed in the following sections, starting with the separation processes.

5.3.1 Separation Processes

Separation processes are physical processes that rely on specific physical properties of crude oils or their components to fractionate or isolate their constituents. The most prominent physical separation process in a refinery is the crude distillation process, which fractionates a crude oil into several cuts with respect to their boiling points that range from gases at ambient conditions (e.g., propane and butane that constitute LPG) to heavy vacuum gas oils that have end points (higher boiling point of a distillation cut) of approximately 1000°F. Distillate fractions of crude oil that are directly sent to a finishing step or require minimal processing before entering a product pool are designated by the phrase "straight-run," such as straight-run naphtha, straight-run kerosene, etc. The higher boiling crude oil fractions and the distillation residua obtained from the atmospheric distillation and vacuum distillation towers are sent to subsequent separation and conversion processes as described in the overall flow diagram to produce the desired fuels and materials. In addition to boiling points, other physical properties of crude oil components can be used for separation purposes, such as solubility/insolubility in a

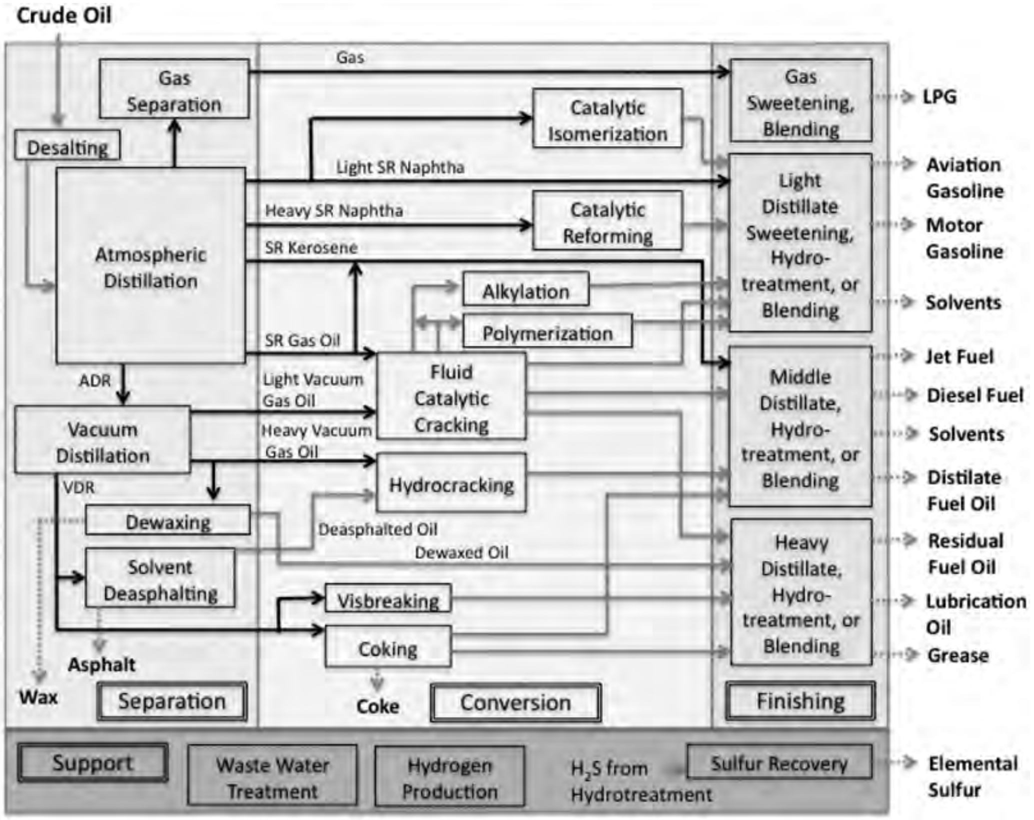


Figure 5.1—An overall refinery block flow diagram indicating an integrated network of major separation, conversion, finishing, and supporting processes.

solvent (e.g., in desalting to remove salt from crude oil and in deasphalting to separate asphalt from vacuum distillation residue) and freezing point (e.g., in dewaxing to separate wax to decrease the freezing point of the dewaxed oil).

5.3.2 Conversion Processes

Because separation processes do not produce the desired yields of particularly the distillate fuels (e.g., gasoline, jet fuel, and diesel fuels) as premium products, conversion processes are used to induce chemical changes in the composition of crude oil fractions. In U.S. refineries, fluid catalytic cracking (FCC) processes are particularly important because of their capability to produce high-octane number motor gasoline in high yields from the straight-run gas oil and light vacuum gas oil. Other catalytic conversion processes include catalytic reforming, catalytic isomerization, alkylation, and polymerization processes to further increase the yields of high-octane number motor gasoline. In contrast to catalytic cracking, which is aimed at reducing the molecular size of the compounds in the feed, catalytic isomerization and catalytic reforming do not change the size of the feedstock molecules to any significant extent. Catalytic reforming and isomerization processes increase the octane number of their products through dehydrogenation of cycloalkanes and isomerization of n-alkanes to produce aromatic hydrocarbons (in reformate) and branched alkanes (in reformate and isomerate). On the other hand, alkylation and polymerization processes are used to induce the coupling (combination) of smaller hydrocarbons, such as one i-alkane (e.g., *i*-butane) and one olefin (e.g., propene), in alkylation and two olefins (e.g., *i*-butene and propene) in polymerization to produce i-alkanes and branched olefins, respectively, to obtain high-octane number molecules that boil in the gasoline range. Therefore, the lighter i-alkanes and olefins generated as byproducts in FCC and other conversion processes can be recovered to contribute to high-octane number streams (as alkylate and polymerate) to the gasoline pool.

In contrast to the emphasis on gasoline production and particularly on FCC in the U.S. refineries, European refineries as well as those in some other parts of the world mainly focus on diesel fuel production because of the increasing proportion of diesel cars and the prominent mass transport systems in these countries that rely on diesel fuel. Therefore, challenges associated with the diesel market requirements and the conversions of higher-boiling fractions of petroleum create higher interest in conversion processes such as mild hydrocracking, hydrocracking, and coking compared with that in U.S. refineries.

Catalytic hydrocracking combines hydrogenation and cracking to handle feedstocks that are heavier than those that can be processed by FCC, such as heavy vacuum gas oils and vacuum distillation residua (VDR), because of excessive coke deposition on the catalyst in the absence of hydrogen. Middle distillates (e.g., kerosene and diesel fuel) are the principal products of hydrocracking.

Thermal processes that do not use any catalysts, such as visbreaking and coking, are used to upgrade the VDR to produce distillate fuels from the bottom of the barrel. Visbreaking is a mild thermal cracking process with the principal purpose of reducing the viscosity of VDR by slight carbon rejection in the visbreaking reactor to produce a heavy distillate or residual fuel oil. Lower yields of light and middle distillates can also be produced by visbreaking depending on the severity of thermal cracking used in the process. On the other hand, coking involves a high-severity thermal cracking to reject carbon in substantial quantities to produce a carbon-rich solid byproduct (coke) along with light and middle distillates that are sent to finishing processes to contribute to the respective distillate fuel pools.

5.3.3 Finishing Processes

Finishing processes constitute the final step in the processing history of a commercial product to ensure that it meets the specifications for marketing. These processes, depicted in generic terms in the boxes on the right-hand side of Figure 5.1 for each product, include physical mixing of different refinery streams in proportions to satisfy the product specifications (e.g., octane number and Reid vapor pressure for gasoline, cetane number, and pour point for diesel fuel), sweetening to remove sulfur compounds by absorption in basic solutions, chemical reactions such as hydrotreatment to remove heteroatoms (e.g., S, N, and metals), sweetening to convert certain sulfur species (i.e., mercaptans) into more benign sulfur compounds (i.e., disulfides), and hydrogenation to saturate olefins to the desired levels for storage stability of gasoline and to saturate aromatics to increase the cetane number of diesel fuel.

5.3.4 Supporting Processes

Unlike the three categories of processes described above, support processes do not directly involve the production of hydrocarbon fuels or materials, but they do play critical roles in the operation of a refinery. Support processes include hydrogen production for supplementing hydrogen output from catalytic reforming to meet the hydrogen demand for hydrotreatment, hydrocracking, and hydrogenation processes; acid gas removal to separate hydrogen sulfide (H_2S) and other gases from hydrocarbon streams; sulfur recovery from H_2S separated in the acid gas removal unit; and wastewater treatment. With the increasingly heavy and sour crudes being processed in refineries, the demand for hydrogen and the need for removal and conversion of acid gases to elemental sulfur have become critically important for refinery operation. Supporting processes also include the production of oxygenated hydrocarbons (e.g., ethyl tertiary butyl ether), particularly in Europe, which are used as gasoline additives to increase the octane number and control exhaust emissions. Benzene removal from gasoline (to comply with environmental regulations) and the wastewater treatment units in refineries also constitute important supporting processes.

5.4 REFINERY PROCESSES

5.4.1 Separation Processes

Separation processes constitute the initial stage of processing in a refinery and they prove a fractionation of products from conversion processes. Separation processes are physical processes in which the chemical structure of the feedstocks does not change. Constituent compounds or groups of compounds are separated through processes such as desalting, distillation, stripping, gas absorption, solvent extraction, and gas adsorption.

5.4.1.1 DESALTING

Although distillation is usually referred to as the first process in petroleum refineries, desalting takes place before distillation. Salt dissolved in water to form brine enters the crude stream as a contaminant during the production or transportation of oil to refineries. If salt is not removed from crude oil, serious damage can result, especially in the heater tubes, because of corrosion caused by the presence of chloride. Salt in crude oil also causes a reduction in heat transfer rates in heat exchangers and furnaces. Salt concentration in crude oil is usually expressed in terms of pounds of equivalent sodium chloride per thousand barrels of clear (water-free) crude and is reported as lb/1000 bbl, or simply PTB. In the United States and Europe, desalting is done in the refineries to reduce the PTB of crude to 1. PTB can be calculated as [2]

$$PTB = 1000\,\frac{\%S\,\&\,W}{100-\%S\,\&\,W}\,(350SG_{brine})\,\frac{ppmw}{10^6} \qquad (5.1)$$

where:

$\%S\&W$ = volume percentage of salt and water in oil $[0.1 \rightarrow 1]$,

$ppmw$ = salt content of water in ppmw, and

SG_{brine} = specific gravity of brine (>1), which depends on the salt concentration of water.

For example, seawater with salinity of 35,000 ppmw (or 3.5 wt %) has a specific gravity of 1.02 [1]. The relation between specific gravity of brine and its salt content can be expressed as $SG_{brine} = 1 + 6.7 \cdot 10^{-7}(ppmw)$ or $SG_{brine} = 1 + 0.0067(S\%)$, in which $S\%$ is the salt content (total dissolved solid) of brine in percentage weight.

Processes that reduce the PTB of a crude to 1 may include

- Adding demulsifier (soaps, sulfonates),
- A wetting agent for solid removal,
- Heating to 200–300°F, and
- Electrostatic coalescence.

Desalting in refineries is more economical than in the field because heat is readily available from the refinery flue gases. General methods of desalting are shown in Figure 5.2 as modified from Manning [2]. By adding hot water to crude, salt associated with brine in the crude is dissolved in the hot water and then the same amount of water is removed as brine. In this way, the salt concentration of brine associated with the crude is decreased although the percentage volume of brine may remain the same as before the desalting process. The efficiency of a desalting process largely depends on the level of mixing of the added hot water with the crude and the separation of brine. One of the most effective means of this process is mixing/coalescing using high voltage. By creating a voltage of approximately 30,000–40,000 V within 1–2 s, small particles are formed that make mixing very effective. After just 1 s of application, the voltage is reduced to 0 (i.e., within 3–4 s) for reagglomeration of the small particles to form larger units (coalescing process) and enhance the separation of brine from oil. This cycle is repeated until the desired level of separation is obtained. The desalter unit is simply an electrostatic heat treater to separate crude from the dilution water through extensive subdivision and better exchange of salt between the oil and dilution water. As the electric field is reduced, large water droplets are formed and settle down according to Stokes law. By use of electrostatic coalescence, the $\%S\&W$ of crude can be reduced to 0.1–0.15 (in vol %) whereas without an electric field it can only be reduced to 0.5–1 % [2]. Dehydration of crude is best obtained at a pH of 6. However, the pH should never exceed 8 because of emulsion formation. The pH can be controlled by the addition of acid to recycled water. During the desalting process, some other elements in crude such as V, Mg, and Fe can also be reduced between 30 and 75 % whereas salt, Ca, and Na can be reduced by 90 %. Therefore, the stages of the desalting process can be summarized as

1. Adding dilution (or less saline) water to crude,
2. Mixing dilution water with crude by a mixer, and
3. Dehydration of crude to separate crude and the diluted brine (salt and water) phase.

Desalting can be performed in a single- or two-stage unit. The amount of water wash and the temperature of the mixing process mainly depend on the crude API gravity, as shown in Table 5.1.

The main parameters that should be considered before the installation of a desalting unit are

- The number of desalting stages,
- The dehydration level achieved (vol % of salt and water) remaining in the crude leaving the desalter,
- The salinity of the brine remaining in the crude,
- The efficiency of the mixing of dilution water and crude,
- The salinity of dilution water, and
- The required PTB specification.

As a rule of thumb, if the required PTB is 20–50, then seawater may be used as dilution water. The number of stages depends on the level of dehydration in the remaining crude [2]:

- *Single-stage:* 5–7 vol % (salt and water) remaining in crude,
- *Two-stage:* 1–2 vol % (salt and water) remaining in crude,
- *Three-stage:* Used for desalting heavy and viscous crudes (API gravity of 10–20).

The design calculations related to the level of dehydration and desalting in a desalter are based on material balances for the salt and water.

5.4.1.2 DISTILLATION

In this section, the principles of distillation and various methods are introduced, followed by a description of distillation towers in refineries, straight-run products, and the intermediate streams obtained from distillation processes.

5.4.1.2.1 Operation and Types of Distillation Processes

Distillation is the main physical process in refineries that separates hydrocarbon compounds into distillate fractions on the basis of their boiling points or volatility [3–5]. More volatile compounds (with low boiling points) tend to vaporize more quickly than heavy compounds, and this forms the basis of separation through distillation. In a distillation column, light components appear in the top as top product and the heavier part of the mixture appears in the bottom. For a crude that is a mixture of hundreds of hydrocarbons, some very light compounds such as ethane and propane only appear in the top whereas extremely heavy and nonvolatile compounds such as asphalts only appear in the bottom. The condensed top product is also referred to as “distillate,” or overhead product.

Figure 5.3 shows a flow diagram for a typical crude distillation unit (CDU) [6]. The CDU consumes a significant fraction of the energy consumed in a refinery, and, as shown in Figure 5.3, it has a complex heat exchanger network (HEN) for energy economy. The HEN consists of several heat exchangers in series or parallel configurations to extract energy from the distillation column pumparounds or side streams. The crude is heated at three stages before entering the column at approximately 400ºC. A preflash drum (or a

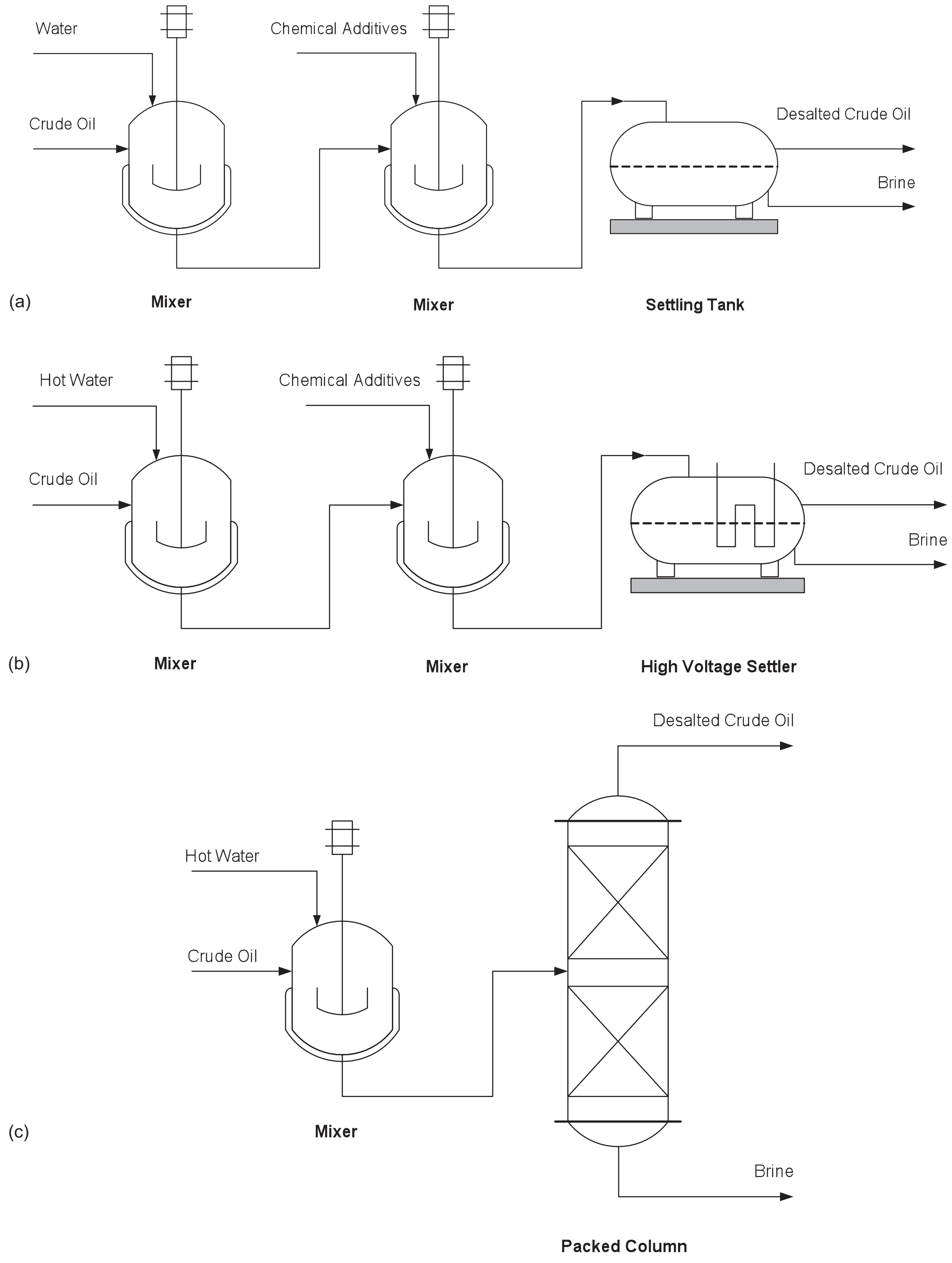


Figure 5.2—Three general methods for the desalting of crude oil based on three oil/water separation methods: (a) settling, (b) use of an electric field, and (c) use of a packed column. *Source*: Figure modified from [2].

TABLE 5.1—Amount of Water Wash and Temperature vs. Crude Gravity [2]

°API	Water Wash (vol %)	Temperature (°C (°F))
API > 40	3–4	115–125 (240–260)
30 < API < 40	4–7	125–140 (260–280)
API < 30	7–10	140–150 (280–300)

preflash column) may be included in the crude preheater train. This preflash step separates volatile fractions such fuel gas, LPG, and light naphtha to reduce the quantity of feed into the furnace. The separation of the light fractions before the furnace allows a better separation of the products in the distillation column and conserves energy. The crude preheat train is one of the most complex units that need to be controlled effectively for an optimal energy balance for the CDU that is important for the refinery's energy economy.

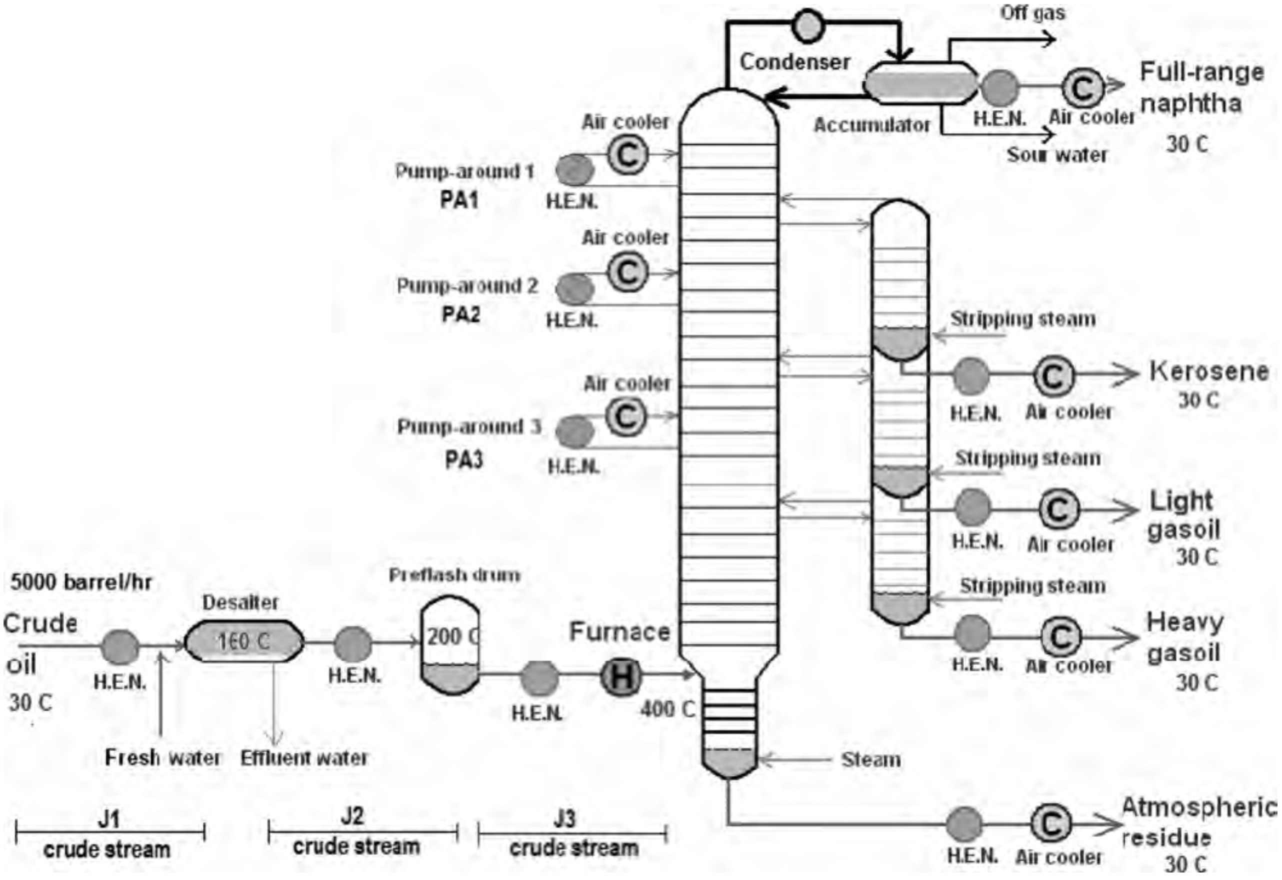


Figure 5.3—A crude distillation unit (CDU) and its HEN [6]. *Source*: Figure used with permission.

Siemanond and Kosol [6] have studied the energy requirements for a light (Arabian) and a heavy (Bacha quero) crude. The yields of distillate products from these crudes are given in Table 5.2, indicating larger distillate yields and lower residue yield from the Arabian light. Table 5.3 gives the heat exchanger and condenser duties for the distillation of two crudes for which the temperature of the crude and distillation products is set at 30ºC. It should be noted that most of the energy necessary for distillation is added in the external furnace, as can be seen in Table 5.3. The total energy required for distillation includes the energy needed to evaporate the side stream products and a small amount needed to provide internal reflux that is called "overflash." Keeping the amount of overflash to a minimum is also important for the energy economy in the CDU.

TABLE 5.2—Products from a Light and Heavy Crude Obtained from a CDU [6]

Products	Product Boiling Range (°C)	Products from Light Crude at 30°C (vol %)	Products from Heavy Crude at 30°C (vol %)
Naphtha	0–171	23	6
Kerosene	171–271	18	10
Gas oil	271–473	28	22
Residue	>473	31	62

TABLE 5.3—Heat Exchanger Duties for Distillation of Two Crudes [6]

	Energy Consumption of CDU (10^6 W)	
Utility	Light Crude Feed at 5000 bbl/h	Heavy Crude Feed at 5000 bbl/h
Steam and steam duty	7.67	8.07
Condenser duty	62.3	13.9

The performance of a CDU can be significantly improved if part of the top liquid product after the condenser is returned into the distillation column as reflux. The contact between the upward vapor phase and the downward liquid phase (as a result of reflux) would increase the exchange of components between the two phases. Light components evaporate from the liquid phase, and heavy components condense from the vapor phase into the liquid phase to improve the fractionation in the distillation column.

The distillation columns work as a multistage distillation system in which each stage is equivalent to a single distillation unit. To have a good separation, vapor and liquid leaving each stage should reach vapor/liquid equilibrium. Temperature along the column increases from the top to the bottom, and the crude oil enters on the feed tray. The section above the feed tray is known as the rectification and below the feed is referred to as the stripping section.

To have better vaporization and separation of the heavier components, steam is typically injected into the column at the bottom. The presence of steam decreases the partial pressure of hydrocarbons, and they can be vaporized at lower temperatures. Distillation at lower temperatures is desirable because high temperatures could lead to the degradation of thermally labile compounds.

The top condenser of the distillation column can be a partial condenser to obtain a liquid stream for the reflux, and the product is condensed in a second condenser. The bottom liquid is also partially vaporized in a reboiler, and a further fractionation can occur in the reboiler because it acts like a separation stage. The heat required in the reboiler is provided by high-pressure steam. The reboiler drives the operation of a distillation column as it generates vapor that flows upward in the column. Having a higher reflux rate can increase the purity of the top products; however, it reduces the production and requires the addition of more energy in the reboiler. Therefore, an optimal value of the reflux can be determined through column optimization and minimizing the total column cost as will be discussed in Chapter 13. Distillation columns can be tray or packed columns. Details of different column types and their advantages are discussed in Chapter 13.

A form of single-stage separation is called flash distillation or simply flash, in which the temperature and pressure in the unit are controlled in a way that only a part of the liquid feed is vaporized. The vapor product from the flash can be condensed for recovery. Liquid feed can be partially vaporized either by heating at constant pressure (similar to what happens in a reboiler) or by reducing the pressure at constant temperature. The vapor and liquid streams leaving a flash chamber approach equilibrium if the flash unit operates close to an ideal stage. Such flash units are common in refineries where the light gases are flashed out from a liquid by reducing the pressure.

In a refinery, desalted crude oil usually enters the atmospheric distillation column after going through a preflash drum or column, as described above. Because crude oil is a mixture of thousands of different compounds, the fractional distillation products also contain many different compounds, particularly in fractions with higher boiling points. For every side stream product, five to eight trays are generally needed. There are also several plates below the feed tray. For example, for a column with 4 side streams there may be 25–30 trays.

The residue from an atmospheric distillation column typically has an initial boiling point of approximately 650°F (~350°C). Higher temperatures are not desirable in crude distillation because thermal cracking of some constituent compounds may occur. To avoid thermal cracking in a distillation column, heavy residue from the atmospheric tower is further distilled in a vacuum tower. After desalting, the crude is typically heated up to 550°F by a heat exchanger and then to 750°F in a furnace. The temperature of the bottom product of the atmospheric tower is raised to 850°F before entering vacuum distillation. The pressure in vacuum towers ranges from 10 to 50 mmHg.

The diameter of a typical atmospheric crude tower is approximately 13 ft, and the height is approximately 85 ft, but towers for the fractional distillation of side products such as LPGs could have diameters of 2–3 ft and be up to 200 ft in height with as many as 30–100 trays. This is mainly due to the low relative volatility of components that requires a larger number of trays for a desired level of separation. Heavy residues distilled in a vacuum tower have high molar volumes; therefore, the diameter of vacuum towers is much larger than those of atmospheric towers. The vacuum tower's diameter could be as large as 40 ft depending on the feed rate.

5.4.1.2.2 Straight-Run Products and Intermediate Streams from Distillation

The distillation of crude oil in the atmospheric distillation column gives fractions that include straight-run products, such as LPG, naphtha, kerosene, and light and heavy gas oils [7,8]. The vacuum column generates intermediate streams (i.e., light and heavy vacuum gas oils and vacuum residue) that are subjected to subsequent processing to produce light and middle distillate fuels and nonfuel products. The specifications of all fuels and materials obtained from crude oil are presented in Chapters 2 and 4.

As seen in Figure 5.3, the vapors from the top of the atmospheric column (overhead products) are condensed and separated into gas and liquid streams in the accumulator. The gas is further separated into fuel gas (methane and ethane) that is burned for generating heat or steam in the refinery as well as LPG. LPG that consists of propane and butane is the lightest straight-run product from crude oil distillation. LPG may need to be treated to remove impurities such as H_2S, elemental sulfur, and carbonyl sulfide (COS). Part of the liquid overhead product (full-range naphtha) is returned to the column as reflux. The rest of the overhead liquid is separated into light and heavy naphtha. Light naphtha can be used as specialty solvent, after purification, if necessary, or sent to an isomerization unit to increase its octane number to become a blending component for gasoline. Heavy naphtha is hydrotreated and usually directed to a catalytic reforming unit to produce high-octane gasoline, as shown in Figure 5.1 and discussed in more detail in Section 5.4.2.1.2. Condensed water is sent to a water treatment plant.

The side streams are separated in the side cut steam strippers into middle distillates (i.e., kerosene) and light and heavy gas oils. Kerosene is hydrotreated to produce jet fuel, or to be used as a blending component for diesel fuel, or as a solvent. Light gas oil (LGO) is hydrotreated to produce diesel fuel, and heavy gas oil (HGO) is hydrotreated to produce a blending component for diesel fuel or light fuel oil. In refineries that are focused on maximizing gasoline production, atmospheric gas oils as well as vacuum gas oils are used as feedstocks for FCC to produce more gasoline as the primary product, as discussed later in Section 5.4.2.1.1.

Atmospheric residue is fed into the vacuum distillation column to be fractionated into light and heavy vacuum gas oil (LVGO and HVGO, respectively) and vacuum residue (VR). LVGO can be used for producing lubricating oil basestock after dewaxing to control the freezing point of the basestock. HVGO can be introduced to catalytic cracking or hydrocracking to produce light and middle distillates. Finally, the bottom of the barrel, VR, can be used as feedstock for deasphalting to produce deasphalted oil (DAO) and asphalt, for visbreaking to produce fuel oil, or coked to produce light and middle distillates and petroleum coke. In turn, DAO may be used as feedstock for dewaxing and lubricating oil basestock production or as feedstock for hydrocracking to produce primarily middle distillates (i.e., jet fuel and diesel fuel).

The role of distillation has remained significant in the historical evolution of refinery schemes that have been referred to in the literature as follows:

- *Topping:* Simple distillation only, not currently used.
- *Hydroskimming:* Distillation combined with hydrotreating, still used in some refineries.
- *Conversion:* Including vacuum distillation with the chemical conversion of vacuum distillates into light products.
- *Deep conversion:* Chemical conversion of VDR into light products.
- *Lubricant production:* Special vacuum distillation incorporated with deasphalting, lubricating oil extraction, dewaxing, and finishing.

5.4.1.3 OTHER SEPARATION PROCESSES: ABSORPTION, STRIPPING, EXTRACTION, AND ADSORPTION

There are several other physical separation processes that are used in refineries to separate components from each other in liquid and gas phases. Absorption is a process in which a gas component is separated using an amine solvent in an absorption column. Stripping is the opposite of absorption and occurs when a volatile component is evaporated from a liquid phase into a gas phase. This process is usually used to recover enriched solvent from an absorption column as will be discussed in Chapter 13.

An absorption column is similar to a distillation column (tray or packed) in which good contact between gas and liquid streams is needed to have good performance in the column. However, absorption columns do not have a condenser or a reboiler. Rich gas enters from the bottom and solvent enters from the top, whereas rich solvent leaves the column through the bottom. Absorption columns usually operate at low temperatures but high pressures. Good absorption solvents should be nontoxic, cheap, nonvolatile, and possess a high absorption capacity. In general, the phrase "like dissolves like" works for absorption as well. For example, to separate C_3 and C_4 from a gas mixture of C_1, C_2, C_3, and C_4, a hydrocarbon solvent such as a paraffinic oil would be suitable. A heavier component (e.g., C_4) tends to be absorbed more than C_3 and the other light components because C_4 is closer in structure to that of a paraffinic solvent such as decane. The absorption capacity of a solvent increases for a given compound that has similar chemical and physical properties to those of the solvent.

Another physical separation process is solvent extraction, in which a component is separated from a liquid mixture using a liquid solvent. A separation of two components, A and B, by distillation is possible when the difference between vapor pressure (or boiling points) of the components is large (high relative volatility). However, if the boiling points of the components are close to each other, the separation by distillation requires a large column with a high cost. If the boiling points of two components are the same (i.e., relative volatility of unity), then separation by distillation is not possible, and an alternative technique is needed. Consider a solution of acetic acid (component A) in water (component B). Solvent isopropyl ether (component C) is added in which C is partially soluble with component A but not soluble in B. The three-component mixture of A, B, and C will then separate into two phases, A and B and A and C. The phase rich in solvent C (in this example ether is the rich phase) is called the "extract" whereas the phase rich in component B (water layer phase in this example) is called the "raffinate." The extract phase then can be sent to a distillation column to separate A and C. In this way, one can separate component A from B and recover the solvent C for recycling. In an ideal separation, the two phases of extract and raffinate are in equilibrium and principles of liquid-liquid equilibrium will be used for the design and operation of the extractor. A multistage countercurrent extraction unit is commonly used in the form of a column to separate two miscible liquids to a certain degree of purity. In the process, the heavy liquid usually enters from top of the column whereas light liquid (usually solvent phase) enters countercurrently from the bottom. The number of stages or trays necessary for the desired separation in such columns can be determined through equilibrium data and the operating line. As an example, liquid-liquid extraction separates aromatics from aliphatic hydrocarbon mixtures by using a mixture of diethylene glycol (90–92 %) and water (8–10 %). Aromatics such as benzene, toluene, and xylene(s) can be separated from oil by use of sulfolane in a liquid-liquid extraction process [1]. The design of such units is discussed in Chapter 13.

Another physical separation process used in refineries is adsorption, in which usually a gas is separated from a gas mixture by a solid phase called the adsorbent. This process can also be used for adsorption of a component in liquid mixtures such as removal of hydrocarbons from water. Adsorption is a useful process when a component exists in small quantities. For example after separation of H_2S from natural gas through a gas absorption process, the remaining amount of H_2S in the gas mixture can be removed through an adsorption process yielding a gas with a very low concentration of H_2S. This process is also quite useful to remove odors and pollutants from air.

The effectiveness of an adsorption process largely depends on the characteristics and types of adsorbents (the solid phase). The adsorbents are typically in the form of small beads or pellets ranging from 0.1 to 12 mm in size, with the larger particle being used in packed beds. Columns are filled with adsorbent beads and gas feed enters from the bottom of the column. The porosity of particles is approximately 50 %, and the adsorption usually occurs as a monolayer on the surface of a solid. When gas is introduced into a solid bed column, it first diffuses into the bulk of the gas phase and then through pores of the solid before reaching the solid surface. The overall performance also depends on the diffusion rates in the gas and solid pores as well as the kinetics of the adsorption process. Good adsorbents have a high surface area up to 2000 m^2/g whereas a value of 1200 m^2/g is considered a good surface area. Various kinds of adsorbents in the order of surface area include activated carbon, silica gel, activated alumina, molecular sieve zeolites, and synthetic polymers and resins in which activated carbons usually have surface areas of 300–1200 m^2/g and alumina has a surface area of 200–500 m^2/g [3].

5.4.1.4 DEWAXING AND LUBRICATING OIL PRODUCTION

Dewaxing processes are designed to remove wax from precursor lubricating oils (LVGOs or DAOs) to give the lubricating oil basestock good fluidity characteristics at low temperatures. An oil can generally be dewaxed by separation of wax as a solid that crystallizes from the oils at low temperatures in a process called "solvent dewaxing."

Before the 1930s, naphthenic and paraffinic oils were used as lubricants for motors, and both were solvent (i.e., phenol) extracted to improve their quality [1]. However, lubricating oils are mainly composed of normal and branched paraffins. Lubricating oils were produced in early refineries as byproducts of paraffin wax. Lubricating oil typically has high boiling points (>400°C) and high viscosity. The carbon number range for lubricating oil is usually between 25 and 35–40 [1]. Lubricating oil can be produced in four steps:

1. Distillation to remove lighter components,
2. Solvent refining or hydrogen treatment to remove non-hydrocarbon compounds,
3. Dewaxing to remove wax constituents and to improve low-temperature properties, and
4. Clay treatment (or hydrogen treatment) to prevent instability of the product [1].

SAE has classified lubricating oils into different classes on the basis of their kinematic viscosity. For example, the viscosity of grade SAE 20 oil should have a minimum value of 5.6 cSt and a maximum value of 9.3 cSt at 100°C (212°F).

The solvents used in the solvent dewaxing of oils are naphtha, propane, sulfur dioxide, acetone-benzene, methyl ethyl ketone-benzene (benzol), and methyl-*n*-propyl ketone. Currently, ketone solvents are commonly used in dewaxing processing. Processes of dewaxing include contacting the feedstock with the solvent, precipitating the wax from the mixture by chilling, and recovering the solvent from the wax and dewaxed oil for recycling. Recent dewaxing processes include catalytic dewaxing, which is a mild hydrocracking process and is conducted at temperatures in the range of 280–400°C and pressures in the range of 300–1500 psi, depending on the type of feedstock used and the product required. The catalyst used for the process is the ZSM-5 catalyst (MFI according to the IUPAC Framework Type Code). This catalyst is selective for n-paraffin cracking through molecular sieving. A catalytic dewaxing process developed by Mobil is shown in Figure 5.4.

5.4.1.5 DEASPHALTING: ASPHALT AND DAO PRODUCTION

Asphaltenes, as discussed in Chapter 2, consist of a high-molecular-weight aromatic hydrocarbon containing heteroatoms such as sulfur and nitrogen. Asphaltenes are associated with heavy residues from a vacuum tower and can be separated from the residue through a solvent separation process. As much as 80 % of the residue from vacuum crude oil towers is paraffinic material that can be upgraded to diesel fuel. Low-molecular-weight paraffins such as propane, butane, or pentane can be added to asphaltenic oils, and asphaltenes are separated as solid asphalt. The mechanism of separation is through the density difference between asphaltenes and the oil/solvent solution. Undesirable heteroatoms such as sulfur, nitrogen, and metals are also removed through deasphalting of oil. Deasphalting is usually applied to vacuum gas oil, feedstocks for lubricating basestocks, and distillation. Upgrading of heavy oils through deasphalting can be done at the production site of an oil field, which results in better quality crude for export and processing, as discussed in Chapter 8. Removal of asphaltene through solvent extraction is common in refineries to remove asphaltene from heavy residues and asphaltenic oils. LPG can be used to precipitate asphaltic materials. When propane is added to oil containing asphaltene, propane dissolves in oil, but it rejects asphaltene because of a considerable difference in their chemical structure and molar size. Propane can then be recovered through an evaporation process as shown in Figure 5.5 [1]. In this process, the heavy feedstock and 3–10 times its volume of liquefied propane are pumped together through a mixing device and then into a settling tank. The temperature is maintained between 27 and 71°C, in which the higher the temperature, the greater the tendency of asphaltic materials to separate. However, the temperature should be above the asphaltene pumping temperature, and the propane is maintained in the liquid state by a pressure of approximately 200 psi. The final products of the deasphalting process are asphalt and DAO, as shown in Figure 5.5. Other methods of deasphalting are discussed by Speight [1]. Another process is proposed by Honeywell's UOP and is shown in Figure 5.6 [9]. The UOP deasphalting process produces DAO that is

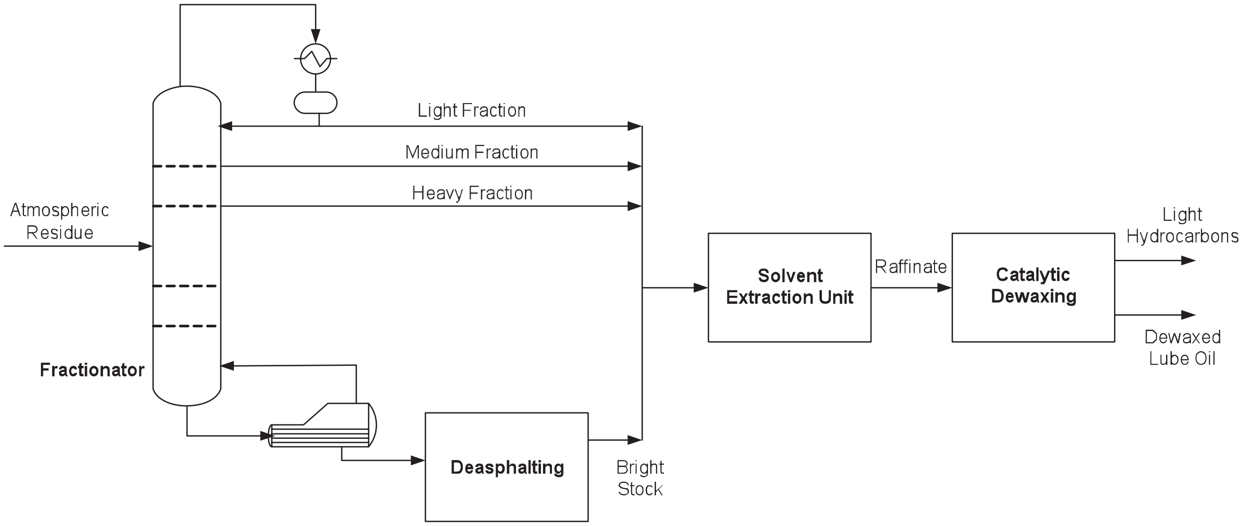


Figure 5.4—Catalytic dewaxing process that is based on the Mobil process as given in [1].

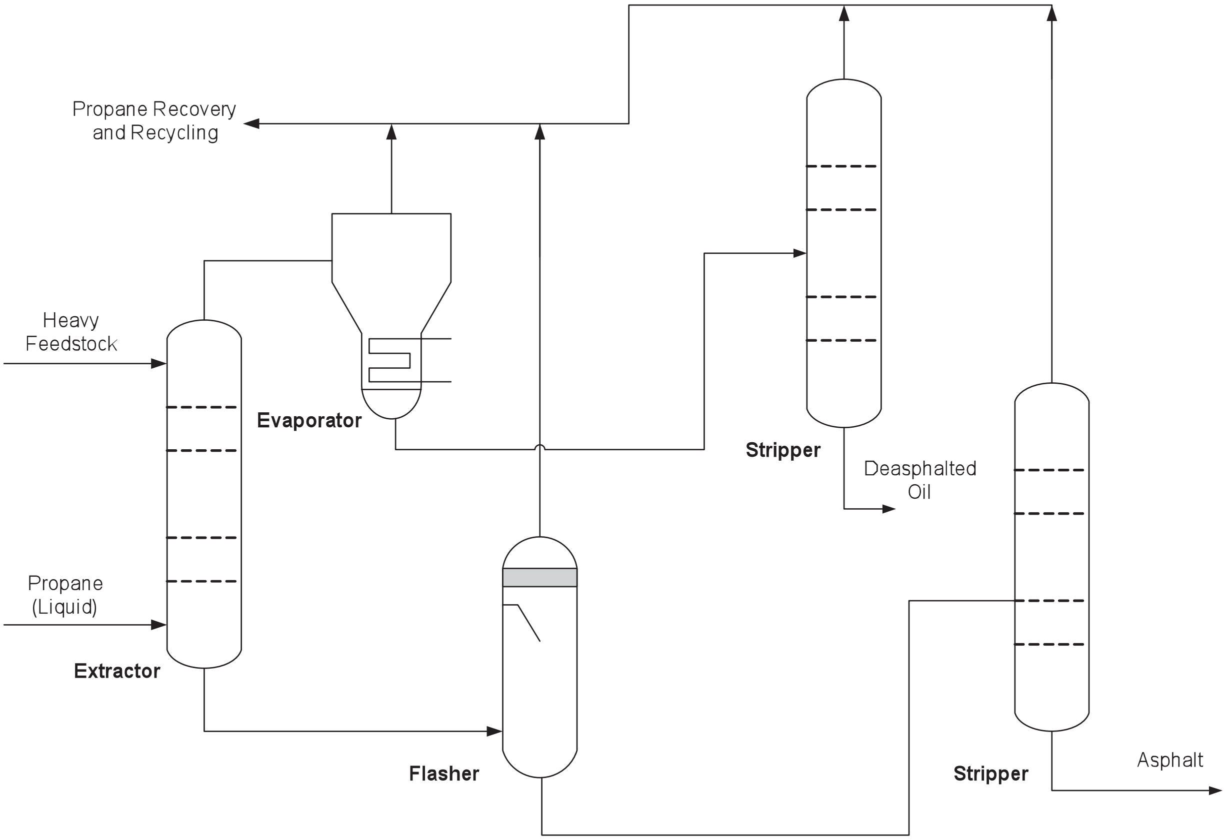


Figure 5.5—Schematic of deasphalting process by propane that is based on the method recommended in [1].

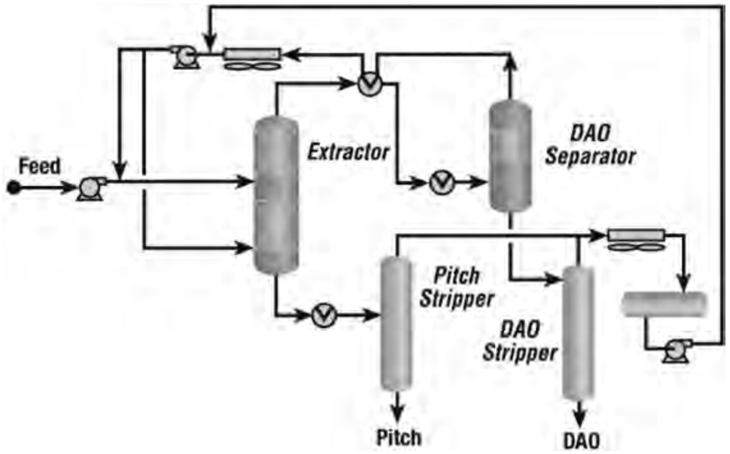


Figure 5.6—UOP/FWUSA solvent deasphalting process [9]. *Source*: Figure used with permission from UOP LLC, a Honeywell company.

rich in paraffinic-type molecules that can later be converted in an FCC unit or hydrocracking unit. The pitch product contains most of the residue's contaminants (metals, asphaltenes, Conradson carbon) and is rich in aromatic compounds and asphaltenes. The feed (normally VR) is mixed with a light paraffinic solvent, typically butane, where the DAO is solubilized in the solvent. The insoluble part will precipitate out of the mixed solution (Figure 5.6). The solvent can be recovered and recycled back to the beginning of the process. Considering the solvent selection, as the solvent gets heavier, the yield of DAO increases, but its quality declines. As the DAO yield increases, the concentration of contaminants in the DAO also increases. Changing solvents is not usually considered as a day-to-day operating practice [9].

5.4.2 Conversion Processes

Conversion processes change the molecular structure of the crude oil fractions from distillation processes and other intermediate products from different refinery units to increase the quantity and quality of premium distillate fuels such as gasoline, jet fuel, diesel fuel, and fuel oils. This subsection covers the principal conversion processes used in a refinery that are grouped on the basis of the targeted distillate fuel product starting with gasoline production.

5.4.2.1 GASOLINE PRODUCTION

Gasoline is the principal product in U.S. refineries, accounting for 40 % by volume of all refinery products [10] because of the high demand for motor gasoline as the primary fuel for automobiles. Properties and specifications of gasoline products are discussed in Chapters 2 and 4. Among all of the processes used for producing gasoline, the process of FCC accounts for the largest volume of gasoline production through the cracking of gas oils. Catalytic reforming and isomerization processes are performed to increase the octane number of heavy naphtha and light naphtha fractions, respectively, without a major change in molecular weight or boiling point range of the feedstocks to provide high-octane number gasoline streams to the blending pool. On the other hand, alkylation and polymerization are used to combine lighter hydrocarbons (C_3 and C_4 alkanes and olefins) generated in conversion processes (e.g., FCC and coking) to produce branched alkanes and olefins (i-C_7-i-C_8) with high octane numbers for the gasoline pool. These processes are introduced in more detail in the following sections. It should be noted that there are other refining processes that produce gasoline blending streams as byproducts, as will be pointed out when discussing these processes.

5.4.2.1.1 FCC

The FCC process is the most widely used refinery process to produce high-octane gasoline mainly from straight-run atmospheric gas oil and LVGO. This process involves breaking up long chains of n-alkanes into shorter chains of branched alkanes (isoalkanes), cycloalkanes (naphthenes), and aromatics by using acidic catalysts. In addition to high-octane gasoline, FCC produces LPG, cycle oils, and olefin-rich light hydrocarbons (C_3, C_4) that can be used in alkylation and polymerization reactions to produce higher molecular weight branched alkanes and olefins to contribute to the blending pool of high-octane gasoline in refineries. Because of the central importance of FCC in petroleum refining, a separate chapter (Chapter 6) is devoted to discussing this process in detail. Only a brief description of the process is presented here.

Increasing demand for gasoline along with the need to produce high-octane gasoline for increasingly more powerful spark ignition engines led to the development and maturation of catalytic cracking processes just before and during World War II. After the development of a fixed-bed (Houdry process, 1936) and a moving-bed (Thermofor Catalytic Cracking, 1941) catalytic cracking process, fluid-bed catalytic cracking (FCC, 1942) became the most widely used process worldwide because of the improved thermal efficiency of the process and the high product selectivity achieved, particularly after the introduction of crystalline zeolites as catalysts in the 1960s.

In general terms, the FCC process can be divided into three components: the reactor, the catalyst regenerator, and the product fractionator. In the reactor, the cracking reactions initiate on the active sites of the catalysts with the formation of carbocations (positively charged hydrocarbon ions), and the subsequent ionic chain reactions produce branched alkanes and aromatic compounds to constitute the crackate (cracked gasoline with high octane number), light olefins, cycle oils, and slurry oil that are sent to the fractionator. A carbon-rich byproduct of catalytic cracking, termed "coke," deposits on catalyst surfaces and blocks the active sites. The coked catalysts are sent to the regenerator unit to burn off the coke deposit, and the regenerated catalysts are returned to the reactor to complete the catalyst cycle. The heat necessary for the endothermic cracking reactions can thus be supplied by the hot catalyst particles that are heated by burning the coke deposit off their surface. For most FCC units, there exists a good heat balance between the reactor and the regenerator for effective thermal integration. FCC is considered a carbon rejection process because the coke deposited on the catalyst surface and eventually burned off for heat is rich in carbon and thus enables the production of large quantities of a light distillate (crackate) in the process.

Two different configurations of the FCC process exist depending on the positions of the reactor and the regenerator: they can be side by side or stacked, where the reactor is mounted on top of the regenerator. Major licensor companies that offer FCC processes with different configurations include Kellogg Brown & Root, CB&I Lummus, ExxonMobil Research and Engineering, Shell Global Solutions International, Stone & Webster Engineering Corporation, Institut Francais du Petrole (IFP), and UOP.

The flow diagram of a UOP FCC process is shown in Figure 5.7 [11]. The gas oil feed mixed with steam is introduced to the bottom of the riser (reactor) with the hot catalyst particles from the regenerator. Most of the cracking reactions take place in the riser. After steam stripping in the upper part of the reactor, the coked catalysts are sent to the regenerator and the products are directed to the fractionator section that consists of a main column and a gas concentration (separation) unit. UOP engineers are also proposing two-stage regenerator units for FCC plants. The advantages of a two-stage regenerator over a single-stage regenerator are

- Easier to operate,
- Uniform coke burn,
- Low carbon residue (<0.05 wt %),
- Higher conversion of carbon monoxide (CO) to carbon dioxide (CO_2),
- Lower nitrogen oxide (NO_x) emissions, and
- Minimizing catalyst deactivation.

Addition of a third-stage catalyst regenerator may control the emission of particulate matter (PM) in flue gases. It could reduce the PM to meet the 50-mg/Nm^3 clean gas requirement, help axial flow separation, and reduce PM to less than 0.8 lb_{PM}/1000 lb (coke).

Another modification to FCC plants could be installation of a catalyst cooler, which may provide better control of the catalyst/oil ratio; the ability to optimize the FCC operating conditions, increase conversions, and process heavier residual feedstocks; and better catalyst activity and catalyst maintenance. Recent advancements in FCC processes are discussed in Chapters 6 and 7.

5.4.2.1.2 Catalytic Reforming

Catalytic reforming converts low-octane straight-run naphtha fractions (particularly heavy naphtha that is rich in naphthenes) into a high-octane, low-sulfur reformate, which is a major blending product for gasoline. The most valuable

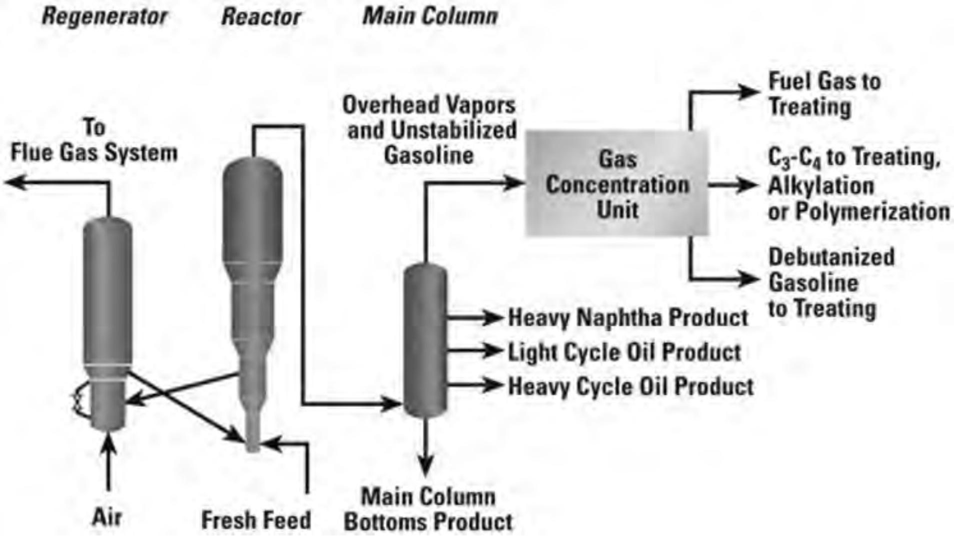


Figure 5.7—A UOP FCC process flow diagram [11]. *Source*: Figure used with permission from UOP LLC, a Honeywell company.

byproduct from catalytic reforming is the hydrogen needed in a refinery with the increasing demand for hydrotreating and hydrocracking processes. Most reforming catalysts contain platinum supported on alumina, and some may contain additional metals such as rhenium and tin in bi- or trimetallic catalyst formulations. In most cases, the naphtha feedstock needs to be hydrotreated before reforming to protect the platinum catalyst from poisoning by sulfur or nitrogen species. With the more stringent requirements on benzene and the total aromatics limit in the United States and Europe, the amount of reformate that can be used in gasoline blending has been limited, but the function of catalytic reforming as the only internal source of hydrogen continues to be important for refineries.

The first commercial catalytic reforming process was introduced by UOP in 1949 as the Platforming™ process that used three fixed-bed reactors. The reactors operate in series with furnaces placed before each reactor to heat the feedstock and the reactor effluents to 500–530°C before entering each reactor because the predominant reforming reactions are highly endothermic. These units, called "semiregenerative catalytic reformers," need to be shut down once every 6–24 months for the in situ regeneration of catalysts that are deactivated by coke deposition. Later designs included an extra reactor (a swing reactor) to enable isolation of one reactor at a time to undergo catalyst regeneration whereas the other three reactors are running. This configuration enables longer on-stream times (up to 5 years) before scheduled shutdowns for catalyst regeneration, but it has not become popular.

A continuous catalyst regeneration (CCR) scheme for reforming came on stream in 1971. Figure 5.8 shows a flow diagram for the UOP CCR Platforming process [12]. The reactors are stacked with a moving bed of catalyst trickling from the top reactor to the bottom reactor by gravity. Partially deactivated catalyst from the bottom of the reactor stack is continuously withdrawn and transferred to the CCR regenerator. The regenerated catalyst is reinjected to the top of the first reactor to complete the catalyst circulation cycle.

Hydrotreated naphtha feed is combined with recycle hydrogen gas and heat exchanged with the reactor effluent. The combined feed is then raised to reaction temperature

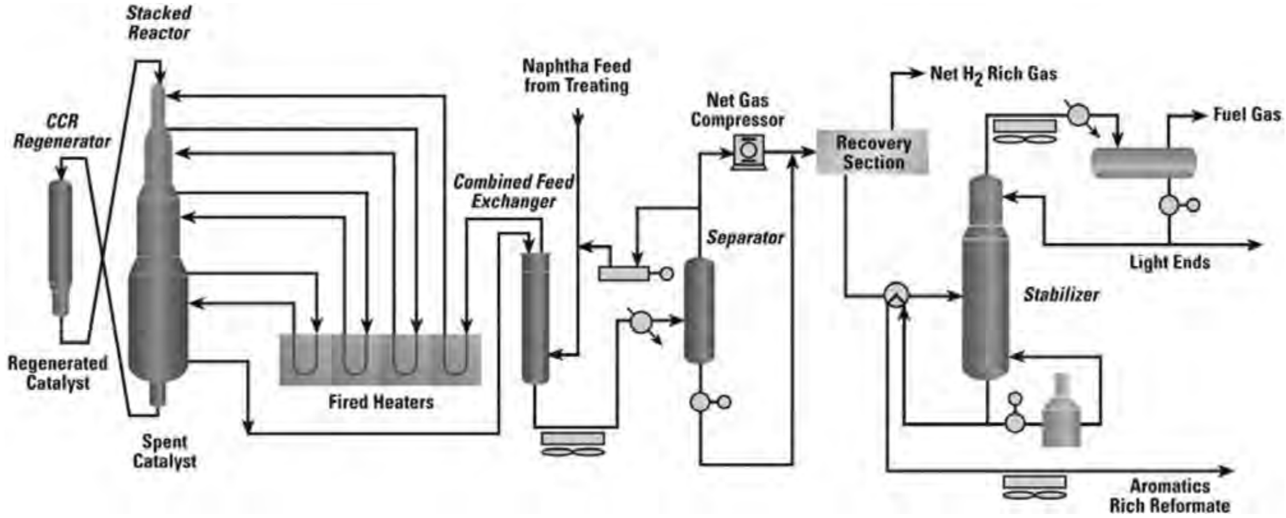


Figure 5.8—UOP CCR Platforming process [12]. *Source*: Figure used with permission from UOP LLC, a Honeywell company.

in the charge heater and sent to the first reactor section. Because the predominant reforming reactions are endothermic, an inter-reactor heater is used to reheat the charge to reaction temperature before it is introduced to the next reactor. The effluent from the last reactor is heat exchanged with the combined feed, cooled, and separated into vapor and liquid products in a separator. The vapor phase is rich in hydrogen gas, and a portion of the gas is compressed and recycled back to the reactors. Recycling hydrogen is necessary to suppress coking on the catalysts. The hydrogen-rich gas is compressed and charged together with the separator liquid phase to the product recovery section. The performance of the unit (i.e., steady reformate yield and quality) depends strongly on the ability of the CCR regenerator to completely regenerate the catalyst.

In addition to UOP's Platforming process, the major commercial catalytic reforming processes include Powerforming™ (ExxonMobil), Ultraforming™ and Magnaforming™ (BP), Catalytic Reforming (Engelhard), Reforming (IFP), and Rheniforming™ (Chevron).

The principal reactions of interest in catalytic reforming, shown in Figure 5.9, are

- Dehydrogenation of naphthenes to aromatics,
- Dehydroisomerization of alkyl-C_5-naphthenes,
- Dehydrocyclization of n-paraffins to aromatics, and
- Isomerization of n-alkanes to i-alkanes.

All of these reactions significantly increase the octane number (research octane number [RON] from 75 to 110 in Reaction 1, from 91 through 83 [cyclohexane] to 100 in Reaction 2, from 0 to 110 in Reaction 3, and from –10 to 90 in Reaction 4). Large quantities of H_2 are produced in the highly endothermic Reactions 1–3. High temperatures and low hydrogen pressures strongly promote the conversion Reactions 1–3. However, it is necessary to maintain a sufficiently high hydrogen pressure in the reactors to inhibit coke deposition. Hydrocracking is an undesired side reaction in catalytic reforming because it consumes hydrogen and decreases the reformate yield by producing gaseous hydrocarbons. Hydrocracking reactions are exothermic, but they can still be favored at high temperatures because of kinetics and favored obviously by high hydrogen pressures. Typically, reformers operate at pressures from 50 to 350 psig (345–2415 kPa), a hydrogen/feed ratio of 3–8 mol H_2/mol feed, and liquid hourly space velocities of 1–3 [13].

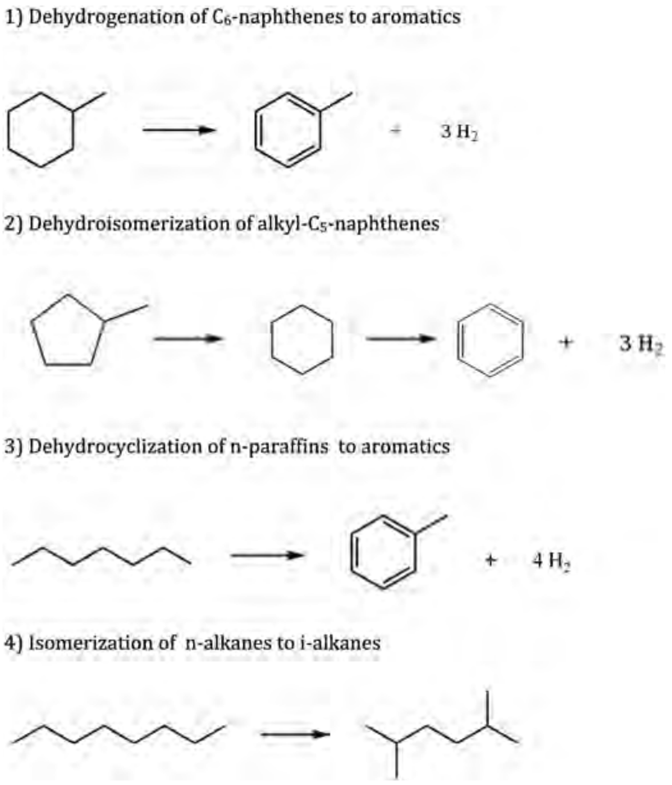


Figure 5.9—Principal reactions in catalytic reforming.

A reaction network for catalytic reforming is shown in Figure 5.10 [14], indicating the role of metallic (M) and acidic (A) sites on the support. The surfaces of metals (e.g., Pt) catalyze dehydrogenation reactions, whereas the acid sites on the support (e.g., alumina) catalyze isomerization and cracking reactions. Metal and acid sites are involved in the catalysis of hydrocracking reactions. Achieving the principal objective of catalytic reforming—high yields and high quality of reformate—can be achieved, to a large extent, by controlling the activity of the catalysts and the balance between acidic and metallic sites to increase the selectivity to desirable reactions.

5.4.2.1.3 *Alkylation and Polymerization*

The alkylation process combines light isoparaffins, most commonly isobutene, with C_3–C_4 olefins to produce a mixture of higher molecular weight isoparaffins (i.e., alkylate) as a high-octane number blending component for the gasoline pool. Isobutane and C_3–C_4 olefins are produced as byproducts from FCC and other catalytic and thermal conversion processes in a refinery. The alkylation process was developed in the 1930s and 1940s to initially produce high-octane aviation gasoline, but later it became important for producing motor gasoline because the spark ignition engines have become more powerful with higher compression ratios that require fuel with higher octane numbers. With the recent restrictions on benzene and the total aromatic hydrocarbon contents of gasoline by environmental regulations, alkylation has gained favor as an octane number booster over catalytic reforming. Alkylate does not contain any olefinic or aromatic hydrocarbons.

Alkylation reactions are catalyzed by strong acids (i.e., sulfuric acid [H_2SO_4] and hydrofluoric acid [HF]) to take place more selectively at low temperatures—40–70°F for H_2SO_4 and 100°F for HF. By careful selection of the operating conditions, a high proportion of products can fall in the gasoline boiling range with motor octane numbers (MONs) of 88–94 and RONs of 94–99 [15]. Early commercial units used H_2SO_4, but more recently HF alkylation has found more common use in petroleum refineries. HF can be more easily regenerated than H_2SO_4 in the alkylation process, and HF alkylation is less sensitive to temperature than H_2SO_4 alkylation [15]. In both processes, the volume of acid used is approximately equal to the volume of liquid hydrocarbon feed. Important operating variables include acid strength, reaction temperature, isobutane/olefin ratio, and olefin space velocity. The reactions are run at sufficiently high pressures to keep the hydrocarbons and the acid in the liquid phase. Good mixing of acid with hydrocarbons is essential for high conversions.

Some examples of desired alkylation reactions (combination of isoparaffins with olefins) are given in Figure 5.11.

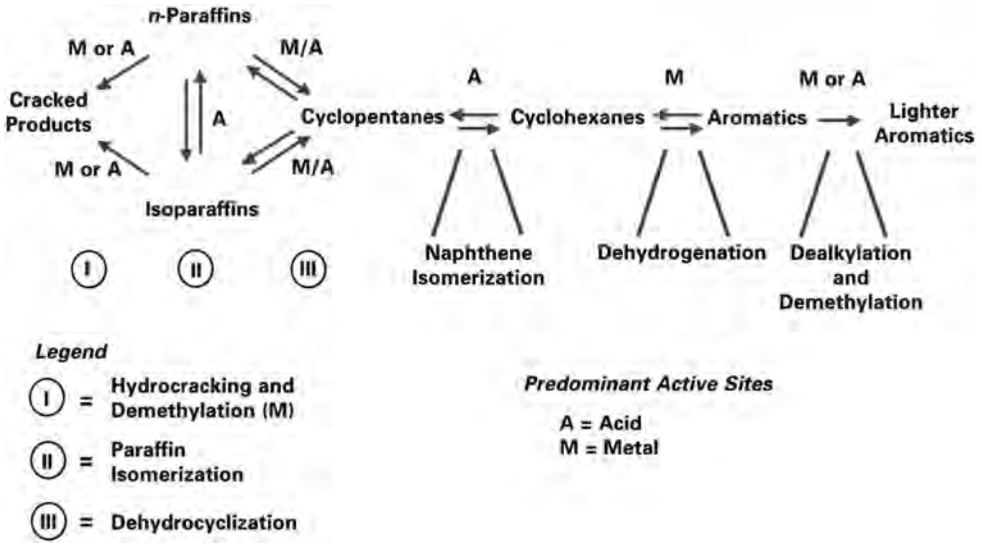


Figure 5.10—A reaction network for catalytic reforming [14]. *Source*: Figure used with permission from UOP LLC, a Honeywell company.

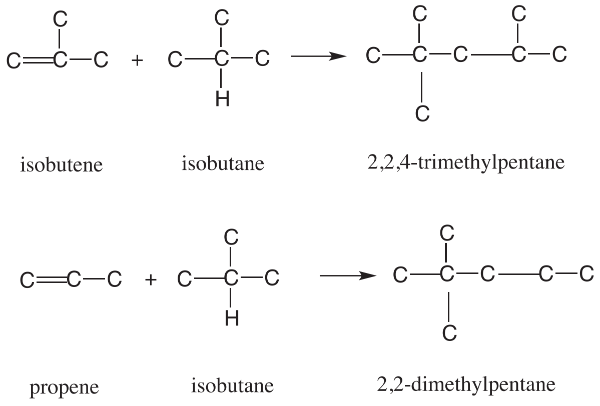


Figure 5.11—Desirable alkylation reactions [15].

These reactions are believed to occur through ionic chain reactions initiated by donation of a proton from the acid catalyst to an olefin to produce a carbocation that reacts with isobutane to form a tert-butyl cation. Subsequent propagation reactions involve the reactions of a tert-butyl cation with olefins to form larger isoparaffin cations that lead to final products through reactions with isobutane to form a new tert-butyl cation to sustain the chain reaction [15]. The alkylation reaction is highly exothermic, and cooling the reactor contents during alkylation is important.

Figure 5.12 shows a flow diagram for a UOP HF alkylation process [16]. Olefin and isobutane feed streams are dried to remove water before they are mixed with the isobutane recycle stream. The mixture is fed to the reactor, where it is highly dispersed into an incoming stream of acid catalyst. Conversion of reactants to high-quality alkylate takes place quickly, and the mixture flows up to the settling zone. In the settler, the catalyst is separated out as a bottom phase and flows, by gravity, through the catalyst cooler and returns to the reactor. The hydrocarbon phase from the settler, which contains propane, recycled isobutane, normal butane, and alkylate, is charged to the main fractionator. High-purity propane is sent overhead to pass through the HF- propane stripper, defluorinator, and potassium hydroxide (KOH) treater before it is recovered. Recycled isobutane is drawn from the side of the fractionator and returned to the entrance of the reactor after it is mixed with the dried olefin and isobutane feed. The *n*-butane product is taken from the side of the fractionators as vapor, condensed and KOH-treated before recovery. The alkylate product is obtained from the bottom of the fractionator. The HF catalyst is regenerated onsite in the regeneration section where heavy oils (tars) are removed from the catalyst.

Transporting and working with concentrated acids pose safety risks. In particular, HF tends to form a vapor cloud that is difficult to disperse. As examples for recent developments to mitigate the risks associated with using HF, one could cite the Reduced Volatility Alkylation Process (ReVAP™) and the Inventory Management Process (IMP®) [16]. The ReVAP process drastically reduces the volatility of HF acid, and IMP allows safer transfer of the catalyst inventory to a dedicated receiver vessel. The major licensor of the HF alkylation processes is UOP, whereas ExxonMobil and Stratford Engineering Corporation license H_2SO_4 alkylation processes. A newly designed alkylation process by UOP uses a solid catalyst called Alkylene®. Advantages of this new process over traditional HF alkylation processes (liquid acid technology) include no acid transportation, no acid spills, no corrosion, and reduced maintenance cost. Efforts to develop alternative processes that use solid acid catalysts instead of concentrated HF and H_2SO_4 for alkylation are discussed in Chapters 9 and 10.

The polymerization process combines propenes and butenes to produce higher olefins with high-octane numbers (97 RON and 83 MON) for the gasoline pool. The polymerization process was used extensively in the 1930s and 1940s, but it was replaced to a large extent by the alkylation process after World War II. It has gained favor after phasing out the addition of tetraethyl lead (TEL) to gasoline, and the demand for unleaded gasoline has increased. Typical polymerization reactions are shown in Figure 5.13 [15].

The most commonly licensed polymerization process is the UOP polymerization process, which uses phosphoric

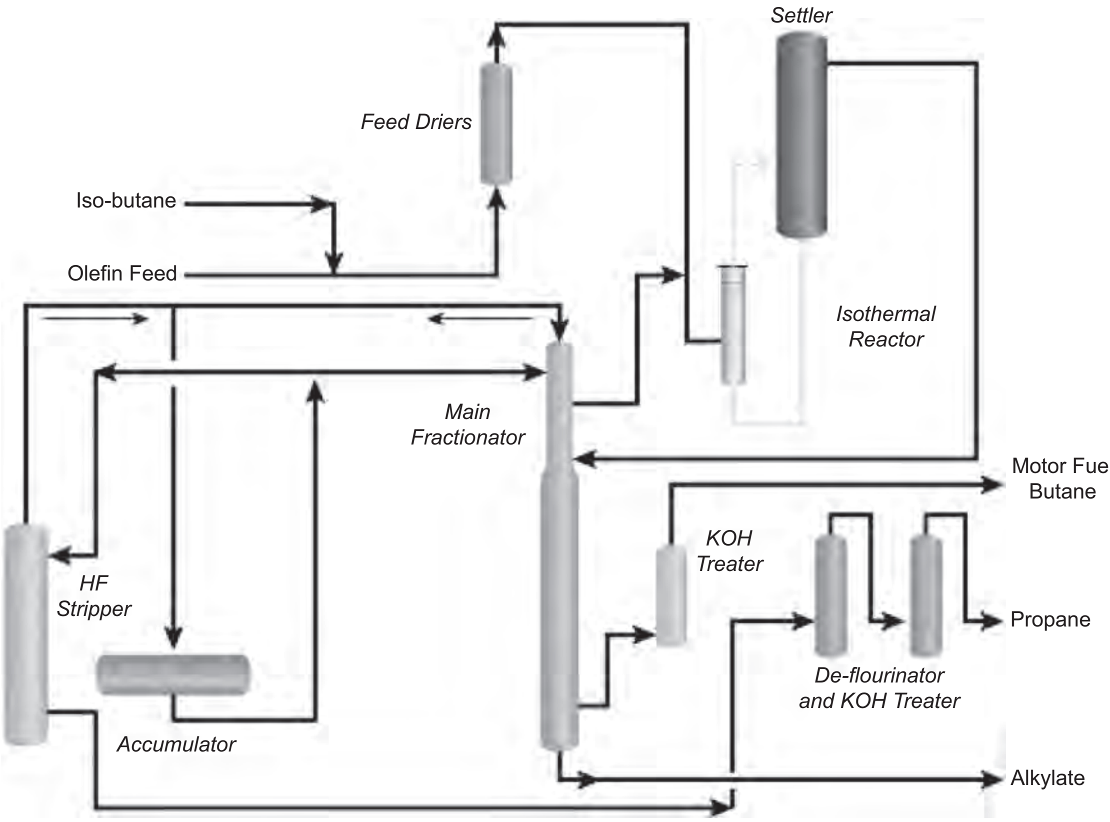


Figure 5.12—UOP HF alkylation (Alkylplus®) process [16]. *Source*: Figure used with permission from UOP LLC, a Honeywell company.

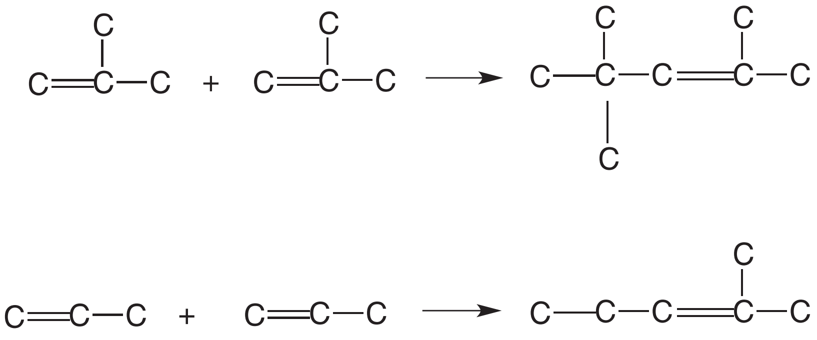


Figure 5.13—Typical polymerization reactions [15].

acid as catalyst. IFP licenses a Dimersol® process that produces dimers from propene or butene using a homogeneous aluminum alkyl catalyst.

5.4.2.1.4 *Isomerization*

Isomerization processes have been used to isomerize *n*-butane to isobutane used in alkylation and C_5/C_6 n-paraffins in light naphtha to the corresponding isoparaffins to produce high-octane number gasoline stocks after the adoption of lead-free gasoline. Catalytic isomerization processes that use hydrogen have been developed to operate under moderate conditions. Chapter 7 reviews the chemistry of hydroisomerization and the development and evolution of hydroisomerization catalysts as well as the associated future challenges and opportunities. A brief description of the process is given here using the UOP Par-Isom™ process as an example.

Figure 5.14 shows a simple flow diagram of a UOP Par-Isom process [17]. Typical feed sources for this process include hydrotreated light straight-run naphtha, light natural gasoline, or condensate. The fresh C_5/C_6 feed combined with make-up and recycled hydrogen is directed to a heat exchange for heating the reactants to reaction temperature. Hot oil or high-pressure steam can be used as the heat source in this exchanger. The heated feed is sent to the reactor. The reactor effluent is sent to a product separator and stabilizer to separate H_2 to be recycled, the isomerate product, and off gas. Typical isomerate product (C_5+) yields are 97 wt %

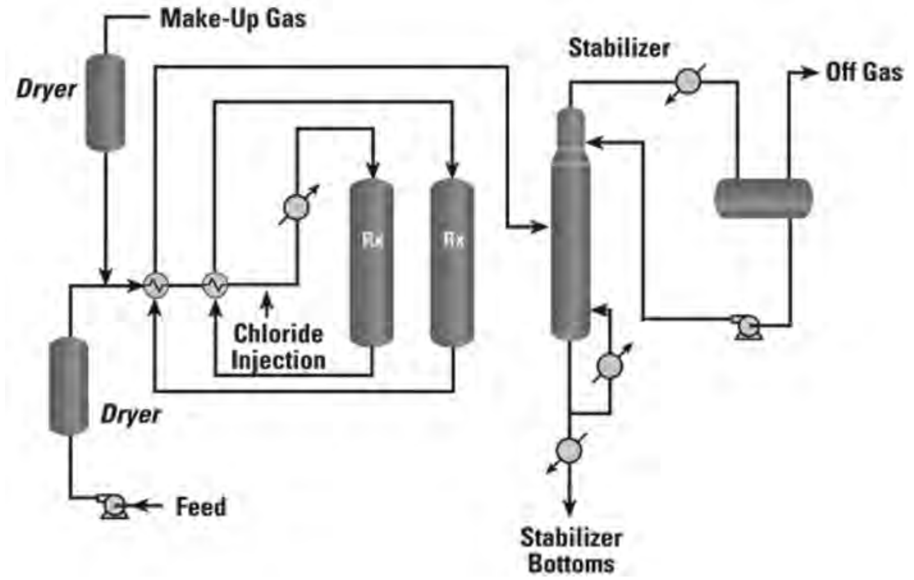


Figure 5.14—UOP Par-Isomer Process [17]. *Source*: Figure used with permission from UOP LLC, a Honeywell company.

of the fresh feed, and the product octane number ranges from 81 to 87, depending on the flow configuration and feedstock properties.

5.4.2.2 JET FUEL, DIESEL, FUEL OIL, AND COKE PRODUCTION

Although gasoline production can be a primary focus of crude oil refining, as in the United States, 40–50 % of the crude oil refined goes into the production of other fuels and nonfuel materials. Many countries rely on diesel fuel as the primary fuel for ground transportation, and, in general, marine transportation relies heavily on diesel or heavier fuel oils. The demand for jet fuel as the gas turbine fuel for jet aircraft has been steadily increasing. Considering that the crude oil available for refining is getting heavier and more contaminated, processes to convert heavy fractions of crude oils or heavy oils into clean distillate products have become important, as discussed in Chapter 8. A brief description of hydrocracking, visbreaking, thermal cracking, and coking is given here because these processes are discussed in some detail in Chapters 8 and 9.

5.4.2.2.1 Catalytic Hydrocracking

Catalytic hydrocracking is one of the latest additions to petroleum refining processes, with the first modern commercial unit started up by Chevron in 1958. The interest in hydrocracking has been attributed to the increasing demand for light and middle distillates, the availability of byproduct hydrogen in large quantities from catalytic reforming, and the environmental regulations limiting sulfur and aromatic hydrocarbons in motor fuels [18]. The advantages of hydrocracking include its ability to handle a wide range of feedstocks that may be difficult to process by catalytic cracking and its flexibility in selectivity between light and middle distillates. As a hydrogen-addition process, hydrocracking provides high yields of valuable distillates without producing low-grade byproducts (e.g., heavy oils, gas, or coke) as experienced in carbon rejection processes such as coking.

Hydrocracking processes most commonly include two reaction stages: hydrotreating to remove heteroatom (S, N, O) species and hydrocracking to increase the H/C ratio of the hydrocarbons in the feeds by hydrogenation and to decrease their molecular weight by cracking. As shown in Figure 5.15 [19], the hydrotreating reactor packed with cobalt-molybdenum catalysts precedes the hydrocracking reactor typically packed with nickel-tungsten catalysts (for hydrogenation) supported on alumina/silica (for cracking). The products from the hydrocracker are sent to a fractionator to be separated into gas and light distillates (LPG and naphtha), middle distillates (kerosene and diesel [or LGO]), and HGO. HGO may be recycled to the hydrocracker for a deeper conversion into light and middle distillates or to extinction, as desired. The reactions are performed at 300–400°C and 8–15 MPa of hydrogen pressure.

In a refinery, hydrocracking complements catalytic cracking by taking on the more aromatic feedstocks that resist cracking, including the byproducts of FCC, such as light cycle oil (LCO). In the United States, hydrocracking of LCO (from FCC) provides a large proportion of the diesel fuel production because straight-run LGO is a preferred stock for FCC to produce gasoline as the principal product. The major licensors of hydrocracking processes include Chevron, UOP, ExxonMobil Research and Engineering, BP, Shell, and BASF-IFP.

Recent advances in hydrotreating/hydrocracking processes and the hydrotreating/hydrocracking catalysts for processing the residual fractions of crude oils and heavy oils, including bitumen conversion to synthetic crude oil, are discussed in Chapters 8–10.

5.4.2.2.2 Visbreaking and Thermal Cracking

Thermal cracking is the first commercial conversion process developed in the early 1900s principally to produce more motor gasoline from crude oils and produce high-octane gasoline for aircraft use, initiating the evolution of the petroleum refinery. With the advent of catalytic cracking in the 1930s and 1940s and its capability to produce higher yields of gasoline with higher octane number, thermal

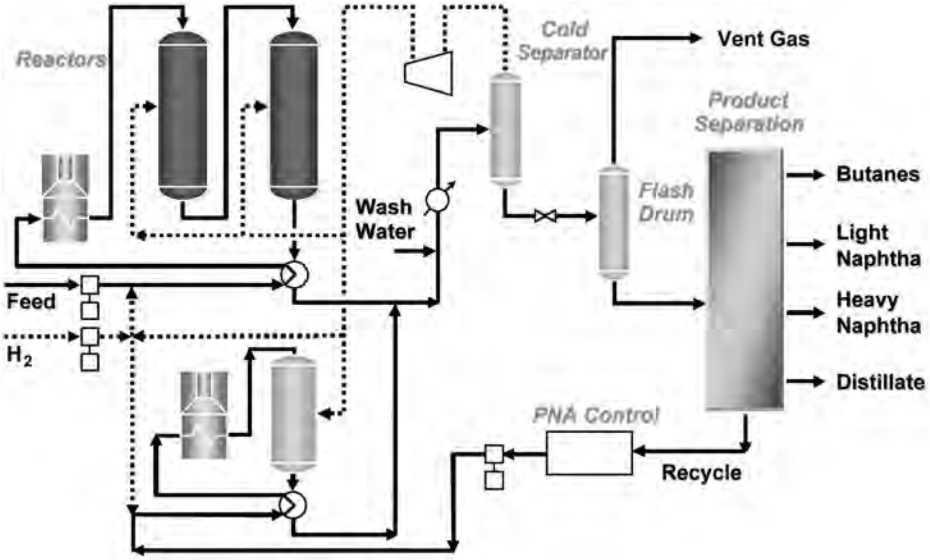


Figure 5.15—A two-stage UOP hydrocracking process [19]. *Source*: Figure used with permission from UOP LLC, a Honeywell company.

cracking of gas oils has ceased to be an important process for gasoline production in modern refineries. As opposed to ionic chain reactions controlling catalytic cracking, free radical chain reactions govern the thermal cracking chemistry that generates high yields of gas, particularly methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4), and produces straight-chain alkanes in liquid products with low octane numbers. Therefore, a principal application of the thermal cracking of distillate fractions in current refineries is limited to naphtha cracking for the purpose of producing C_2H_4 for the petrochemical industry. However, thermal cracking of residual fractions, particularly VDR, is still practiced in association with visbreaking and coking processes in the refineries.

Visbreaking is a mild thermal cracking process applied to reduce the viscosity of VDR to produce fuel oil and some light products to increase the distillate yield in a refinery. Commercial visbreaking processes and their significance in the overall refinery scheme are discussed in Chapter 8.

5.4.2.2.3 Coking

Despite the development of catalytic cracking processes, coking processes in particular, the delayed coking process has survived as a popular refining process all over the world to refine the heavy end of crudes or heavy oils through carbon rejection as coke. Chapter 8 discusses coking technologies and processes (including fluid coking and flexicoking) in some detail. Here, a brief description of the delayed coking process is given with focus on the properties and the applications of the coke products. The petroleum coke produced through the delayed coking process has reached 100 million t/year in the world, and 20 million t are calcined for use in metallurgy for processing alumina and titania as well as raw material in the carbon industry for producing graphite electrodes for electric arc furnaces and nuclear graphite.

There are basically three kinds of coke produced by delayed coking: high-density shot coke, porous sponge coke, and needle coke. Figure 5.16 describes the appearances, specifications, and applications of these cokes. The formation of shot coke is usually troublesome because of difficulties in removing the coke from the drums and problems with grinding, although shot coke has some niche applications such as in titanium dioxide (TiO_2) production. Sponge coke is used as solid fuel and manufacturing anodes for aluminum production. Among the delayed coking products, needle coke is a specialty coke produced mostly from coking the FCC decant oil; its production is approximately 1 million t almost exclusively in the United States, United Kingdom, and Japan.

The major properties of the needle coke include

- A low coefficient of thermal expansion,
- A low puffing tendency during graphitization because of lower nitrogen and sulfur contents, and
- High mechanical strength.

The anode coke has limits on metal contaminants, requiring less than 500 ppm of Ni and V in the coke. The price of fuel coke depends on its carbon purity (S, N, and metal contaminants); however, the fuel coke is traded at a price comparable to that of the coal.

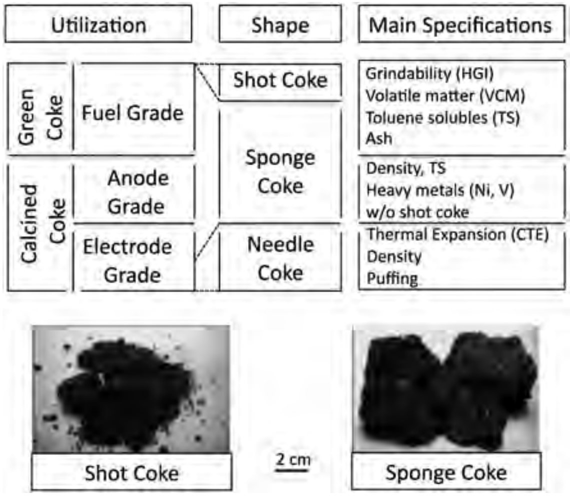


Figure 5.16—Appearances, properties, and applications of cokes produced from delayed coking of vacuum residue.

Producing a high-quality coke (e.g., anode coke from the delayed coking process) as a byproduct adds to the benefit of producing distillate liquid fuels from very heavy feedstocks. Therefore, the pretreatment of the feed to increase the coke quality becomes feasible.

Delayed coking can deal with the heavy feeds that cannot be upgraded by other refining processes because of the high coking yield and high contamination with metals, sulfur, and nitrogen. However, the feeds are recently being treated before delayed coking to obtain better performance in the processes and higher quality products. The treatment must be well designed in terms of objectives and procedures because the treatment itself must overcome the difficulties as expected from the composition of the feed. The objectives of pretreatment are summarized in Table 5.4.

The variety of feeds for delayed coking is now expanded because of the larger variety of crudes and products from a greater variety of processes in petroleum refining and petrochemical processes. To keep the coking process feasible and to improve the products' quantity and quality from the particular feed, the feed can be adjusted. The delayed coker requires limited viscosity and coking reactivity of the feed, which must pass rapidly through the heating tube (preheated) without any coke deposit on the tube wall. The heating of the feed may lead to the phase separation of the heavy fractions because of the vaporization and thermal cracking of the particular fraction. The phase separation may result in the deposition of coke precursors on the heater tube and heterogeneous coking in the coker drum. Heterogeneous coking often leads to the considerable degradation of coke quality and causes the formation of shot/ball coke in the bottom of the drum. Some feed produces such coke in the whole zone of the drum.

The quality and quantity of the products are controlled as desired by the refiners. Usually refiners want high yields of the distillates such as coker gasoline and gas oil. A higher quality of distillates such as low sulfur content is also desired. Low-grade coke obtained from a low-grade feed does not have much value; therefore, its yield is minimized by design. However, a high-quality coke, such as premium needle coke, is highly desired and its yield is maximized. Quality factors for delayed cokes are summarized in Table 5.5. These factors are defined by their application of coke as fuel, aluminum anode, or steel electrode coke, respectively.

TABLE 5.4—The Objectives for Feed Pretreatment in Delayed Coking

Feed Properties	Effects
Fluidity	No coking in the heater tubes Liquid phase coking
Non-fusible component	Fluidity and coking properties
Contamination	Quality of distillate and coke
Coke yield or Distillate Yield	Higher yields of desired products
Coke structure	Density Porosity Optical texture Graphitization
Coking reactivity of the feed	Coking in the heater and coke drum

Operational control factors in the delayed coker are mainly drum pressure, recycle ratio, and heater outlet temperature. Their effects are not so significant on the properties of the products, although there are optimal conditions that can be selected. The properties of the products depend strongly on the properties of the feedstocks.

For a better performance of delayed coking operation and higher product values, several feed pretreatment options are available and practiced. These procedures are summarized in Table 5.6. One extreme is to charge the heaviest feed into the delayed coker. Other thermal or catalytic processes can refine the light fraction. Another extreme is to reject the particular fraction, often the heaviest end, to improve the coke quality. SDA (solvent deasphalting process) is proposed as an effective way to remove the heaviest end (the metal and S compounds present in the feed) to improve the coke quality. This also improves the liquid product quality and makes the process easier to control. The issue that needs to be addressed with this option is how to use the separated asphaltene fraction.

The feed can also be catalytically or thermally treated to obtain a better performance in terms of product yield and quality. Blending feeds with particular additives (e.g., aromatic and hydroaromatic compounds) could also improve the process and the quality of products and provide a better control of the coking process.

The refining of the coker feed includes removal of contaminants, conversion of the heavy fraction, aromatization/condensation of light paraffinic fractions, and hydrogenation of the aromatic fraction. Such refining reactions are combined for better performance. Selective hydrogenation is a

TABLE 5.5—Quality Factors for Cokes from the Delayed Coking Process

Quality Factor	Fuel Coke	Electrode Quality
Free carbon contaminants Ash and minerals Metal Sulfur Nitrogen	 Lower fuel quality SO_x NO_x	 Lower electrode quality Puffing Puffing
Metal	Metal deposition	Contamination in electric refining
Sulfur	SO_x	Puffing
Nitrogen	NO_x	Puffing
Density	Very strong coke is not desirable	Coke strength and density of carbon electrode
Porosity cracks and their distribution		Large coke size desired
Graphitization extent		Steel production
Optical texture isotropic, mosaic, needle		Aluminum production Steel production
Thermal expansion		Steel production

TABLE 5.6—Pretreatments of Feeds for Delayed Coking

Procedure	Objectives
Fractionations	
Heavy end cut (SDA is typical.)	Uniform fluidity
Light component cut	Higher coke yield Treatment of lower quality feed (reactor volume efficiency)
Blending with	Coking control
Aromatic additive	Solvent fraction to keep liquid phase during the coking
Hydroaromatic additive	Hydrogen donative additive to induce and keep liquid phase
Acidic treatment	
Dealkylation Aromatization	Aromaticity enhancement to control coking reactivity
Hydrogenation	Hydroaromatic feed controls coking reactivity to increase the distillate and coke quality
Hydrocracking	Hydroaromatic feed controls coking reactivity to increase the distillate and coke quality
Hydrorefining	
HDM	Metal reduction for coke quality
HDS	Sulfur reduction for coke quality
HDN	Nitrogen reduction for coke quality

particular reaction that can control the coking through moderating the condensation reactions via hydrogen transfer and enhancing the thermal cracking and ring-opening reactions.

The catalytic process is ideal; however, the catalysts must be designed to function under severe conditions. Solvolytic and thermal reactions constitute another choice to modify the feed.

5.4.3 Finishing Processes

5.4.3.1 HYDROTREATMENT

As a natural substance, crude oil contains heteroatom (S, N, and O) compounds as well as metals (mainly Ni and V) in addition to hydrocarbons. The sulfur content of crude oils normally ranges from 0.05 to 6 wt %, nitrogen content varies from 0.1 to 1 wt %, oxygen from 0.1 to 2.0 wt %, and metals from 10 to 1000 ppm. Once crude is fractionated by distillation, the heteroatoms (particularly S, N, and metal compounds) are distributed in the products. Heteroatom compounds are mainly associated with the higher boiling fractions and the residues that are rich in aromatic compounds. The presence of heteroatom compounds in petroleum products is undesirable because they reduce fuel stability, contribute to the emission of pollutants, and damage engines. Heteroatom compounds in refinery streams (e.g., basic nitrogen compounds, sulfur compounds, and metals) can deactivate catalysts and promote coke formation.

The light products such as LPG and naphthas have low concentrations of sulfur and require minimal treatment, such as absorption in alkaline solvents (e.g., H_2S or mercaptan sulfur) or conversion of mercaptans to sulfides to eliminate odor. For example, the UOP Merox™ process is widely used to remove H_2S and mercaptan sulfur (Merox extraction) or to convert mercaptan sulfur to less-objectionable disulfides (Merox sweetening) [20]. The Merox process can be used to treat liquids such as LPG, naphtha, and kerosene. Removing sulfur from higher molecular weight and more complex molecules requires hydrotreatment processes that use hydrogen. The advancement in hydrotreatment processes to desulfurize higher boiling distillate fractions and FCC products are discussed in Chapters 9 and 10. A brief introduction to hydrotreatment processes is given later in this section.

Particularly strict sulfur limits have recently been imposed on diesel fuels so that the particulate emissions from diesel engines can be reduced. In the United States, the government regulations [21] require that highway and nonroad, locomotive, and marine engines that use diesel fuel meet a maximum specification of 15 ppm sulfur by 2014 with a full compliance for highway use and nonroad diesel fuel since December 2010. It also requires full compliance for locomotive and marine diesel fuel use by 2012.

Table 5.7 shows the evolution sulfur limit of diesel fuels in the United States, Europe, and Japan. In 2006, new U.S. standards for ultralow-sulfur diesel (ULSD) took effect under a 2001 rule issued by the U.S. Environmental Protection Agency (EPA). Diesel fuel sulfur content must be reduced to no more than 15 ppm from the 500 ppm that was established by a 1993 rule that reduced the level from 5000 ppm (0.5 wt %). To account for pipeline contamination, refiners may have to produce diesel fuel with a sulfur content as low as 7 ppm. EPA estimates that the marginal cost of producing ULSD ranges from 2.5 to 6.8 cents per gallon in the United States. The Energy Information Administration (EIA) projects that the total investment in U.S. refineries to meet the requirements for ULSD ranges from \$6.3 to \$9.3 billion. Because the energy content of

TABLE 5.7—Limits of Sulfur Content of Diesel Oil in Europe, Japan, and in the United States (in ppmw) [22]

	1953	1976	1990	1992	1996	1997	2000	2005	2006	2011[a]
European Union	–	–	–	–	500	–	350	50	–	10
Japan	12,000	5000	–	2000	–	500	–	50	–	–
United States	–	–	500	–	–	–	–	–	15	–

[a]Proposal of European Union commission.

ULSD is somewhat less than that of the 500-ppm sulfur content of diesel, fuel efficiency may be affected, requiring higher demand on diesel and more consumption [23]. Desulfurization of fuels is commonly achieved by heterogeneously catalyzed hydrodesulfurization (HDS), in which the organic sulfur species are converted to H_2S and the corresponding hydrocarbon: $R\text{-}SH + H_2 \rightarrow R\text{-}H + H_2S$. Here R represents an alkyl group, such as methyl (CH_3–) or ethyl (C_2H_5–). The reactivity of R-SH compounds is higher than that of disulfides (R-S-S-R). The H_2S is easily removed from the desulfurized oil by absorption in a gas treatment unit and subsequently converted to elemental sulfur by the Claus process [24].

Sulfur ring compounds such as methylated dibenzothiophenes have the lowest reactivity in HDS reactions because of the shielding of the S atom by the methyl groups. Removing sulfur from these compounds (i.e., deep desulfurization) requires more hydrogen consumption to saturate the aromatic rings in dibenzothiophene to form nonplanar compounds and eliminate the steric hindrance of methyl groups to make the S atom accessible to active sites on the catalyst surface for removal as H_2S.

Hydrodenitrogenation (HDN) is a similar process in which hydrogen is used to remove nitrogen, and for this reason during HDS the nitrogen content of fuels is also reduced. Pyridine (C_5H_5N) can be reduced to pentane (C_5H_{12}) and ammonia (NH_3) by adding $5H_2$ in three steps that consist of saturating the aromatic ring with $3H_2$ to form piperidine ($C_5H_{11}N$), a ring-opening reaction with one H_2 to form amylamine ($C_5H_{11}NH_2$), and forming *n*-pentane by removing nitrogen as NH_3 with one H_2. The overall HDN reaction is $C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$.

Removal of basic nitrogen compounds such as C_5H_5N is an important pretreatment step before a process that uses acidic catalysts, such as FCC. On the other hand, HDS is an important pretreatment process for feedstocks that would be exposed to noble metal catalysts that are poisoned by sulfur compounds, such as Pt in the catalytic reforming process.

HDS reaction conditions are typically 350°C and 7 MPa. With respect to the increasing demand for practically sulfur-free fuels (<10 ppm), sulfur species with very low reactivity such as dibenzothiophene derivatives have to be converted in a second-stage deep HDS step that leads to additional high investment and operating costs [22].

Shih et al. [25] developed a simple correlation for prediction of reactivity over a temperature range of 520–780°F. The reactivity is defined as the temperature (°F) required to achieve a 500-ppm sulfur product ($T_{500ppmS}$) and is given as a function of two feed properties:

$$T_{500ppmS} = 454°\text{F} + 31\exp(S_{600F+}) + 25\ln(N) \tag{5.2}$$

where:

S_{600F+} = weight percent of sulfur in the 600°F+ fraction of the feed, and

N = feed nitrogen content (ppmw).

For ULSD fuel (10 ppm sulfur), usually alumina-supported CoMo or NiMo-sulfide (NMA) catalysts are used. An alternative to this is carbon-supported Ni-Mo-sulfide (NMC) with surface areas ranging from 900 to 3000 m^2/g as discussed in reference 26. Kunisada et al. [27] show that a hydrotreated gas oil containing 340 ppm sulfur can be successfully desulfurized to less than 10 ppm sulfur under the presence of 1.67 % H_2S over CoMoS and NiMoS supported on acidic supports. Such supports are believed to enhance the sulfur release from active sites and the hydrogenation of refractory sulfur species to accelerate their deep desulfurization.

5.4.3.2 PRODUCT BLENDING

As a major finishing process, product blending plays a key role in preparing the refinery products for the market in compliance with all of the product specifications and quality control measures. The objective of product blending is to assign all available blend components to satisfy the product demand and specifications to minimize cost and maximize overall profit. Almost all refinery products are blended for the optimal use of all of the intermediate product streams for the most efficient and profitable conversion of petroleum to marketable products. For example, typical motor gasolines may consist of straight-run naphthas, crackates, reformates, alkylates, isomerates, polymerates, pyrolysis gasoline, etc., in proportions to make the desired grades of gasoline and the specifications. Chapter 4 describes the specifications of the petroleum fuels and materials and Chapter 19 is devoted to discussing the fuel blending technology and management in petroleum refineries. Until the 1960s, the blending was performed in batch operations. With computerization and the availability of the required equipment, online blending operations have replaced blending in batch processes. Keeping inventories of the blending stocks along with cost and physical data has increased the flexibility of and profits from online blending through optimization programs. In most cases, the components blend nonlinearly for a given property (e.g., octane number, cetane number, freezing point), and geometric programming is required for reliable predictions of the specified properties.

5.4.4 Supporting Processes

Supporting processes are not directly involved in the production of fuels or materials, but they are essential for the operation of a petroleum refinery. Major supporting processes include hydrogen production, environmental remediation of refinery emissions, and sulfur recovery. Hydrogen production and environmental remediation issues are discussed in detail in Chapters 12 and 29, respectively, and will not be covered here. The following section reviews sulfur recovery.

Sulfur exists in natural gas and refinery gases (i.e., overhead gas from crude distillation and hydrotreating units) as H_2S. An acidic gas, H_2S is removed by absorption in basic solutions of ethanol amines and sent to the Claus process. In the Claus process, H_2S is converted to elemental sulfur, which can be safely stored and sold as a byproduct. The process consists of two steps that take place consecutively in burner and converter reactors. In the burner, part of H_2S is oxidized to form sulfur dioxide (SO_2), which subsequently reacts with the remaining H_2S over an alumina catalyst in the converter reactor to produce elemental sulfur [24]:

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \text{ (Burner reaction)}$$

$$2H_2S + SO_2 \leftrightarrow 2H_2O + S \text{ (Converter reaction)}$$

The overall reaction in the Claus process becomes

$$3H_2S + \frac{3}{2}O_2 \rightarrow 3H_2O + S$$

Because of equilibrium limitations, the sulfur recovery is usually limited to 94–95 %. Therefore, the Claus offgas contains small amounts of H_2S, SO_2, and other sulfur gases such as COS and carbon disulfide (CS_2) formed in the side reactions. Using a separate process (e.g., the Shell Claus Off-gas Treatment [SCOT]), SO_2, COS, and CS_2 are converted to H_2S upon reaction with hydrogen on a tungsten catalyst. The H_2S product is absorbed by an amine solvent and recycled to the Claus unit feed. A combination of the Claus process with a tail gas clean-up process such as SCOT leads to sulfur recovery in excess of 99 % [24].

5.5 EVOLUTION OF REFINERY PROCESSES AND REFINERY CONFIGURATIONS

5.5.1 Development of Refinery Processes

Consumer demand has driven a continuous evolution of petroleum refining with the introduction of new processes to increase the quantity and quality of refinery products in a long path from producing just one main product, kerosene, by simple atmospheric distillation in 1861 with the byproducts tar and naphtha to the multitude of hydrocarbon fuels, chemicals, and petrochemicals produced in the complex refineries of the present day. Table 5.8 shows a timeline of the refinery processes introduced in the time period from 1861 to 1975 as the development of the internal combustion engine has demanded the production of gasoline and diesel fuels, and the aviation industry has demanded high-octane aviation gasoline for the turbo engine and kerosene-based jet fuel for the gas turbine engine of jet aircraft. The increasing demand for distillate fuels that has exceeded the supply that can be obtained from distillation alone has ushered in thermal and catalytic conversion processes in addition to physical separation processes such as vacuum distillation (1870), dewaxing (1935), and deasphalting (1950) to produce lubricating oils along with byproducts such as wax and asphalt that have found other industrial applications.

In 1913, the thermal cracking process was developed to break the large molecules into smaller ones to produce additional gasoline and distillate fuels. Visbreaking and coking were developed in the late 1930s to treat the heavy ends. Catalytic cracking and polymerization processes were also introduced in the mid- to late 1930s to meet the demand for higher octane gasoline required by the higher-compression gasoline engines. Other catalytic processes, such as alkylation and isomerization, were developed in the early 1940s to produce high-octane aviation gasoline and petrochemical feedstocks. Catalytic reforming and isomerization were developed in the 1950s to increase the gasoline

TABLE 5.8—A Timeline for the Development of Petroleum Refining Processes from 1861 to 1975 [28]

Year	Process	Purpose	Byproducts, etc.
1861	Atmospheric distillation	Produce kerosene	Naphtha, tar, etc.
1870	Vacuum distillation	Lubricants (original) and cracking feedstocks (1930s)	Asphalt, residual coker feedstocks
1913	Thermal cracking	Increase gasoline	Residual, bunker fuel
1916	Sweetening	Reduce sulfur and odor	Sulfur
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulfur	Sulfur
1932	Coking	Produce gasoline basestocks	Coke
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Solvent dewaxing	Improve pour point	Waxes
1935	Catalytic polymerization	Improve gasoline yield and octane number	Petrochemical feedstocks
1937	Catalytic cracking	Higher octane gasoline	Petrochemical feedstocks
1939	Visbreaking	Reduce viscosity	Increased distillate, tar
1940	Alkylation	Increase gasoline octane and yield	High-octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield and octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
1954	Hydrodesulfurization	Remove sulfur	Sulfur
1956	Inhibitor sweetening	Remove mercaptan	Disulfides
1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality and reduce sulfur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking and flexicoking	Increase gasoline yield from residual	Heavy residuals

TABLE 5.9—Evolution of the Demand for Petroleum Products in the World from 1970 to 2010 [30]

	1970		1980		1990		2000		2010	
	10^6 tons	%	10^6 tons	%	10^6 tons	%	10^6 tons	%	10^6 tons	%
Gasoline	492	25.4	626	26.6	750	26.8	876	26.2	1047	26.0
Middle distillates	530	27.4	721	30.6	950	33.9	1163	34.8	1472	36.6
Heavy fuels	608	31.4	645	27.4	500	17.9	426	12.8	456	11.3
Others	307	15.8	363	15.4	600	21.4	875	26.2	1046	2.0
Total	1937	100	2355	100	2800	100	3340	100	4021	100

Middle distillates = jet fuels, heating oil, and diesel oil. Others = refinery gas, LPG, naphthas, lubricants, wax, bitumen, petroleum coke, etc. 1 bbl/day = ~50 t/year.

yields with high octane numbers and improve antiknock characteristics. Throughout the 1960s and 1970s, new catalysts were developed for hydrocracking and residue hydrocracking processes to produce higher yields of light and middle distillates and for catalytic dewaxing to improve the pour point of lubricating oils.

In parallel to the development of conversion processes, various treatment (finishing) processes have been developed to remove heteroatoms and other impurities. Treating processes can involve chemical reaction or physical separation or both. Typical examples of such treating processes are chemical sweetening (1916), hydrogenation (1932), and HDS (1954).

5.5.2 Changes in Refinery Configurations

Until the 1960s and 1970s, refineries had relatively simple configurations consisting primarily of distillation, catalytic reforming, and HDS units. Such simple refineries produced a large amount of fuel oils (~40 %). In the late 1970s, the oil shocks caused a decrease in the demand for heavy fuels and a need for lighter products. This was the main reason for using more cracking units such as visbreakers, catalytic crackers (FCC), and hydrocrackers to produce low-sulfur products. For example, in France, 15 million t of fuel oil were used in 1973 whereas in 1993 this number reduced to only 2 million t [29]. Heating oil has been largely replaced by gas and electricity. In France, nuclear power plants generate 75 % of electricity. In the meantime, the demand for the petroleum products with no easy substitute such as gasoline and middle distillates continued to increase.

Table 5.9 shows the evolution of the demand for petroleum products in the world from 1970 to 2010 as given by Marcilly [30], clearly showing the significant drop in the demand for heavy fuels from 31.4 % of the petroleum refined in 1970 to 11.35 % in 2010.

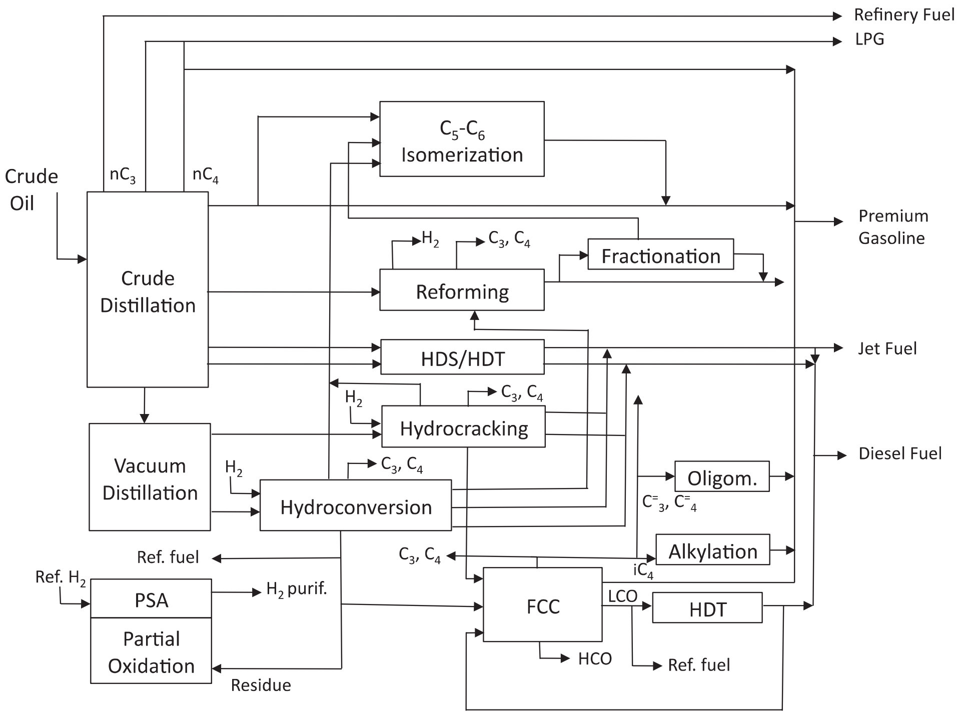


Figure 5.17—A refinery scenario for 2010. *Source*: Figure modified from Marcilly [30], a European model.

Figure 5.17 shows a flow diagram for the sophisticated and ultracomplex refineries of the present day [30]. The principal feature of these refineries is the high level of conversion of heavy ends into light products. Most of the conversion takes place through FCC-type units with high yields of gasoline at low cost. In Western Europe conversion processes in refineries increased from 6 % in 1975 to more than 30 % in 1977 [29]. In 1977, only one third of 143 refineries in Western Europe were equipped with FCC units whereas in 2000 this is more than 80 %. Furthermore, environmental regulations require fuels with less sulfur, and production of ultralow-sulfur fuels (gasoline and diesel fuels) is on the rise. The manufacturing of such high-quality fuels requires more severe conversion and finishing processes in refineries. Table 5.10 shows the evolution of refinery processes in various parts of the world for the last 20 years [30]. The figures represent capacity in million tons per year. In all three regions, hydrotreatment and cracking processes have been on the rise and the trend continues.

A future scenario for refineries in the United States is shown in Figure 5.18 [31]. In this scenario, a light Saudi Arabian crude is considered with a sulfur content of 1.78 wt %. The produced gasoline has a sulfur content of 5–10 ppm. In this scenario, coking provides the principal carbon rejection as coke, and all of the liquid products from coking are further treated to manufacture light and middle distillates and fuel oil. Further discussion on future scenarios for petroleum refineries is given in Chapter 34.

5.6 FUTURE OUTLOOK—MARKETS AND TECHNOLOGY

Factors that would affect future refineries over time include financing, technology, people/organizations, business, and the environment. Regardless of government regulations,

TABLE 5.10—Development in the Structure of World Refining Capacities from 1979 to 1999 for the Main Geographical Zones in Million Tons per Year [30]

	1979			1999		
	North America	Western Europe	Asia-Pacific	North America	Western Europe	Asia-Pacific
HDT	437	346	214	577	404	374
FCC	260	49	30	298	106	125
HDC	46	6	1	84	34	35
Atmospheric distillation	997	998	520	923	723	982

HDT = hydrotreatment, HDC = hydrocracking.

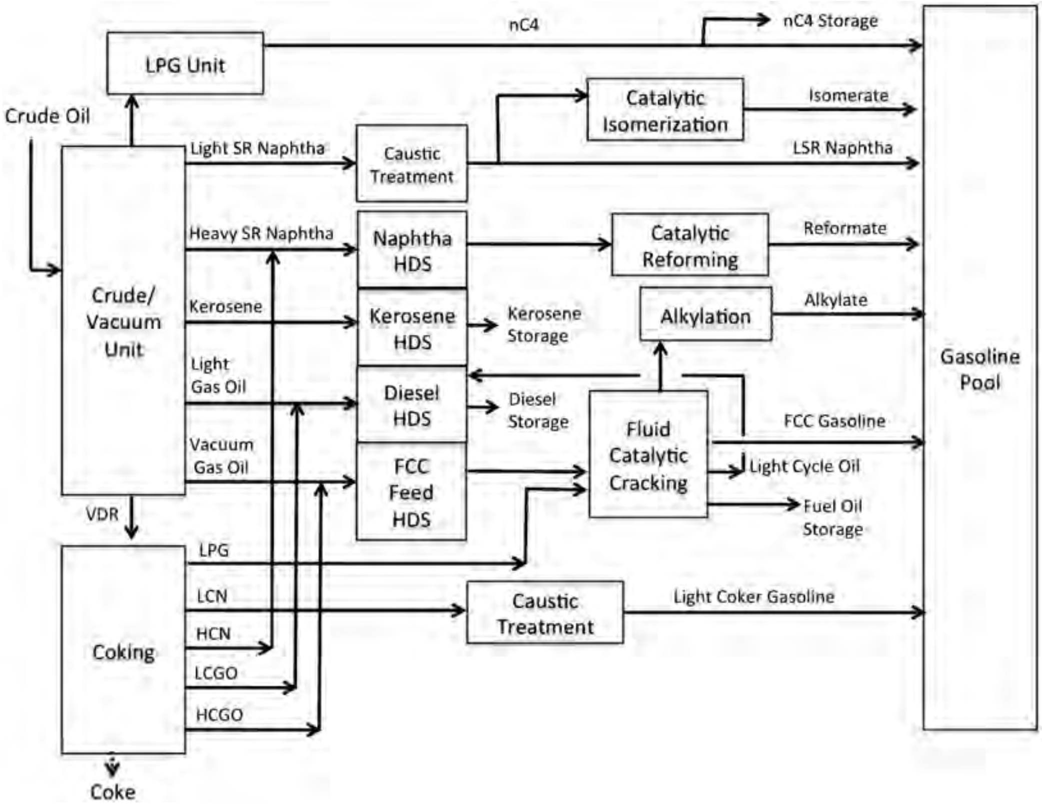


Figure 5.18—A scenario for a future refinery for light Arabian crude (a U.S. model). Sulfur in the feed is 1.78 wt % and refinery capacity is 150,000 bbl/day. *Source*: Figure modified after [31].

future refineries should have safer operations to prevent explosions, fires, spills, and environmentally undesirable emissions with strict commitment to the production plan and economical operation.

Petroleum refining involves physical and chemical processes, and the complexity of refining depends on the crude quality and the required specifications of the products. Crude quality varies from one part of the world to the other; it also changes with time. Usually the crude quality in terms of API gravity and sulfur content decreases with time. For example, the API gravity of crude oils refined in the United States has decreased from 33.8 to 32.0 in the period of 1 decade from 1980 to 1990. During the same period, the sulfur content of U.S. crudes has increased from 0.86 to 1.1 wt % [1]. Such quality changes require more advanced crude refining. In conflict with the trend of crudes getting heavier, on the product side in the past few decades there has been higher demand on distillates such as gasoline, jet fuel, and diesel fuel and less demand on heavy fuel oil and residues. This conflict, along with the environmental regulations that demand cleaner fuels, requires more extensive conversion processes to transform heavy oils into lighter and cleaner products.

A high-sulfur and heavy crude costs up to one third less than lighter or better crudes. However, high-sulfur crudes require more processing and therefore more fixed expenses and labor. They also require more energy. Energy accounts for roughly half of the operating cost of a refinery. A refinery close to crude oil sources and a high-demand market entails lower transportation cost. A refinery can make good profits if it is well equipped to run some of the heaviest, cheapest crudes in the world. Large investments are needed to meet the environmental constraints and product quality (i.e., high-octane unleaded gasoline, ultralow-sulfur fuels). To increase the octane number of gasoline without the use of TEL, refineries must operate at greater severity for catalytic reforming, have more isomerization and alkylation units, and use oxygenated compounds as additives. Changing market conditions also affect future refineries.

The evolution of investment, energy consumption, and hydrogen consumption for three categories of refineries as of 2000 in the European Union is given in Table 5.11 [30]. The cost of refinery investment as well as the amount of hydrogen consumption for classical refineries depends on the product quality.

TABLE 5.11—Evolution of Investment, Energy, and Hydrogen Consumptions for the Refineries of 2000 [30]

Type of Refinery	Investment (billion $)	Energy Consumption (wt % of crude)	Hydrogen Consumption[a]
Simple	0.5	≈ 4	α
Classical conversion	1–1.5	≈ 6	2α
Deep conversion	2.5	≈ 10	5α

[a] The figures are not absolute because the hydrogen and therefore Â will depend on operating conditions (nature of crude and S content of products, etc.). Investment costs are given for a typical refinery of ~150,000- to 160,000-bbl/day capacity.

The hydrotreatment required for deep conversion demands additional hydrogen to supplement what was supplied traditionally by the refinery reformer. The additional sources of hydrogen include a natural gas steam-reforming unit or partial oxidation of the residue to totally convert the residue into synthesis gas [30].

Looking ahead, five drivers have been identified as having the greatest affect on the petroleum industry in the coming decades [32]:

1. *Environmental concerns:* Lifecycle effects of petroleum fuels on air pollution and global climate change and continuously evolving regulations.
2. *Markets and demand:* Strong demand for petroleum fuel and objectives to reduce this demand by replacing them with cost-effective and renewable energy sources.
3. *Competitive forces:* Increased global competition leading to joint ventures and mergers to reduce cost.
4. *Process improvements:* Capability to respond to changes in the crude slate with more sophisticated and new technology, including new catalysts, new chemistry and concepts in refining, and modeling technologies interfaced with online measurement technologies for optimization.
5. *Energy efficiency:* New technologies, market incentives, and increasing scale of operations to improve energy efficiency and increased engine efficiencies driven by mandates and competitive forces as well as opportunities for treating an engine-fuel combination as a single entity to increase the efficiency of gasoline and diesel engines.

With these major drivers, future refineries will become safer, more reliable, more energy-efficient, and have reduced environmental impact. A high degree of automation with integrated process and energy systems control could effectively address the changing product specifications and respond to the market demand [32]. Further discussion on these issues is provided in Chapter 34.

5.7 SUMMARY

Petroleum refining has evolved from a one-pot batch distillation process to separate kerosene from crude oil for lighting lamps to the most sophisticated network of integrated physical and chemical processes that run around the clock. These processes separate crude oil into hydrocarbon fractions and convert/finish these fractions into a multitude of commercial fuels and materials. The primary objective of a petroleum refinery is to add value to a crude oil feed by producing marketable fuels and materials at the lowest possible cost in accordance with the required product specifications and environmental regulations.

The refinery products include LPG, gasoline, solvents, jet fuel, diesel fuel, fuel oil, asphalt, wax, lubricating oils, and petrochemicals. Considering the variability of crude oils with geography and time and the evolving demand, specifications, and environmental regulations for the refinery products, refineries need to have the flexibility to handle these variations in a competitive market. This chapter provides an overview of how refinery processes work and relate to one another to make use of physical separations and chemical changes to provide the market with the desired quantity and quality of the petroleum products. Most innovations in petroleum refining processes took place around the time of World War II and often with the collaboration of several oil companies to meet the demand for the higher quantity and higher quality of distillate fuels. The recent increase in the demand for distillate fuels, particularly in Asia, could initiate another wave of innovations in refinery operations to exploit the breakthroughs in digital communications and process modeling to yield the demanded products under the current environmental and feedstock constraints.

REFERENCES

[1] Speight, J.G., *The Chemistry and Technology of Petroleum*, 4th ed., Marcel Dekker, New York, 2006.

[2] Manning, F.S., and Thompson, R.R., *Oilfield Processing*, PennWell Publishing, Tulsa, OK, 1995.

[3] Geankoplis, C.J., *Transport Processes and Separation Process Principles*, 4th ed., Prentice Hall, Upper Saddle River, NJ, 2003.

[4] McCabe, W.L., Smith, J.C., and Harriott, P., *Unit Operation of Chemical Engineering*, 7th ed., McGraw-Hill, New York, 2005.

[5] Kister, H.Z., *Distillation Operations*, McGraw-Hill, New York, 1990.

[6] Siemanond, K., and Kosol, S., “Retrofit of Crude Preheat Train with Multiple Types of Crude,” in *SIMULTECH11 Proceedings*, 2011, pp. 303–308.

[7] Elvers, B. (Ed.), *Handbook of Fuels: Energy Sources for Transportation*, Wiley-VCH, Weinheim, Germany, 2008, pp. 29–34.

[8] Gary, J.H., Handwerk, H., and Kaiser, M.J., *Petroleum Refining: Technology & Economics*, 5th ed., CRC Press, Boca Raton, FL, 2007, p. 83.

[9] “UOP/FWUSA Solvent Deasphalting Process,” http://www.uop.com/solvent-deasphalting-sda/ (accessed February 19, 2012).

[10] “U.S. Energy Information Administration, U.S. Department of Energy,” http://www.eia.doe.gov/oil_gas/petroleum/data_publications/petroleum_marketing_monthly/pmm.html (accessed February 20, 2011).

[11] “UOP FCC Process,” http://www.uop.com/fcc/ (accessed February 19, 2012).

[12] “UOP CCR Platforming™ Process,” http://www.uop.com/reforming-ccr-platforming/ (accessed February 19, 2012).

[13] Gary, J.H., Handwerk, H., and Kaiser, M.J., *Petroleum Refining: Technology & Economics*, 5th ed., CRC Press, Boca Raton, FL, 2007, p. 215.

[14] “CCR Platforming,” http://www.uop.com/refining/1031.html (accessed February 20, 2011).

[15] Gary, J.H., Handwerk, H., and Kaiser, M.J., *Petroleum Refining: Technology & Economics*, 5th ed., CRC Press, Boca Raton, FL, 2007, pp. 231–236.

[16] “UOP Alkylplus® Process,” http://www.uop.com/alkyplus/ (accessed February 20, 2012).

[17] “UOP Par-Isomer™ Process,” http://www.uop.com/clean-fuel-specifications-met-light-naphtha-isomerization-technologies-uop/ (accessed February 19, 2012).

[18] Gary, J.H., Handwerk, H., and Kaiser, M.J., *Petroleum Refining: Technology & Economics*, 5th ed., CRC Press, Boca Raton, FL, 2007, p. 161.

[19] “A Two-Stage Hydrocracking Process,” http://www.uop.com/hydrocracking-unicracking-stage/ (accessed February 20, 2011).

[20] “UOP Merox™ Process,” http://www.uop.com/processing-solutions/refining/gas-lpg-treating/ (accessed February 20, 2011).

[21] U.S. Title 40, Part 80 40 CFR 80 § 500-620, http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=e8e7d79c681c4a6fa6a64275952d9c3f&rgn=div6&view=text&node=40:16.0.1.1.9.9&idno=40 (accessed February 20, 2011).

[22] Schmitz, C., Datsevitch, L., and Jess, A., “Deep Desulfurization of Diesel Oil: Kinetic Studies and Process-Improvement by the Use of a Two-Phase Reactor with Presaturator,” *Chem. Eng. Sci*., Vol. 59, 2004, pp. 2821–2829.

[23] Andrews, A., *Oil Shale: History, Incentives, and Policy*, Congressional Research Service Report for Congress, Library of Congress, Washington, DC, 2006.

[24] Gary, J.H., Handwerk, H., and Kaiser, M.J., *Petroleum Refining: Technology & Economics*, 5th ed., CRC Press, Boca Raton, FL, 2007, pp. 283–290.

[25] Shih, S.S., Mizrahi, S., Green, L.A., and Sarli, M.S., “Deep Desulphurization of Distillates,” *Ind. Chem. Res*., Vol. 31, 1992, pp. 1232–1235.

[26] Kouzu, M., Kuriki, Y., Hamdy, F., Sakanishi, K., Sugimoto, Y., and Saito, I., “Catalytic Potential of Carbon-Supported NiMo-Sulfide for Ultra-Deep Hydrodesulfurization of Diesel Fuel,” *Appl. Catal. A*, Vol. 265, 2004, pp. 61–67.

[27] Kunisada, N., Choi, K.-H., Lorai, Y., and Mochida, I., “Effective Supports to Moderate H2S Inhibition on Cobalt and Nickel Molybdenum Sulfide Catalysts in Deep Desulfurization of Gas Oil,” *Appl. Catal. A*, Vol. 260, 2004, pp. 185–190.

[28] “OSHA Technical Manual, Section IV: Chapter 2,” http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html (accessed February 20, 2011).

[29] Wauqier, J.-P. (Ed.), *Petroleum Refining, Vol. 1 Crude Oil*. Petroleum Products, Process Flowsheets, Editions Technip, Paris, 1995, p. 504.

[30] Mracilly, C., “Evolution of Refining and Petrochemicals: What Is the Place of Zeolites,” *Oil Gas Sci. Technol*., Vol. 56, 2001, pp. 499–514.

[31] Lamb, G.D., Davis, E., and Johnson, J.W., “Impact of Future Refinery of Producing Ultra-Low Sulfur Gasoline,” http://www.mustangeng.com/AboutMustang/Publications/Publications/IMPACT.pdf (accessed October 2, 2012).

[32] American Petroleum Institute (API), *Technology Vision 2020—A Report on Technology and the Future of U.S. Petroleum Industry*, Draft, API, Washington, DC, 2000, http://www1.eere.energy.gov/industry/petroleum_refining/tools.html (accessed on February 22, 2011).

6

Fluid Catalytic Cracking

Ravi Kumar Voolapalli[1], Chiranjeevi Thota[1], D.T. Gokak[1], N.V. Choudary[2], and M.A. Siddiqui[3]

6.1 INTRODUCTION

Fluid catalytic cracking (FCC) is a major secondary processing unit in the petroleum industry for converting gas oil streams into high-octane gasoline, cycle oils, liquefied petroleum gasoline (LPG), and light olefins. After the carbon rejection route, it upgrades low-value streams such as vacuum gas oil (VGO), atmospheric residue, deasphalted heavy oils, etc., into distillates while operating at low pressures and moderate temperatures. It has gained a special place in the refining industry because of its feed flexibility, ability to produce diverse products, and quick response to the market demands through minor changes in process operating conditions. The economics of the FCC process are so attractive that it is almost impossible to imagine a modern refinery without this unit.

6.2 HISTORY

FCC technology was originally developed nearly 70 years ago, primarily for producing gasoline from gas oil feedstocks [1]. The first FCC unit was commissioned in 1942 at the Esso refinery in Baton Rouge, LA, using powder catalyst that was made to flow like a liquid through fluidization. The world's leading oil-producing and technology companies such as M.W. Kellogg, Standard Oil (Indiana), BP, Royal Dutch/Shell group, Texaco, and UOP undertook this challenging task through a consortium approach employing approximately 1000 scientific and technical personnel. It was the first time in the history of mankind that such large-scale fluidized reactors were built and solids were made to flow like liquid. Since then, technological innovations have continued over the years for improved operation ease, product selectivity, and feed flexibility, thus spreading the scope of this process in a substantial way [2]. Today, petroleum refiners are viewing FCC not as a high-octane gasoline production unit alone but also as a major source for light olefins and petrochemical feedstock production as well as an important option for upgrading resid feeds.

6.3 PROCESS DESCRIPTION

FCC is a selective cracking process for converting high-molecular-weight hydrocarbon molecules, typically gas oil range, into low-molecular-weight compounds using crystalline zeolite, a silica alumina-based catalyst. Figure 6.1, shows the process scheme of a typical FCC plant. Conceptually, the process can be divided into three main sections: the riser-regenerator section, the FCC main fractionator, and the gas concentration unit. The riser-reactor section is the heart of the process where the cracking reactions take place. In this section, gas oil feed streams are converted to gasoline, LPG, cycle oils, gas, and coke. The main fractionator separates the cycle oils and bottoms whereas the offgas, light olefins, and gasoline are separated from unstable gasoline in the gas concentration section.

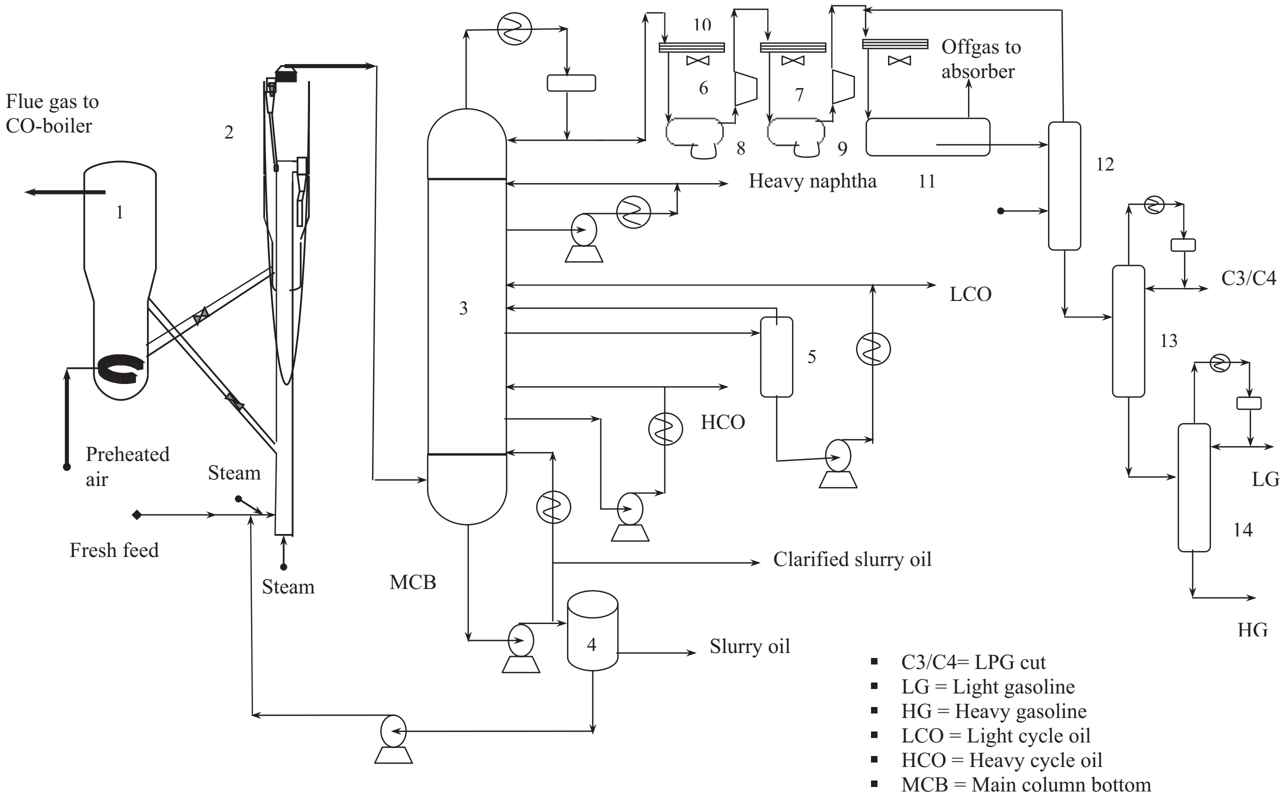
The riser-reactor section consists of three key components: the riser, stripper, and catalyst regenerator. In the riser section, gas oil feed comes in contact with hot regenerated catalyst, feed vaporizes in the first few metres, and concurrently starts cracking as it moves upward along with the catalyst. A substantial amount of enthalpy is consumed from the hot catalyst for feed vaporization and endothermic cracking reactions leading to a drop in temperature and thus reduced cracking severity. The cracking reactions also produce a significant amount of coke, due to which the catalyst loses its activity. Therefore, continuous regeneration of catalyst is vital. The spent catalyst is regenerated by burning the deposited coke in the regenerator. Because of the exothermic heat of coke combustion, the catalyst temperature increases in the regenerator. The enthalpy carried by the hot catalyst is the only source of heat for vaporization and cracking the feed in the riser. Before entering the regenerator, the spent catalyst is efficiently separated from the product stream in the riser termination section and steam is stripped to remove the adsorbed hydrocarbons so that the load on the regenerator is only due to hard coke.

The product stream separated from the catalyst leaves the riser and enters the bottom section of the main fractionator, where it is quenched in the column's bottom circuit producing medium-pressure steam. In the main fractionators, light cycle oil and heavy naphtha are separated as side draws whereas unconverted heavy slurry oil is removed from the bottom. The gas, condensed water, and unstable gasoline are recovered from the column top through a partial condenser. In most applications, the bottom product is used as such except when the catalyst fines content is high, necessitating some type of filtration. The bottom product is used as a cutter for fuel oil production or finds application as carbon black feedstock. The main fractionator bottom temperature is maintained below 370°C to avoid coking while the column top pressure is typically approximately 1.5 bar.

The uncondensed vapor stream mainly contains gas, LPG, and gasoline. The vapors are compressed in a two-stage compressor to a pressure of 15 bar and enter a high-pressure separator (HPS) system. The gases from the HPS are contacted in the primary absorber with unstabilized gasoline and debutanized gasoline to remove the C_3^+ fraction from the C_2^- fraction. The offgases from the primary

---

[1] Bharat Petroleum Corp., Ltd., Greater Noida, India
[2] Hindustan Petroleum Corp., Ltd., Beguluru, India
[3] Guru Gobind Singh Indraprastha University, New Delhi, India



1 = Regenerator, 2 = FCC reactor, 3 = fractionator, 4 = slurry settling drum, 5 = LCO stripper, 6 and 7 = compressor stage I and II, 8 = overhead product collection drum, 9 = interstage collection drum, 10 = air fin cool system, 11 = high-pressure separator, 12 = stripper, 13 = debutanizer, 14 = gasoline splitter.

Figure 6.1—FCC complex configuration including product separation.

absorber are sent to the sponge oil absorber wherein light cycle oil (LCO) is used as absorbing media to remove C_5^+ and LPG from the offgases. The gas with most of the C_3^+ material removed is treated for H_2S removal or sent for further processing before using as fuel gas. The liquid stream from the HPS is fed to a stripper column for the removal of C_2^- and sent back to the HPS. The C_3 and C_4 compounds in the stripper bottoms are separated in a debutanizer column. The stabilized gasoline from the debutanizer bottom, which is free from C_3 and C_4, is sent to further treatment or storage. The FCC main fractionator and gas concentration section designs are more or less the same in almost all FCC units. However, there have been significant differences in the reactor regenerator section, especially with respect to the configurations and integration of various subsystems. These differences are primarily due to different patented licensor designs, product pattern, processing conditions used, and the quality of feeds handled.

6.4 MAJOR REACTIONS

In the FCC riser section, a wide range of complex series and parallel reactions occur, which include primary gas oil cracking reactions and secondary reactions such as hydrogen transfer, isomerization, dehydrogenation, cyclization, etc. [3]. Table 6.1 summarizes the key reactions and the thermodynamic data for a few idealized reactions.

Catalytic cracking chemistry is based on carbenium ion formation, stabilization, and termination. The basic mechanism involves initiation of a charged carbon atom on either a Bronsted or Lewis acid site by protonation or abstraction of hydrogen ion. Propagation then occurs by hydride transfer and cracking by β-scission (cracking at two bonds away from the carbenium ion). Cracking reactions involve C–C bond rupture via formation of carbocations. A scheme for cracking via carbenium ion intermediate is as follows:

1. Initiation (making the carbenium ion)

$$\underset{\text{Olefin}}{\text{R1-CH=CH-R2}} + \underset{\text{Bronsted acid site}}{\text{H}^+} \leftrightarrow \underset{\text{Carbenium ion}}{\text{R1-C}^+\text{H-CH}_2\text{-R2}} \quad (6.1a)$$

$$\underset{\text{Paraffin}}{\text{R1–CH}_2\text{-CH}_2\text{-R2}} - \underset{\text{Lewis acid site}}{\text{H}^-} \leftrightarrow \underset{\text{Carbenium ion}}{\text{R1–C}^+\text{H-CH}_2\text{-R2}} \quad (6.1b)$$

2. Propagation step (hydride transfer)

$$\underset{\text{Carbenium ion}}{\text{R1-CH}_2\text{-C}^+\text{H-R2}} + \underset{\text{Paraffin}}{\text{R3-CH}_2\text{-CH}_2\text{-R4}} \leftrightarrow \underset{\text{Paraffin}}{\text{R1-CH}_2\text{-CH}_2\text{-R2}} + \underset{\text{Carbeniumion}}{\text{R3-CH}_2\text{-CH}^+\text{-R4}} \quad (6.2)$$

3. Cracking step (β-scission)

$$\underset{\text{Carbenium ion}}{\text{R3-CH}_2\text{-CH}^+\text{-R4}} \rightarrow \underset{\text{Carbenium ion}}{\text{R3}^+} + \underset{\text{Olefin}}{\text{CH}_2\text{=CH-R4}} \quad (6.3)$$

TABLE 6.1—Key Reactions and Thermodynamic Data for a Few Idealized Reactions [4] Primary Cracking Reactions

Reaction Class	Reactions	Example	Heat of Reaction Btu/mol (ΔH_R) 950°F
Cracking	Paraffins → Olefin + Paraffin	$n\text{-}C_{10}H_{22} \rightarrow n\text{-}C_7H_{16} + C_3H_6$	32,050
	Olefins → Olefins	$1\text{-}C_8H_{16} \rightarrow 2\text{-}C_4H_8$	33,663
	Naphthene → Olefins		
Dealkylation (cracking)	Alkyl Aromatic → Olefin + Alkyl Aromatic	$iso\text{-}C_3H_7\text{-}C_6H_5 \rightarrow C_6H_6 + C_3H_6$	40,602
Secondary reactions			
Hydrogen transfer	Olefin + Naphthene → Paraffin + Cyclo-Olefin	$2C_6H_{12}+2C_6H_{12} \rightarrow 3C_6H_{14}+C_6H_6$	–109,681
	Carbenium Ion + Paraffin → Paraffin + Carbenium Ion	$RCH^{(+)}CH_2CH_3 + R'CH_2CH_3 \rightarrow$ $RCH_2CH_2CH_3 + R'CH^{(+)}CH_3$	–
	Naphthene + Olefin → Aromatic+ Paraffin	$Cyclo\text{-}C_6H_{12} + C_5H_{10} \rightarrow C_5H_{12} + C_6H_6$	–73,249
Isomerization	n-Olefin → iso-Olefin	$1\text{-}C_4H_8 \rightarrow trans\text{-}2\text{-}C_4H_8$	–4,874
	n-Paraffin → iso- Paraffin	$n\text{-}C_6H_{10} \rightarrow iso\text{-}C_4H_{10}$	–3,420
	Alkyl-o-Aromatics → Alkyl-m-Aromatics	$o\text{-}C_6H_4(CH_3)_2 \rightarrow m\text{-}C_6H_4(CH_3)_2$	–1,310
	Naphthenes → Alkyl Naphthenes	$cyclo\text{-}C_6H_{12} \rightarrow CH_3\text{- } cyclo\text{-}C_5H_9$	6,264
Transalkylation		$C_6H_6+m\text{-}C_6H_4(CH_3)_2 \rightarrow 2C_6H_5CH_3$	–221
Cyclization	Olefin → Naphthenes	$1\text{-}C_7H_{14} \rightarrow CH_3\text{-}cyclo\text{-}C_6H_{11}$	–37,980
Dehydrogenation	Naphthenes → Cyclo Olefins, Aromatics	$n\text{-}C_6H_{14} \rightarrow 1\text{-}C_6H_{12}+H_2$	–
	Aromatics → Multi-Ring Aromatics		–
Polymerization		$3C_2H_4 \rightarrow 1\text{-}C_6H_{12}$	–
Paraffin alkylation		$1\text{-}C_4H_8+iso\text{-}C_4H_{10} \rightarrow iso\text{-}C_8H_{18}$	–

4. Termination (final step)

$$\underset{\text{Carbenium ion}}{\text{R5-CH}_2\text{-CH}^+\text{-R6}} \rightarrow \underset{\text{Olefin}}{\text{R5-CH}_2\text{-CH=CH}_2\text{-R6}} + \underset{\text{Acid site}}{\text{H}^+} \quad (6.4)$$

Primary and secondary carbenium ions tend to rearrange to form a tertiary ion; hence, catalytic cracking leads to formation of more branched compounds. The nature and strength of the catalyst acid sites will influence the degree of occurrence of various reactions. The stability of carbocations depends on the nature of alkyl groups attached to the positive charge. The relative stability of carbenium ions is as follows:

$$\text{Tertiary} > \text{Secondary} > \text{Primary} > \text{Ethyl} > \text{Methyl} \quad (6.5)$$

Catalysts with high acidity are required for enhanced cracking, but they also promote hydrogen transfer reactions. Unfortunately, a hydrogen transfer reaction would lead to lower gasoline octane and higher coke make. For example, rare-earth-exchanged zeolites produce more paraffins and aromatics compared with ultrastabilized zeolite-based catalysts. For maximization of light olefins, catalysts are tailored to minimize the hydrogen transfer reactions. Likewise, temperature has an important role in governing the type of compounds produced. High temperatures encourage more cracking and less hydrogen transfer, because of which the coke production is relatively low. Dealkylation reactions proliferate at high temperatures, producing more aromatics and olefins. Paraffin isomerization with less branching is more favorable under FCC conditions [5].

Thermodynamically, polycondensation reactions are not favored under cracking conditions (i.e., low pressure and high temperature). However, coke is formed through polymerization of unsaturated compounds followed by dehydrogenation by acid hydrogen transfer or catalyzed by metallic impurities. Other pathways suggested were alkylation of aromatics followed by cyclization or condensation of olefins and diolefins and subsequent dehydrogenation. Although there are quite a few exothermic reactions in FCC, because of the predominance of cracking and dealkylation reactions, the net reactions are endothermic. Further, catalysts with less hydrogen transfer activity will cause the net heat of reaction to be more endothermic, requiring higher amounts of catalyst circulation. Thus, temperature and type of catalyst have a significant effect on the product yield pattern and FCC heat balance.

6.4.1 Kinetics of Catalytic Cracking and Coke Combustion Reactions

FCC feed consists of a wide boiling mixture of heavy-hydrocarbon molecules, the reactivities of which differ considerably according to individual hydrocarbon type and molecular weight. Naphthenes and paraffins have a higher cracking tendency over aromatics, whereas heavier molecules crack faster than the lighter ones. The cracking reactions of FCC feed, which consists of diverse compounds, follow pseudo second-order kinetics. This is because the feed becomes progressively difficult to crack with increasing conversion levels. For plug flow systems, the conversion severity relation can be modeled through Eq 6.6 [6,7]. The feed crackability increases with the increase of nonaromatic content and increasing size of the hydrocarbon chain (N_c), whereas feed nitrogen compounds (N_N) inhibit the cracking.

$$\frac{X}{100-X} WHSV = kC(catalyst\ type)F(feed\ crackability) \exp\left(-\frac{E}{RT}\right) t_c^m \tag{6.6}$$

$$F(feed\ crackability) = w_1(N_C - N_C C_A) + w_2 N_N + w_3 \tag{6.7}$$

where:

X = weight percentage conversion (total yields of liquid fraction boiling below 221°C, coke and gas products);

$WHSV$ = weight hourly space velocity (h^{-1});

k = kinetic constant (h^{-1});

t_c = catalyst residence time (h);

E = activation energy (kJ);

T = average temperature (K);

N_C = carbon number of the average hydrocarbon molecule;

N_N = number of nitrogen atoms in the average hydrocarbon molecule;

C_A = aromatic carbon content;

C and F = functions of catalyst and feed properties, respectively; and

m, w_1, w_2, and w_3 = correlation constants.

6.4.1.1 COKE

The coke yield of an FCC unit is primarily a function of conversion, temperature, and feedstock characteristics and can be correlated to second-order conversion as shown in Figure 6.2. Through extensive studies, Voorhies [8] suggested that coke on catalyst (C_C) is primarily influenced by the exposure time (T_c) and can be related through a nonlinear relationship,

$$Cc = A \cdot T_c^n \tag{6.8}$$

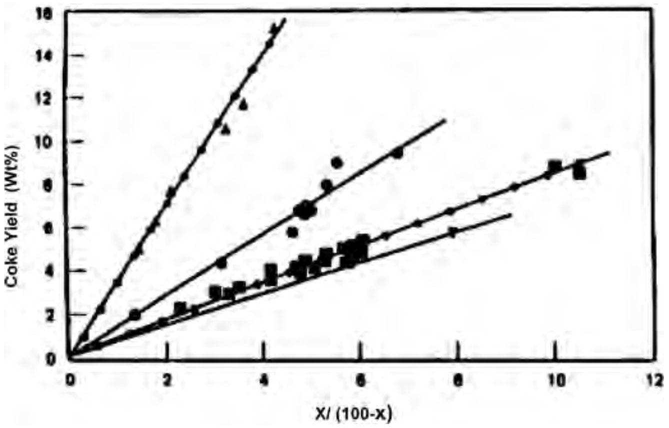


Figure 6.2—Coke yield vs. second-order conversion with different feedstocks [9]. *Source:* Figure used with permission from Exxon Mobil.

in which A is a function of feed quality and n is a constant dependent on the type of catalyst. Zeolite-rich catalysts typically yield more coke initially (lower n value) compared with amorphous-rich catalysts. After a certain cross-over contact time, the amorphous-rich catalyst coke will continue to increase whereas the zeolite catalyst coke value tapers off. Hence, while comparing the commercial plant coke yields with small-scale microreactors such as a microactivity test (MAT) unit, it is important to match the commercial plant contact times in the microreactor to have realistic coke yields.

It may be noticed from Eqs 6.6 and 6.8 that for a given feed and catalyst, the second-order conversion and the coke yields are only functions of catalyst residence time. Therefore, at constant catalyst residence time, a linear relation is expected among coke yield and second-order conversion [9,10]. Bollas et al. [7] proposed an equation for coke yield (u_x) similar to Eq 6.6 with a different activation energy (E_u) and coefficient (n_u) for catalyst residence time:

$$u_x WHSV = k_u C_u(catalyst\ type) F_u(feed\ coking\ tendency) \exp\left(-\frac{E_u}{RT}\right) t^{n_u} \tag{6.9}$$

6.4.1.2 GASOLINE

The gasoline yield is a nonlinear function of conversion. The yield increases with conversion and reaches a maximum after which the yield reduces because of gasoline overcracking (Figure 6.3). The maximum gasoline yield is a function of reactor operational severity, catalyst, and feedstock. Among saturates, naphthenic feeds are the most preferred for gasoline production. By hydrogen transfer reactions, a large proportion of naphthenes are converted into monoaromatics, thus enhancing the octane. In contrast, paraffin-rich feeds produce more LPG and low-octane straight-chain paraffins.

The gasoline yield is also affected by the ZSM-5 content in the catalyst. ZSM-5 selectively cracks the low-octane

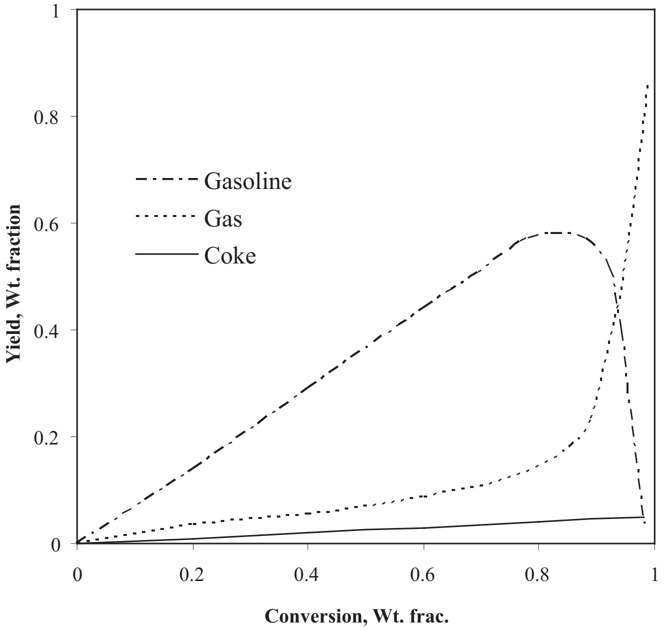
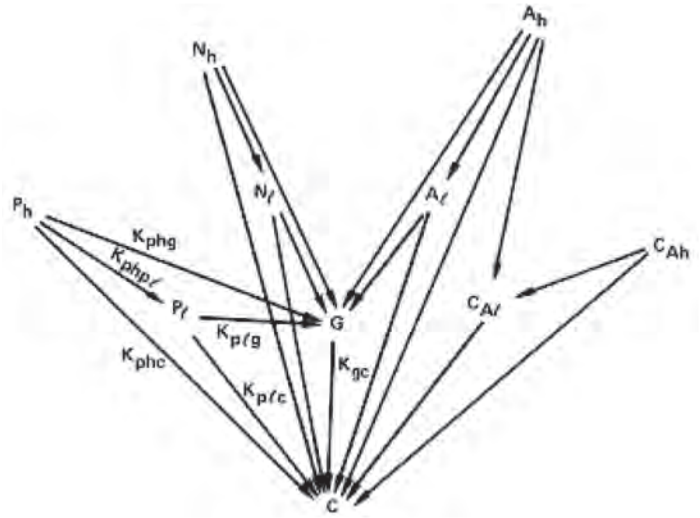


Figure 6.3—Gasoline, coke, and gas yield vs. conversion [11].



P_l = Wt. % paraffinic molecules, (mass spec analysis), 430–650°F
N_l = Wt % naphthenic molecules, (mass spec analysis), 430–650°F
C_{Al} = Wt. % carbon atoms among aromatic rings, (n-d-M method), 430–650°F
A_l = Wt. % aromatic substituent groups (430–65O°F)
P_l = Wt. % paraffinic molecules, (mass spec analysis), 65O°F+
N_h = Wt. % naphthenic molecules, (mass spec analysis), 650°F+
C_{Ah} = Wt. % carbon atoms among aromatic rings. (n-d-M method), 650°F+
A_h = Wt. % aromatic substituent groups (650°F+)
G = Glump (C5–430°F)
C = Clump (C, to C4 + COKE)
$C_{Al} + P_l + N_l + A_l$ = LFO (430–650°F)
$C_{Ah} + P_h + N_h + A_h$ = HFO (650°F)

Figure 6.4—Ten-lump kinetic model of Jacob et al. [12]. *Source:* Figure used with permission from Exxon Mobil.

straight-chain paraffins and olefins into LPG. The LPG yield increases linearly with ZSM-5 content in the catalyst. The combined yields of gasoline and LPG increase almost linearly with conversion.

6.4.1.3 GAS

FCC dry gas is primarily produced because of thermal cracking of the feed and nonselective catalytic cracking; hence, the yields are mainly affected by riser temperatures and feed residence time. Minimizing the residence time helps in substantially reducing the gas yields. The metal content on the catalyst also contributes significantly to the gas and coke production through dehydrogenation reactions.

Rigorous kinetic models attempt to model the cracking reactions in a more detailed manner through a lumping approach that is based on detailed feed characteristics. Figure 6.4 shows the ten-lump model of Jacob et al. [12]. Considering kinetics and reactor hydrodynamics, these rigorous models more accurately predict the FCC yields when tuned with sufficient experimental data and are very useful in tracking the effect of operating parameters or feed changes.

6.4.1.4 KINETICS OF COKE COMBUSTION

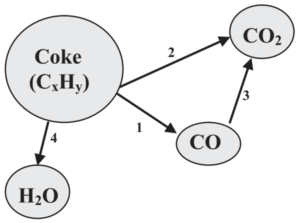
The coke burning kinetics are relatively less complex. There are four (I to IV) key reactions that occur during coke burning (Figure 6.5). Coke burning kinetics are first order with respect to oxygen concentration and coke content on catalyst (reaction I and II of Figure 6.5). During combustion, carbon monoxide (CO) and carbon dioxide (CO_2) are produced at the catalyst surface, and their distribution is given by Eqs 6.10, 6.11, and 6.12 [10,13].

$$-\frac{dC}{dt} = r_1 + r_2 = k_{c0}\exp\left(\frac{-E_c}{RT}\right)\rho_c(1-\varepsilon)CP_{O_2} \tag{6.10}$$

$$\left.\frac{CO}{CO_2}\right|_{surface} = \frac{k_1}{k_2} = \beta_{co}\exp\left(\frac{E_\beta}{RT}\right) \tag{6.11}$$

$$k_c = k_1 + k_{2,} \quad k_1 = \frac{\beta_c k_c}{\beta_c + 1}, \quad k_2 = \frac{k_c}{\beta_c + 1} \tag{6.12}$$

Hydrogen combustion can be assumed to be instantaneous (reaction IV of Figure 6.5), whereas combustion of CO can occur on the catalyst surface and in the homogenous gas phase (i.e., within the void volume). CO conversion is a free radical reaction and hence its combustion rate is relatively slower in the presence of surfaces such as catalyst. The degree of inhibition is a function of temperature, catalyst size, and concentration [10]. Once the catalyst is removed (in cyclones), if excess oxygen (O_2) is present, CO ignition takes place. This effect is known as "afterburn" and is important to control because high temperatures



$$
\begin{array}{llll}
I: & C + 0.5O_2 & \xrightarrow{k_1} & CO \\
II: & C + O_2 & \xrightarrow{k_2} & CO_2 \\
III_c: & CO + 0.5O_2 & \xrightarrow{k_{3c}} & CO_2 \\
III_h: & CO + 0.5O_2 & \xrightarrow{k_{3h}} & CO_2 \\
IV: & H_2 + 0.5O_2 & \xrightarrow{k_4} & H_2O
\end{array}
$$

Figure 6.5—Key reactions of coke burning.

can damage the cyclones. To enhance the CO burning within the dense catalyst bed, CO combustion promoters are added. The effect of CO combustion promoters can be accounted for through k_{3h} as shown in Eq 6.13. The net CO and CO_2 production can be estimated by simultaneously solving Eqs 6.10–6.13.

$$r_3 = \left[k_{3c0}\exp\left(\frac{-E_{3c}}{RT}\right)\rho_c(1-\varepsilon) + k_{3h0}\exp\left(\frac{-E_{3h}}{RT}\right)\varepsilon\right]CP_{O_2}P_{CO} \tag{6.13}$$

where:
C = coke on the catalyst, (weight coke/weight catalyst);
P_{O2} and P_{CO} = partial pressures of O_2 and CO, respectively (Pa);
k_c = total coke combustion rate constant (1/Pa·s);
k_1 and k_2 = coke combustion reaction rate constants in reactions I and II, respectively (Figure 6.5);
$\in$ = regenerator bed porosity;
ρ_c = catalyst density (kg/m^3);
β_c = CO/CO_2 ratio at the catalyst surface;
k_{c0} and β_{c0} = pre-exponent constants for k_c and β_c, respectively;
k_{3c0} = pre-exponent constant for catalytic combustion in reaction III_c;
k_{3h0} = pre-exponent constant for homogenous combustion in reaction III_h; and
E_c, E_β, E_{3c}, and E_{3h} = activation energies corresponding to equations (kJ/K) (6.10–6.13).

The coke combustion kinetic parameters are a function of the catalyst properties and remain constant as long as equilibrium catalyst properties (apparent bulk density [ABD], pore volume, surface area, and fines content) are relatively constant [14].

6.5 FEED, PRODUCT QUALITY, AND OPERATING CONDITIONS

FCC can handle various feedstocks, such as straight-run and VGO streams, hydrotreated VGO, solvent deasphalted oil, coker gas oil, portions of atmospheric or vacuum column bottoms, and other heavy materials. The typical FCC feed boiling range is from 350 to 580°C, and densities are normally greater than 0.87. Table 6.2 presents some of the FCC feeds processed in industry.

Lower feed density values indicate a higher degree of hydrocarbon saturation and hydrogen content. The product yields and product quality of an FCC unit are directly related to the feed hydrogen content. Hydrogen-rich paraffins and naphthenes produce more gasoline compared with aromatic feeds, which are difficult to crack. Figure 6.6 shows the feed conversions with variations in feed density [15] along with the potential conversion values. Potential conversions were calculated based on the paraffin and naphthene content of the feed. The actual conversions are

TABLE 6.2—Typical FCC Feedstocks Processed in Industry

	Nigerian VGO	Mumbai VGO	Hydrotreated VGO
Density, kg/L	0.9265	0.8811	0.8524
Sulfur, % wt	0.37	0.58	0.015
Total nitrogen % wt	0.1413	0.0726	0.0037
Conradson carbon, % wt	0.4	0.49	0.03
Nickel (Ni) (ppm wt)	0.55	0.53	—
Vanadium (V) (ppm wt)	0.08	0.32	—
Sodium (Na) content (ppm wt)	0.33	0.24	—
Distillation D-1160 (°C)			
5 %	370	372	358
30 %	403	419	407
50 %	438	442	427
95 %	539	552	506
Final boiling point (FBP)	572	581	530

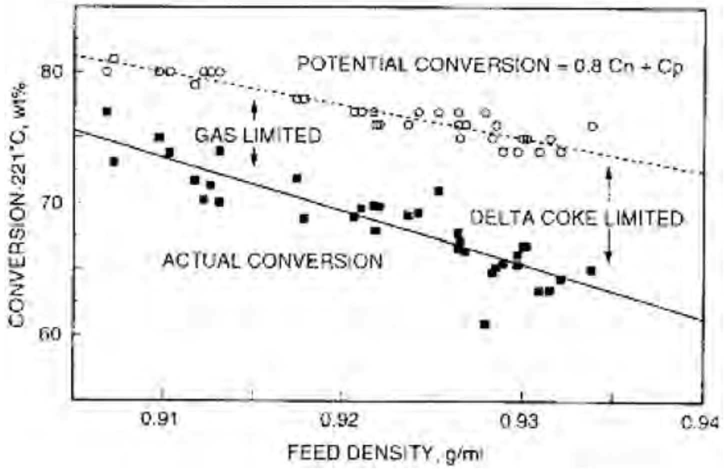


Figure 6.6—Conversion variation with changes in feed density. *Source:* Reproduced with permission from [14].

lower than the potential figures because of limitations of either air blower or gas compressor capacity. In addition to feed density, aniline point and refractive index are also commonly used to assess the feed aromaticity and they correlate well with feed conversion. Aniline point increases with paraffin content, whereas aromatics will have a lower value [16]. Likewise, the refractive index increases with increase in aromaticity [17].

Aromatic-rich feeds produce less gasoline and yield more LCO and coke. The LCO is of poor quality, whereas the gasoline octane is high because of high aromatics. Figure 6.7 shows the pilot plant data of Bollas et al., in which the crackability and coke selectivity exhibited strong correlation with feed aromaticity. When the feed boiling ranges differ widely, correlations based on UOP or Watson K factor, calculated from average boiling point and density, or PONA content are expected to be more accurate [15].

Higher feed distillation temperatures and Conradson carbon (CCR) content indicate the presence of residue, metals, and asphaltene in the feed. Handling high-CCR feeds is difficult because they tend to produce more coke, leading to higher regenerator temperatures, which limits their processability. Because of their high viscosity and high boiling points, heavy hydrocarbons pose a challenging task of vaporization at the riser entry and significantly affect the yield pattern. Further, heavier feeds also contain a higher level of metals, which require more catalyst per barrel of feed to compensate for the metal deactivation. Therefore, beyond a point (>10 wt %), it is uneconomical to process high-CCR feeds and hence feed should be pretreated to reduce the CCR content (e.g., by hydroprocessing or solvent deasphalting).

Another important feed property that affects the feed crackability is organic nitrogen, especially basic nitrogen content, which has a detrimental effect on zeolite by temporarily inhibiting the acid sites of the catalyst. The activity is regained by burning the nitrogen in the regenerator. To overcome the nitrogen inhibition, higher catalyst activity and catalyst-to-oil ratio are needed.

Hydrotreating is a useful option for reducing nitrogen inhibition and metal deactivation as well as for improving product quality. The yields of aromatic-rich feedstocks can be substantially improved by subjecting them to either mild hydrotreating or hydrocracking upstream and integrating with FCC. The key benefits of feed hydroprocessing are higher gasoline yields, lower coke and gas make, and improved quality of distillates (w.r.t. sulfur content and LCO cetane). Sulfur is not inhibitory to the catalyst. However, its removal helps in meeting the product quality on most occasions without further treatment and also helps in reducing sulfur oxide (SO_x) and nitrogen oxide (NO_x) emissions. The benefits due to feed hydrotreatment for improving yield and quality can be seen in the data presented in Table 6.3 [18].

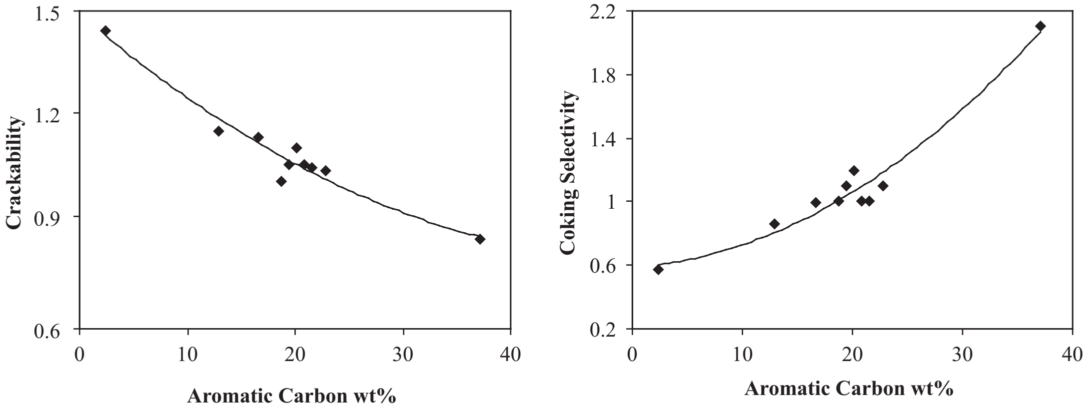


Figure 6.7—Crackability and coking tendency dependency on feed aromatic content. *Source:* Reproduced with permission from [7].

TABLE 6.3—Benefits of Hydrotreating on FCC Yields [18]

	Untreated Feed	Hydrotreated Feed
Conversion, vol %	55.9	74.8
Gasoline, vol %	39.6	55.1
LCO, vol %	26.3	17.3
Decant oil, vol %	17.8	7.9
Sulfur in products		
Gasoline	0.303	0.002
LCO	2.38	0.09
Decant oil	3.25	0.23
SO_x emission, kg/m^3 of feed	1.3	0.09

Although FCC feed hydrotreatment offers excellent benefits in the form of improved product quality and yields, excessive treatment beyond the optimum does not always correspond with higher gasoline yields. A study by UOP [19] suggests that the optimal feed hydrogen content should be between 12.3 and 12.5 wt %. Beyond this, more naphthenes and paraffins are produced in the feed, which leads to higher LPG, gas make, and reduced gasoline yields with lower octane.

6.6 MODES OF FCC OPERATION

In addition to feed flexibility, the FCC process also offers versatility with respect to product slate. By appropriate selection of catalyst and process conditions, FCC can be operated to maximize middle distillates, gasoline, or light olefins [20]. Diesel or middle-distillate mode is characterized by lower operational severity with milder temperature and catalyst-to-oil ratios. In this mode of operation, to maximize the bottoms conversion, recycling of heavy cycle oil is usually practiced. Intermediate temperatures, higher catalyst-to-oil ratios, and higher catalyst activity are associated with the gasoline mode of operation. In light olefins or the LPG mode of operation, reactor temperatures are usually maintained above 540°C and higher catalyst-to-oil ratios are preferred. The liquid products in this mode are highly aromatic, and in some units the propylene yield could be as high as 20 % [21,22]. Table 6.4A presents the typical operating conditions and product yields obtained with a Middle Eastern VGO.

TABLE 6.4A—Operating Conditions, Product Yields, and Properties with Different Modes of FCC Operation [20]

	Middle Distillate Mode	Gasoline Mode	Light Olefins Mode
Operating conditions			
Temperature (°C)	449–510	527–538	538–560
Catalyst to oil	<Base	Base	>Base
Recycle, CFR	1.4 (HCO)	optional (HDT LCO)	optional (HN)
Product yields			
H_2S wt %	0.7	1.0	1.0
C2-, wt %	2.6	3.2	4.7
C3, LV %	6.9	10.7	16.1
C4, LV %	9.8	15.4	20.5
C5+ gasoline, LV %	43.4	60.0	55.2
LCO, LV %	37.5	13.9	10.1
HCO, LV %	7.6	9.2	7.0
Coke, wt %	4.9	5.0	6.4
Product properties			
LPG, vol/vol			
C3 olefins/saturates	3.4	3.2	3.6
C4 olefins/saturates	1.6	1.8	2.1
Gasoline			
ASTM 90 % point, °C	193	193	193
ASTM 90 % point, °F	380	380	380
Research octane number clear (RONC)	90.5	93.2	94.8
Motor octane number clear (MONC)	78.8	80.4	82.1
LCO			
ASTM 90 % point, °C	350	316	316
ASTM 90 % point, °F	670	600	600
Flash point °C (°F)	97 (207)	97 (207)	97 (207)
Viscosity, cSt at 500 °C (1220°F)	3.7	3.1	3.2
Sulfur, wt %	2.9	3.4	3.7
Cetane index	34.3	24.3	20.6
Clarified oil			
Viscosity, cSt at 1000°C (2100°F)	10.9	9.0	10.1
Sulfur, wt %	5.1	6.0	6.8

TABLE 6.4B—Operating Conditions and Product Yields with Two Different Modes of DCC Operation [23]

	Type I	Type II
Operating conditions		
Temperature (°C)	530–575	505–555
Catalyst to oil (w/w)	8–15	7–12
Steam dilution rate, wt % of feed	20–30	10–15
Type of cracking	Riser and bed	Riser
Material balance, wt %		
C2-	11.9	5.6
C3 and C4 LPG	42.2	34.5
Naphtha	26.6	39.0
LCO	6.6	9.8
DO	6.1	5.8
Coke	6.0	4.3
Loss	0.6	1.0
Total	100.0	100.0
Light olefin yield, wt %		
Ethylene	6.1	2.3
Propylene	21.0	14.3
Butylene	14.3	14.7
In which isobutylene	5.1	6.1
Amylene	–	9.8
In which isoamylene	–	6.8

Feed: waxy Chinese VGO pilot plant data

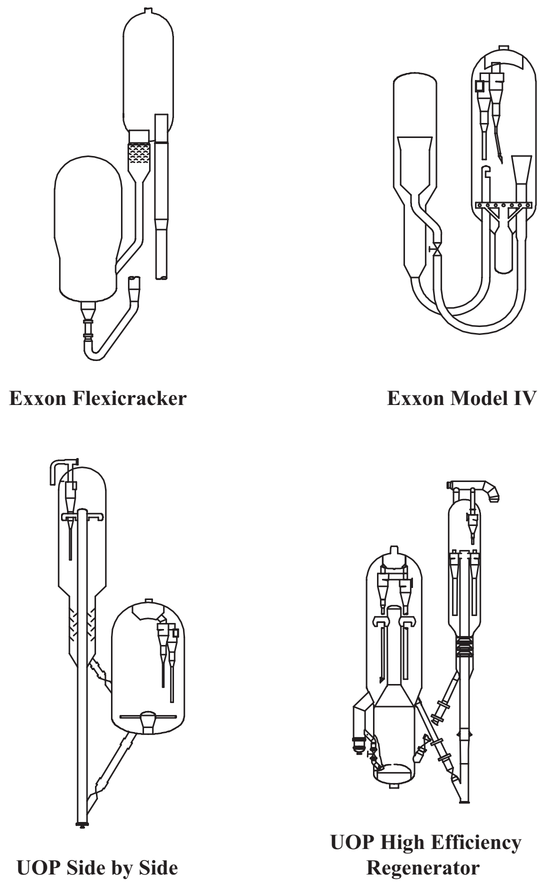
Over the past few years, the light-olefin mode of operation has gained major importance because of the growing demand for propylene. The key advantages of producing propylene through the FCC route are the higher ratio of propylene-to-ethylene yields and relatively less severe operating conditions compared with steam cracking. Almost all major licensors offer light-olefin production technology through their patented processes [21,22,24,25]. Table 6.4B presents the yields and operating conditions with the two different modes of deep catalytic cracking (DCC) operation of Shaw through maximum propylene or high-severity operation (type I) and maximum iso-olefin or lower severity operation (type II) [23]. Because a significant amount of ethylene is also produced in olefin mode, the option of recovering ethylene is worth examining.

FCC LPG is a rich source for other light olefins such as butylenes and amylene and hence is an ideal feedstock for methyl tertiary butyl ether (MTBE)/tert-amyl methyl ether (TAME) or alkylation. The ratio of isobutylene to total butylenes is much higher in olefin-mode operation compared with gasoline mode. Because of the high conversion, all of the C_5^+ liquid products are highly aromatic and the naphtha is octane rich. The BTX content of the naphtha is over 25 wt %, making it suitable for extraction [26]. The di-olefins in naphtha need to be selectively hydrotreated to improve its stability. The cycle oil from FCC, particularly in olefin mode, is low in cetane and hence it needs further upgradation for blending in a diesel pool. Alternatively, it can be used as an excellent cutter stock because of its low viscosity and pour point. The heavy cycle oil (HCO) and small amounts of slurry oil can go directly to fuel oil blending, or the slurry oil can be used as carbon black feedstock (CBFS).

6.7 COMMERCIAL FCC DESIGNS

Subsequent to the first commercial operation of an FCC unit in 1942, the original design has undergone several changes. Availability of highly active catalysts, demand for higher feed capacities, improved yields, product selectivity, changes in feed quality, operational ease, reliability, and longer cycle lengths are some of the key drivers for these changes. Nevertheless, in all of these designs, the basic function of the FCC components such as reactor, stripper, regenerator, and transfer lines, etc., remain the same.

Among the new designs, the most popular ones are UOP's side-by-side configuration, KBR's Orthoflow™, Exxon's flexicracker unit, Shaw/Axens's two-stage regeneration unit, etc. Figures 6.8 and 6.9 present the schematics of some of these designs. Each of these designs incorporates their proprietary know-how and brings in their own strengths and weaknesses. Nevertheless, there have been many engineering advancements in these designs from the point of view of basic reaction engineering, heat and mass transfer, and fluid mechanics. Some of the recent developments include high-efficiency feed nozzles for improved feed vaporization, short contact time reactors for better yield and selectivities, catalyst coolers and riser quench for handling excess heat with residue feedstocks, two-stage regenerators for reduced deactivation and improved regeneration, improved stand pipe design/operation for higher catalyst circulation, etc. [21,22,24,25,27–29]. The following sections cover some of these engineering and design aspects


Exxon Flexicracker

Exxon Model IV

UOP Side by Side

UOP High Efficiency Regenerator

Figure 6.8—Some commercial FCC configurations. *Source:* Reproduced with permission from Exxon Mobil and UOP.

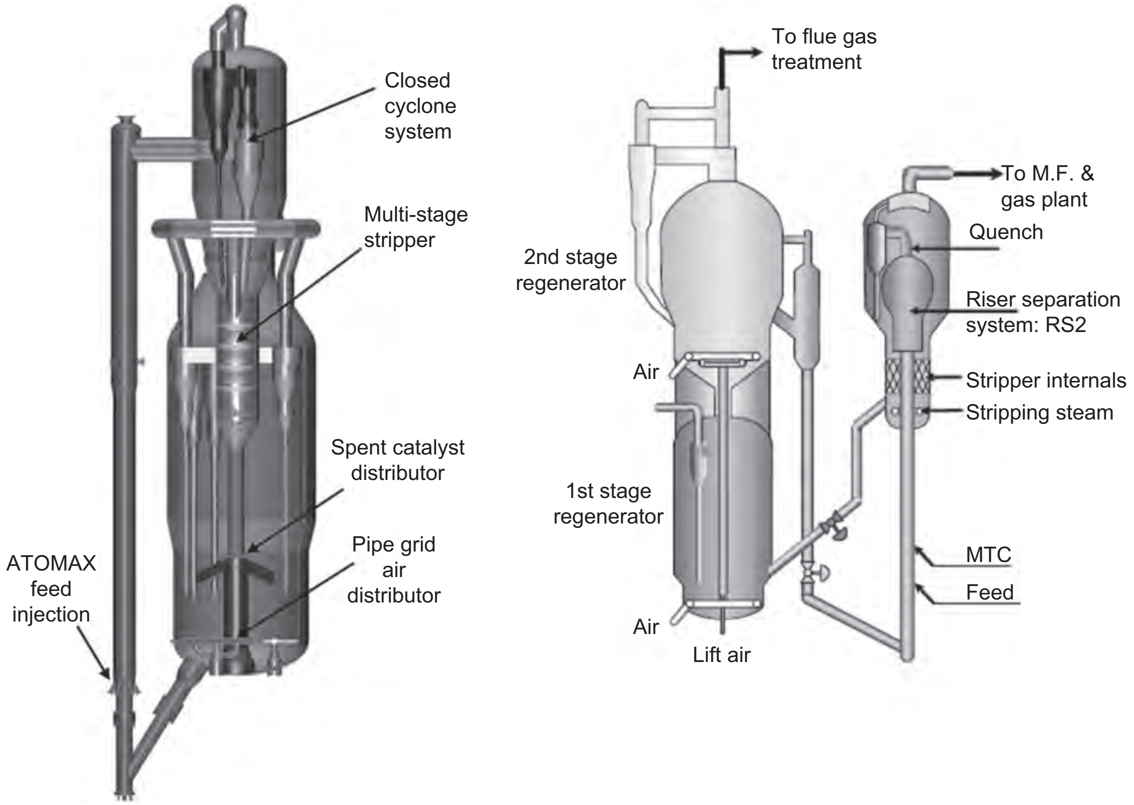


Figure 6.9—KBR FCC configuration (courtesy KBR Inc.) (left) and Shaw & Axens configuration (right). *Source:* Reprinted with permission from *Hydrocarbon Processing*, by Gulf Publishing Co., © 2005; all rights reserved.

in detail. Useful guidelines for FCC hardware design are given in Table 6.5.

6.7.1 FCC Riser

It is well known from basic reaction engineering principles that to maximize intermediates, plug flow configuration is the optimal choice [30]. VGO cracking reactions being consecutive, the plug flow scheme is ideal for maximal yields of gasoline at a given conversion. Back-mixing of the gasoline leads to higher LPG yields because of overcracking. Fortunately, the advent of highly active zeolite catalysts also helped in moving toward dilute phase, plug flow, all-riser cracking from early dense bed cracking.

Catalyst residence time, which depends on catalyst hold up and circulation rates, is another important factor in FCC design. Lower catalyst residence times are preferred because they produce substantially reduced coke make for a given hydrocarbon flow [8,31]. In plug flow reactors, the catalyst hold up time is dependent on slip factor (ratio of gas to catalyst velocity). The following equation can be used for estimating catalyst hold up in any section of the riser [4]:

$$dH = \frac{(CCR)(SF)dL}{60V} \tag{6.14}$$

where:
H = catalyst hold up (t),
CCR = catalyst circulation rate (t/min),
SF = slip factor,
L = length (m), and
V = vapor velocity (m/s).

Higher slip factors would lead to higher catalyst hold up and hence coke make. In straight FCC risers the slip factors typically range from 1.5 to 2. The slip factors are high in the feed vaporization zone in various bends, slopes, and curves. When operating conditions are not widely different, lower catalyst-to-oil ratios give lower slip factors.

Curves and bends promote uneven distribution of catalyst, poor oil contact across the horizontal cross section, and catalyst maldistribution to the riser termination device. In FCC, the base of the wye section is highly turbulent as the regenerator catalyst flow changes its direction. Therefore, elevated nozzles are recommended so that the liquid spray can come in contact with the hot catalyst, the radial density profile of which is uniform. Modern FCC units are designed for all-riser cracking with reduced back-mixing. This is accomplished through efficient feed injection and vaporization at the riser entry zone and rapid separation of catalyst and product at the riser exit. The all-riser cracking maximizes the gasoline yield and eliminates secondary dilute-phase cracking and postriser thermal cracking. Short contact time reactors with all-riser cracking and cracking temperatures above 530°C are now common to produce high-octane gasoline and light olefins [32].

6.7.2 Feed Nozzles

An efficient feed injection system helps in the rapid vaporization of feed and simultaneously quenches the hot regenerated catalyst. Faster feed vaporization results in reduced liquid-phase cracking, hot spots, catalyst slip, and back-mixing, leading to less coke and dry gas make [33]. In an ideal scenario, the cracking should only take place in the

TABLE 6.5—Useful Guidelines for FCC Hardware Design [34]

Stand pipe	• Minimum catalyst flux: 100 lb/ft^2·s • Maximum catalyst flux: 300 lb/ft^2·s • Typical flux: 150–250 lb/ft^2·s • Orientation: Vertical or not more than 35° to vertical • Aeration: 20–25 SCF/t of catalyst per 100-ft vertical drop
Controlling catalyst slide valve	• 2 psi minimum for control • 15 psi maximum for wear • 25–75 % open for control • Design for ~7 psi and 50 % open • Slide valve port area ~0.25–0.45 of stand pipe area
Riser	• Minimum velocity for vertical spent catalyst riser: 8–10 ft/s • Minimum velocity for vertical feed riser: 15–20 ft/s (at bottom) • Maximum riser velocity: 90 ft/s (for wear) • Typical feed riser exit velocity: 50–70 ft/s • Feed riser residence time: 1.8–2.4 s (based on outlet moles) • Feed riser L/D: at least 20 preferred • Feed riser turndowns: 80–95 % separation efficiency
Feed nozzle	• L/D : 3–10 • Steam flow rate: 3–5 wt % of feed (depends on feed properties) • Nozzle tip: depends on type of feed distribution and yield pattern required (generally pattern of distribution is hollow cones or flat sprays)
Reactor vessels	• Maximum operating velocity: 3.5 ft/s (with efficient cyclones) • Typical operating velocities: 2–3 ft/s • Disengaging height (riser turndown to cyclone inlet): 15 ft minimum
Stripper	• Superficial steam velocity: 0.5–1 ft/s • Typical steam rates: 2-4 lb of steam per 1000 lb of catalyst • Typical operating velocities: 0.5–1 ft/s • Typical catalyst residence time: 60–90 s • Typical catalyst flux: 1200 lb/ft^2·min • Stripper L/D: at least 1 • Free area between baffles: 45–55 % of stripper area • Unbaffled strippers not recommended if stripper steam efficiency a concern

Regenerator vessels	• Maximum operating velocity: 3.3 ft/s
	• Typical operating velocity: 2-3 ft/s
	  • 3.5–5.5 ft/s(UOP high efficiency)
	• Catalyst residence time: 5–10 min (one-stage regeneration)
	  • 1 min (UOP high efficiency)
	  • 3–5 min (each stage is two-stage design)
	• Bed L/D: 0.3–0.7 in conventional designs
	• Disengaging height: 18–20 ft (bed surface cyclone inlet in conventional design)
	• Grid pressure drop: typical 1–2 psi, at least 30 % bed head
	• Minimum grid pressure drop: 0.7–0.8 psi

Cyclones	• Reactor 1 stage design: typical collection efficiency: 99.995 %
	• Typical pressure drop: 0.5–0.7 psi
	• Inlet catalyst loading ~0.25–0.5 lb/ft^3
	• Regenerator 2 stage design: typical overall collection efficiency: 99.998 %
	• Typical pressure drop: 1 psi
	• Inlet velocities (ft/s):
	  • Riser cyclones: 60–70
	  • Reactor cyclones: 60–80
	  • Regenerator first stage 60–80
	  • Regenerator second stage 75–85
	• Outlet velocities (ft/s):
	  • Riser cyclones: 70–80
	  • Reactor cyclones: 80–100
	  • Regenerator first stage 70–80
	  • Regenerator second stage 100–200
	• Dipleg mass velocities (lb/ft^2·s): 120–130

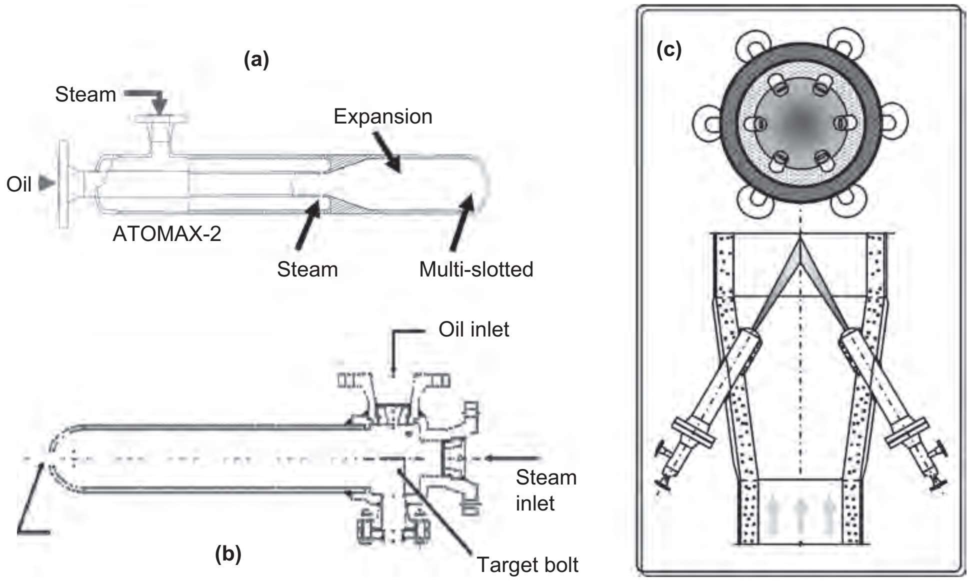


Figure 6.10—Schematic of FCC nozzles [Kellogg (a), Shaw (b)] and their arrangement in riser (c). ATOMAX is a trademark of M.W. Kellogg. *Source:* Figure used courtesy of KBR Inc., and Axens and Shaw.

vapor phase, and modern nozzles attempt to achieve this target. In these nozzles, oil is atomized into fine droplets of narrow size distribution and then distributed uniformly over the riser cross section for intimate contact with the catalyst. The key liquid-phase variables that affect the vaporization are droplet size, liquid flux and spray pattern, and penetration into the flowing catalyst. Catalyst-phase variables include temperature, velocity, density, and distribution [2].

FCC nozzles are designed, through extensive cold flow testing, to produce a flat fan spray pattern of liquid feed distribution with small droplets of narrow size. Figure 6.10 shows the schematics of a few commercially available FCC feed nozzles.

In Shaw/Axens's feed injectors, the oil inlet orifice directs a high-velocity jet of oil onto a target bolt. Steam enters the nozzle at high velocity and shears the oil droplets formed on the target. It is claimed that the oil then filaments and further atomizes as it passes down the barrel of the nozzle and is then shaped into a fan spray pattern at the tip. The optimal use of atomization steam and feed oil pressure drop to achieve fine atomization depends on the type of feedstock. In Kellogg's atomization nozzle ATOMAX™, most of the mixing energy comes from medium-pressure steam. Likewise, the Lummus Micro-Jet™ and UOP Optimix™ also uses steam energy for shearing the oil and atomization [14]. It was suggested that atomization closer to the nozzle tip is important for flat plane contacting and reduced re-coalescence. An improved mixing chamber through proprietary internals, tip design, and nozzle orientation are key technology aspects. Lower oil-side pressure drop and the independent control of steam flow are claimed to be some of the advantages of these nozzles. The typical steam dispersion rates reported for Optimix nozzles were 1–2 wt %, and the pressure drops range from 30 to 60 psi [2].

To uniformly cover the riser radial cross section, multiple feed nozzles are used. Further segregated feed injection systems are also practiced to create a more severe cracking atmosphere while processing heavy feeds. In this scheme, the riser is separated into two zones where a part of the fresh feed or quench stream is injected at higher elevation so that high mix zone temperature and catalyst-to-oil ratio are achieved at the bottom. Such designs allow independent control of mix temperature without any metallurgical constraints from the reactor [29]. Riser quench acts as a heat sink and is similar to a catalyst cooler; however, it increases load on the downstream section.

6.7.3 Riser Termination Device

Disengaging designs were previously used to separate the riser product stream from the spent catalyst through inertial separation devices or rough-cut cyclones. The key disadvantages of such systems were longer hydrocarbon residence time in the dilute phase and higher back-mixing, thus promoting undesirable secondary cracking reactions and thermal cracking, leading to higher coke and gas make. However, some key advantages of such designs were operational simplicity and the absence of dead pockets, which prevents coke formation on reactor walls, etc. [35]. Modern riser termination devices ensure smooth separation of the catalyst from the product stream without disturbing the plug flow to a great extent and directing hydrocarbons more efficiently toward the reactor plenum, thus producing less coke and gas make, as shown in Figure 6.11 [36].

The close coupled cyclones of Lummus and Kellogg, the Vortex Separation System (VSS™) of UOP, and the Riser Separation System or RS^{2SM} design of Axens and Shaw are some of the new disengaging devices. In close coupled systems, the catalyst and hydrocarbons enter directly into the cyclone and the hydrocarbons are efficiently separated from the spent catalyst, thus drastically reducing the hydrocarbon leakage into the dilute phase (Figure 6.12). The cyclone can operate under positive or negative pressure relative to the reactor free board pressure (i.e., dilute bed). The close coupled cyclones can reduce the hydrocarbon residence time to as low as 2 s. The negative pressure

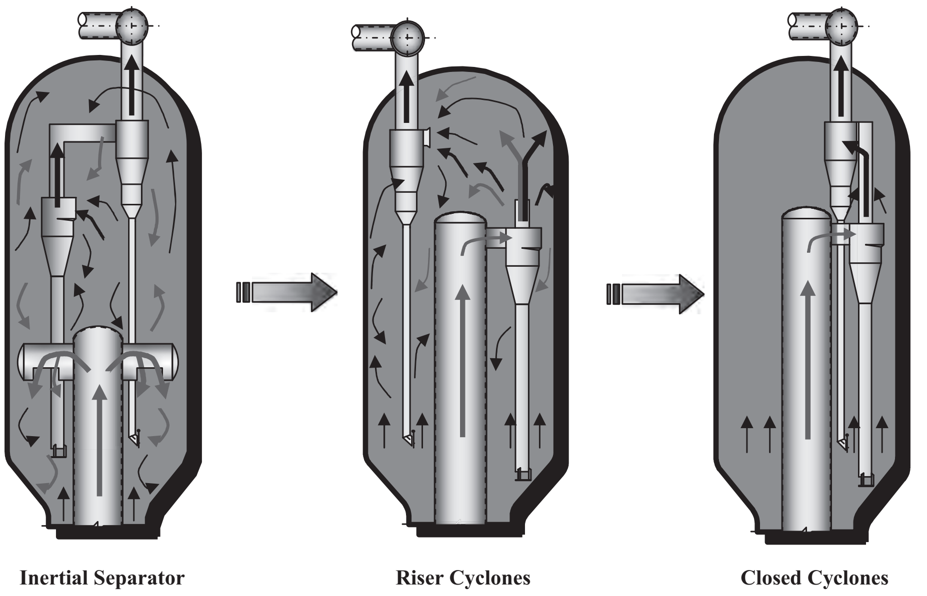


Figure 6.11—Evolution of riser termination designs. *Source:* Figure used courtesy of KBR, Inc.

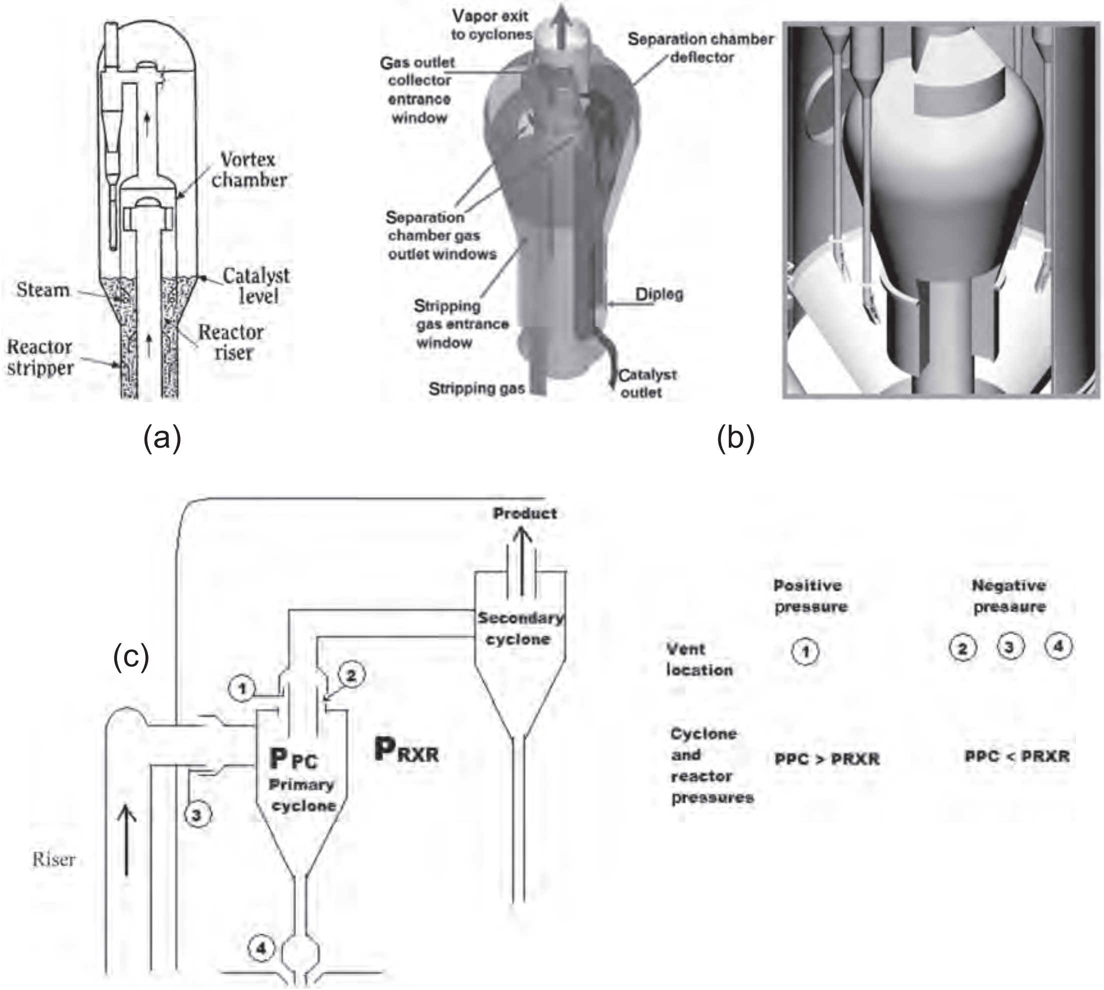


Figure 6.12—Schematic of FCC riser termination designs: (a) VSS (UOP), (b) RS^2 (Shaw). (*Source:* Used with permission of UOP and Shaw), and (c) close-coupled cyclones [37].

systems minimize the hydrocarbon seepage through primary cyclone diplegs. Although advantageous, the close coupled systems are thought to be susceptible to upsets and can lead to catalyst carryover to the main fractionator [35].

The VSS^{TM} and $\text{RS}^{2\text{SM}}$ designs are claimed to be less susceptible to upsets with enclosed separation of hydrocarbons. These designs attempt to provide operational ease while simultaneously reducing the hydrocarbon residence time. Using the momentum, most hydrocarbons are separated from the spent catalyst and directed toward the cyclones through proprietary designs. The separated catalyst is prestripped in an enclosed chamber to minimize the hydrocarbon release, thus attaining higher levels of hydrocarbon containment.

6.7.4 Stripper Internals

FCC catalyst that is separated from the riser contains a significant amount of hydrocarbons in the pores and interstitial voids. The entrapped hydrocarbons are separated by displacement with steam in the stripping section, which otherwise would land in the regenerator, increasing the combustion load. Steam is typically introduced through two steam distributors. Most of the volatile light hydrocarbons will be removed through prestripping steam introduced in the upper stripper bed. The prestripped catalyst flows down through a series of baffles such as disk and donuts, sheds, tube bundles, etc., against a countercurrent stripping steam (Figure 6.13).

The baffles arrangement improves the catalyst steam contact and catalyst residence time, leading to more efficient diffusion of hydrocarbons from catalyst pores into the upflowing steam. In unbaffled strippers, catalyst segregates toward the walls whereas steam flows exclusively in the center, leading to poor stripping. The baffled strippers force the two phases to flow in truly countercurrent fashion with reduced back-mixing. Papa and Zenz [38] proposed a design criterion for strippers following the analogy of separation units. According to this criterion, to achieve true countercurrent plug flow for both of the phases requires operating the unit at approximately 75–80% of flooding flow rates. The maximal flooding flow rate of either phase can be estimated from the following relation [38,39]:

$$\left[\frac{(ACFM/A)\,4^{0.5}}{\left(\Delta\rho/\rho_g\right)^{0.5} D^{0.5}}\right]^{2/3} = 43.86 - 0.794\left[\frac{(Bulk\,CFM/A)\,4^{0.5}}{\left(\Delta\rho/\rho_D\right)^{0.5} D^{0.5}}\right] \tag{6.15}$$

where:
$ACFM$ = actual gas flow rate (ft^3/min),
$Bulk\ CFM$ = catalyst flow rate (ft^3/min),
A = total area of the slot or hole (ft^2),
D = width of slot or diameter of hole (ft),
ρ_g = gas-phase density (lb/ft^3),
ρ_D = catalyst bulk density (lb/ft^3), and
$\Delta\rho = \rho_D - \rho_g$ (lb/ft^3).

The effect of pressure due to static head can be accounted for through a similar equation [40]. Under steady-state conditions, the pressure drop across each

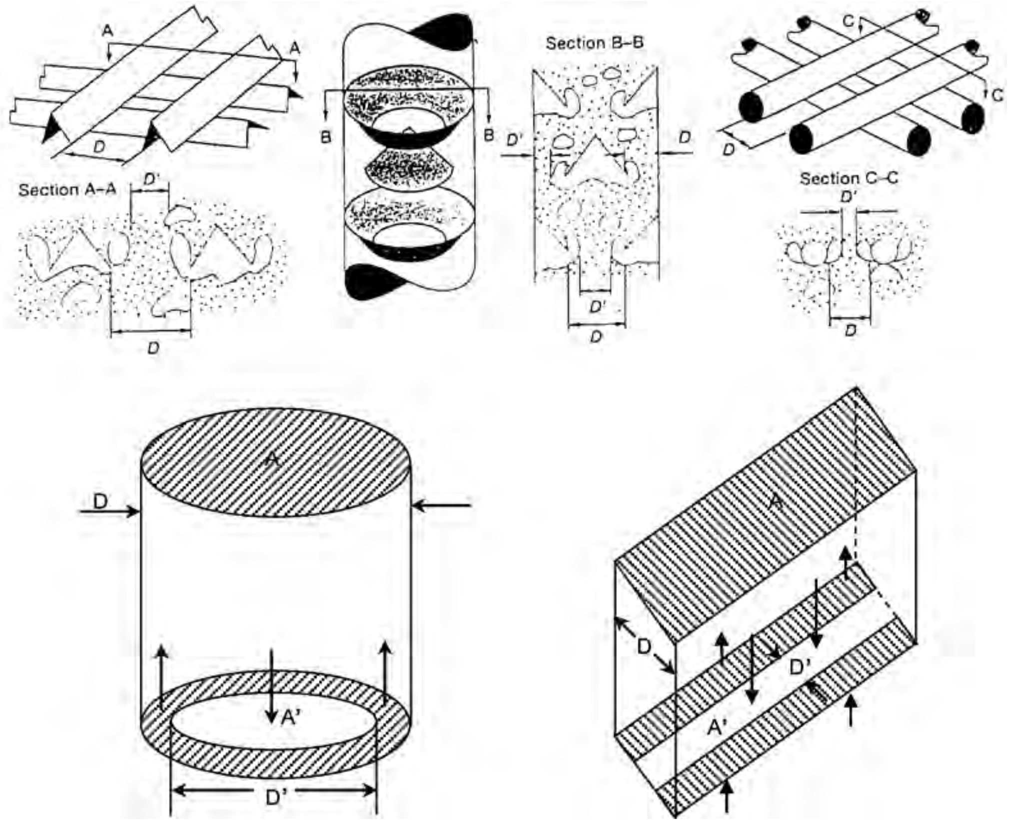


Figure 6.13—Various types of stripper baffles (Chevron grids, disk and donut, tube bundles) (top) and flow areas and diameters as defined in stripper performance equations (bottom). *Source:* Reprinted with permission from [38].

baffle is expected to be the same for constant catalyst flux. The back-mixing can be reduced through closer baffle spacing. However, there is a penalty on capacity due to reduced head. Another parameter that influences stripper efficiency is the length to diameter (L/D) ratio. Strippers with larger L/D ratios are observed to give higher efficiency because of lower effective diameter.

Hydrogen content in the coke fraction of spent catalyst, referred to as "hydrogen in coke," is often considered as an indication of stripper efficiency. Because the hard coke on spent catalyst is expected to contain much less hydrogen compared with the hydrogen content of the volatile material (soft coke), this parameter is easily distinguishable and is hence widely followed. In industry, a value less than 7 % is considered to be good whereas 6 % is ideal [14,41]. Nevertheless, the hydrogen in coke depends on other factors such as stripper temperature, catalyst, type of feed being processed, etc. Generally, catalysts with small pore diameter (high surface area and low pore volume) require more steaming and residence time due to poor "strippability" of heavier molecules. Higher stripper temperatures are likely to help in desorbing these compounds efficiently due to improved volatilization and/or further cracking [42].

Typically, 2–5 kg of stripping steam is used for every ton of circulating catalyst; needless to say the optimal value depends on catalyst, feed, and operating parameters. Often refiners optimize the steam flow rates on the basis of regenerator temperature. Up to a point, an increase in stripping steam reduces the regenerator temperature; beyond optimum, the reduction in coke content would be minimal.

6.7.4.1 STAND PIPES

Stand pipes are circular pipes for the transportation of solids from one section of the unit to another. These can be vertical, angled, or a combination of these two. The two primary stand pipes in FCC units are spent catalyst transfer line and the regenerator transfer line. In these stand pipes, the solids flow against a positive pressure differential, using the gravity head generated by the fluidizing solids, whereas the fluidizing gas flows upward relative to the solids. The stand pipes are typically designed in such a way that they generate more pressure than required so that excess pressure can be wasted across the valves to maintain the pressure balance in the unit. The slide valves generally operate with a pressure drop of 15–100 kPa with valve opening between 25 and 75 % [43].

It is desirable to have vertical standpipes. In vertical standpipes the pressure build-up is high, and hence higher solid fluxes are possible [44]. When the gas flow is below minimum fluidization, the solids cannot exert the pressure at the base of the stand pipe as solids loose their fluidity, leading to reduced flow [45]. Likewise, overaeration leads to excessive interstitial void volume and hence reduced pressure. The stand pipes should ideally be operated around incipient bubbling and incipient buoyancy. Aeration taps are usually provided uniformly along the length of the stand pipe to keep the solids in a fluidized state and avoid large bubbles. The amount of aeration required to maintain the solids in a fluidized state can be computed using the following equation [44]:

$$Q = 1000\left[\frac{P_b}{P_t}\right]\left(\frac{1}{\rho_{mf}} - \frac{1}{\rho_{sk}}\right) - \left(\frac{1}{\rho_t} - \frac{1}{\rho_{sk}}\right) \tag{6.16}$$

where:

Q = aeration required to prevent defluidization (m^3/s);

P_b and P_t = pressures at the bottom and top of the stand pipe, respectively (Pa);

ρ_{mf} and ρ_t = fluid bed density at minimum fluidization velocity and at top of stand pipe, respectively (kg/m^3); and

ρ_{sk} = skeletal density (kg/m^3).

Catalyst fines play an important role in promoting catalyst circulation by improving the fluidity [45]. The ratio of minimum bubbling (U_{mb}) to minimum fluidization (U_{mf}) velocities, which is a strong function of fines content, is given below [46]. The higher ratio indicates a larger operating window for stand pipe operation and a less frequent aeration requirement.

$$\frac{U_{mb}}{U_{mf}} = 2300\frac{\left(\rho_g^{0.126}\mu^{0.523}e^{0.716F45}\right)}{\left(d_p^{0.8}\left(\rho_p - \rho_g\right)g\right)^{0.934}} \tag{6.17}$$

where:

ρ_g = gas density (kg/m^3),

μ = gas viscosity ($kg/m\cdot s$),

F_{45} = fraction of fines < 45 μm,

d_p = mean particle size,

ρ_p = particle density, and

g = gravitational constant.

6.7.5 *Regenerator*

An FCC regenerator design is decided primarily based on the coke burning capacity and catalyst circulation rates. In most situations, single-stage regeneration with or without catalyst cooler may be adequate. For handling high-CCR feeds, two-stage configuration or two stages with catalyst cooler are required. Occasionally, single-stage regenerators are also used in partial combustion mode while processing moderate CCR feeds so that the heat release is restricted.

Single-stage regenerators are typically bubbling fluidized beds where the gas superficial velocities are in the range 0.5–1 m/s. There is a distinguishable dense catalyst bed and a dilute phase in these regenerators. In the dilute bed, the entrained catalyst travels along with the flue gases into the cyclones. The design velocities are decided by optimizing the regenerator diameter and the catalyst entrainment. To keep the cyclone loading to a minimum, the regenerator height should be more than the transport disengagement height (TDH).

Most coke burning reactions occur in a dense bed, but a small fraction of CO escaping from the bed can react with residual O_2 in the dilute phase, leading to a slight temperature rise. In partial combustion units the difference between the dense and dilute bed temperatures, often referred to as "afterburn," could be as high as 20°C, whereas in full combustion units this value is normally less than 10°C. The catalyst entry and its distribution and withdrawal are important for achieving good regeneration and uniform radial distribution. Figure 6.14 shows the catalyst distributor system of KBR Technology.

In the Kellogg Orthoflow™ FCC regeneration configuration, the spent catalyst is introduced at the top of the dense catalyst bed and distributed uniformly through a specially designed spent catalyst distributor, whereas air is introduced from the bottom so that catalyst and air flow in

Figure 6.14—Schematic of spent catalyst distributor and air distributors in KBR's FCC regenerator. *Source:* Figure used courtesy of KBR, Inc.

a countercurrent manner. Countercurrent flow avoids the spent catalyst coming in direct contact with fresh air, thus preventing high particle temperature and catalyst deactivation. Likewise, because of the low O_2 content at the spent catalyst entry, the NO_x produced in the bed is expected to react with coke, leading to reduced NO_x in the flue gas.

The UOP high-efficiency regenerator operates in a fast fluidized bed mode with complete coke combustion. The spent catalyst enters the bottom of the combustion chamber and flows upward along with the air in a combustion riser. The high velocities and low catalyst densities promote the combustion and significantly reduce the regeneration time. The regenerated catalyst is collected in the upper containment vessel from the combustion riser through cyclones. Hot catalyst from this section is recycled to the bottom combustion section to preheat the spent catalyst for accelerated combustion. The key advantages claimed for this design are a smaller regenerator, reduced catalyst inventory, complete coke combustion, etc.

Two-stage regenerator designs are licensed by UOP and Total (jointly by Stone and Webster and IFP). In the two-stage regeneration, nearly 50–70 % of the coke is burned in the first stage under partial combustion mode whereas the remainder is burned under full combustion in the second stage. The first stage operates under milder partial combustion conditions (620–690°C) with deficit oxygen atmosphere while the second stage is under excess O_2 with temperatures ranging from 670 to 760°C. In the UOP unit, the first stage is located on top of the second stage. The catalyst flows from the top through a stand pipe into the second stage. The second-stage flue gas enters into the bottom of the first stage so that the excess air is consumed during the first-stage regeneration. Therefore, the combined flue gases leave from the first stage through a single line. In contrast, in the Stone and Webster-IFP unit the catalyst is lifted from the first stage to the second stage using lift air. The flue gases from the first stage should not be combined until they are sufficiently cooled to prevent ignition.

While processing resid feeds, regenerators are often designed with catalyst coolers. Catalyst coolers are essentially heat exchangers and act as a sink for rejecting excess heat from coke combustion (Figure 6.15). In these heat exchangers the catalyst flows in the shell side whereas water and steam flow through bayonet tubes. The heat removal is controlled by catalyst circulation and through fluidization rates [35]. According to Letzsch (2003b), single-stage regenerators in full combustion mode can handle feed CCRs of 2.5 wt %; in partial combustion the CCR can be as high as 3.5 % [27]. Two-stage regenerators can handle 6 % feed CCR. With catalyst coolers, the suggested CCR limit for both units is 10 %. Ultimately, issues such as overall economics, operational flexibility, catalyst consumption, etc., are the key factors for the regenerator design.

6.7.6 Air Grid

The air grid is important hardware in an FCC regenerator because it ensures good fluidization characteristics. Improper fluidization results in dense bed instability, leading to inefficient air catalyst contact, poor combustion, catalyst attrition, particulate entrainment, uneven cyclone loadings, erosion, etc. Perforated plate grids, concentric rings, and pipe grids are the typical grid designs used in

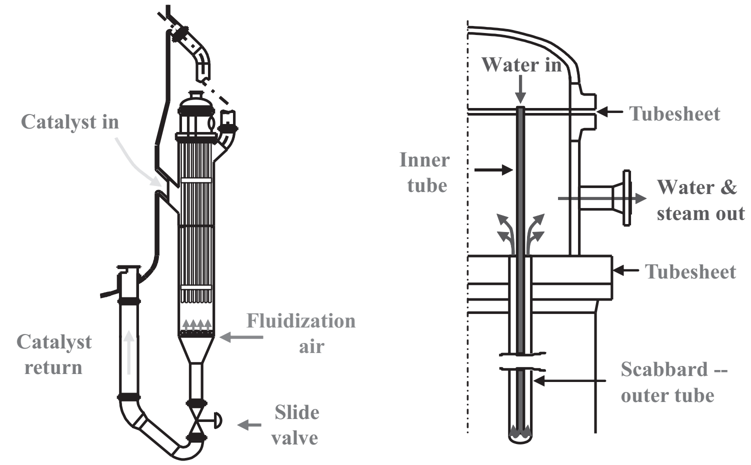


Figure 6.15—KBR's dense-phase catalyst cooler arrangement. *Source:* Figure used courtesy of KBR, Inc.

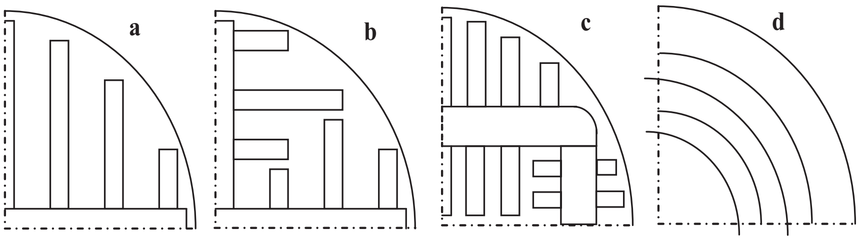


Figure 6.16—Sectional view of typical FCC air grid arrangements: (a) single central pipe, (b) double central pipe, (c) tuning fork, (d) ring-type distributors. *Source:* Reproduced with permission from [47].

FCC regenerators. Pipe grids are usually preferred because of several advantages such as low-pressure drop, minimum weeping, good turndown ratio, and other thermal and mechanical advantages. Several air grid arrangements such as single and double central pipe grids, tuning fork design, and concentric sparger rings are available for commercial FCC catalyst regenerators. Figure 6.16 shows the schematic of some of these designs.

Ideally, the gas distributes uniformly and covers the entire cross section. This is achieved by providing adequate grid pressure drop so that all of the grid holes discharge evenly. However, on the other hand, excessive pressure drops result in high grid hole velocities, leading to catalyst attrition.

The grid pressure drop is a function of gas flow rate, which can be estimated from the grid hole velocity [45]):

$$V_0 = 0.8\sqrt{\frac{2\Delta P}{\rho}} \tag{6.18}$$

where:

V_0 = velocity through the grid hole (m/s),
ΔP = Pressure drop (N/m^2), and
ρ = fluid density (kg/m^3).

For uniform gas distribution, the following considerations are important [40,45,47]:

- At least 10 nozzles per square metre area to minimize stagnation zones.
- A minimum of 30 % of bed pressure drop is required across the distributor when nozzles are pointed upward, whereas the minimum is 10 % with downward-pointed nozzles.
- $D_{head}{}^2/N_h D_h{}^2$ should be greater than 2.5 for the manifold flow variations and pressure drop requirements to be within acceptable limits (D_{head} is the header pipe diameter and N_h and D_h are the number of grid holes and grid hole diameter, respectively).

A minimum grid hole pitch is to be maintained to avoid coalescence of air bubbles at the grid level. Zenz [48] suggested that the initial bubble size is approximately half of the jet penetration length. There exists around each rising bubble a down-flowing shell of solids for which the outer periphery is concentric with the bubble such that the solids shell diameter is 1.5 D_B. To avoid premature bubble growth by a merger of two bubbles simultaneously leaving the grid, the grid hole pitch should not be closer than ½ D_B. Port shrouding can be used to reduce the grid hole velocity to prevent jet merging as well as to reduce particle attrition. Port shrouding reduces the velocity at the gas-solids interface and therefore reduces particle attrition. To be effective, shrouds must be long enough to contain the expanding (11° included angle) gas jet leaving the grid orifice (Figure 6.17).

6.7.7 Cyclones

Cyclones are used for separating solid particles from a gas stream using the centrifugal forces. The dust-laden gas stream enters tangentially into the cyclone at very high velocity. The centrifugal forces imparted on the solid particles drive them toward the cyclone barrel wall, from where the particles slide down through the conical section into the dipleg, ultimately landing in the catalyst bed. The spiraling gas separated from the solids exits from the top.

The particle collection efficiency is related to the time necessary for a particle to reach the barrel wall according to Stokes' settling velocity within the residence time available for carrier gas. The residence time depends on the number of spiral traverses (N_s) within the barrel, whereas Stokes' velocity is a function of centrifugal force and particle properties. The minimum smallest theoretical particle (D_{th}) that can cross the cyclone width within the available residence time can be estimated from the following equations:

$$D_{th} = \left[9L_w\mu_G/\pi N_S V_i(\rho_P - \rho_G)\right]^{1/2} \tag{6.19}$$

$$N_S V_I^{1.5} = 2.908 \tag{6.20}$$

where:

L_W = cyclone's inlet duct width,
μ_G = gas viscosity,
V_i = gas inlet velocity,
ρ_p = apparent particle density, and
ρ_G = gas density.

It is preferable to have an inlet duct with a height-to-width ratio (h/L_w) greater than 1 for maximizing the number of particles closer to the wall and their efficient collection, whereas the travel distance (L_w) for settling is small. The collection efficiency of the particle with size D_{th} and other fractions can be estimated from the correlations. The collection efficiency increases with dust loading, and correction needs to be applied to account for the "plowing effect" of the larger particles (Figure 6.18). The efficiency correlations available in the literature differ significantly because they have been developed with widely differing geometries, particle properties, loadings, etc. Nevertheless, the mechanistic procedure is simple and effective for new designs and troubleshooting operational problems when used in conjunction with optimal cyclone dimensions [49].

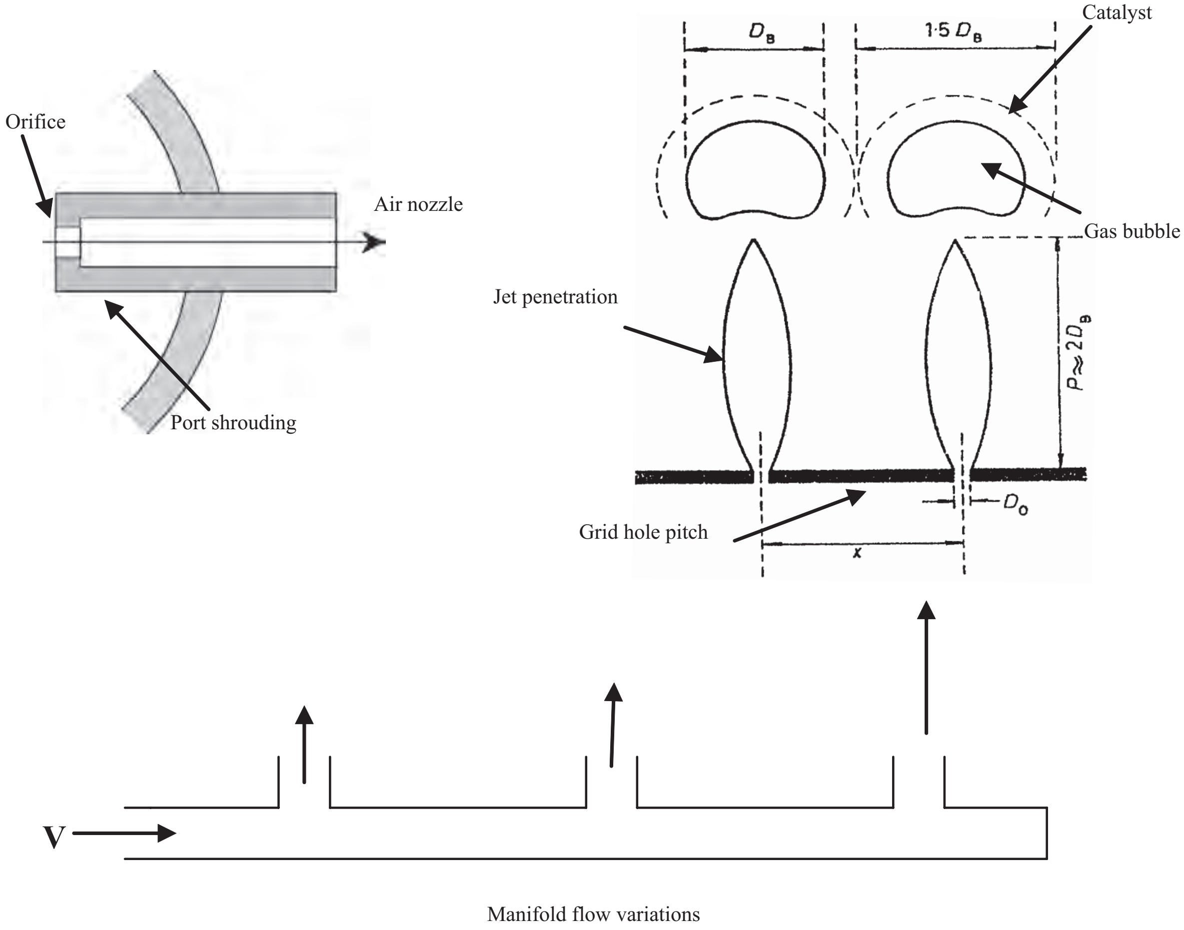


Figure 6.17—Important pipe grid design considerations [40,48,50].

6.8 CATALYSTS AND ADDITIVES

Catalysts and additives play a major role in selectively converting low-value VGO into high-value lighter and middle distillates. FCC catalyst is a fine powder with an average particle size of 60–75 μm and a size distribution ranging from 20 to 120 μm. The catalyst basically consists of four major components: zeolite, active matrix, filler, and binder. Each of these constituents has a unique role in the overall functioning of the catalyst, whereas zeolite is the key component that is more active and selective for gasoline production.

6.8.1 Catalyst Constituents

6.8.1.1 ZEOLITE

Zeolite is mainly responsible for cracking activity. Zeolites are structurally complex inorganic polymers that are based on an infinitely extending three-dimensional, four-cornered network of AlO_4 and SiO_4 tetrahedra. The structure can be considered to arise from the isomorphous substitution of Si by Al in the crystal lattice of SiO_2. The tetrahedra are linked to each other by a sharing of oxygen atoms to give rise to three-dimensional structures containing voids and channels of molecular dimensions.

Zeolite Y, which is isostructural to Faujasite, a naturally occurring zeolite having a pore opening of approximately 8 Å, is used for manufacturing FCC catalyst. The size of the pore opening puts a limit on the size of the hydrocarbon molecules that enter the zeolite cage. A unit cell of zeolite Y contains 192 framework atomic positions occupied by either Si or Al atoms. In the zeolites framework, Al cannot have as its immediate neighbor another Al, thus resulting in a Si/Al ratio of 1 or greater. A unit cell of synthesized zeolite Y, with a Si/Al ratio of 2.5, contains 137 atoms of Si and 55 atoms of Al. Because aluminum is in the +3 oxidation state, each tetrahedra containing alumina has a net negative charge that is compensated for by sodium ions in as-synthesized zeolite. These charge-compensating ions called “extra framework ions” are mobile and can be easily exchanged with other ions such as ammonium ion. When calcined, ammonium ion decomposes, liberating ammonia, which escapes from zeolite leaving a H^+ ion, which is a Bronstead acid site. Hence, the number of acid sites in the zeolite depends on the aluminum tetrahedra in the framework. Zeolite acidity can be moderated by increasing the Si/Al molar ratio. This can be achieved either by synthesizing zeolite with a higher Si/Al molar ratio or through postsynthesis modification of dealumination by steaming or chemical treatment.

6.8.1.2 SYNTHESIS OF ZEOLITES

Zeolite is generally synthesized starting from sodium silicate and sodium aluminate. The sodium ions can be replaced partially by ion exchange with ammonium or rare earth ions in aqueous solutions. The presence of

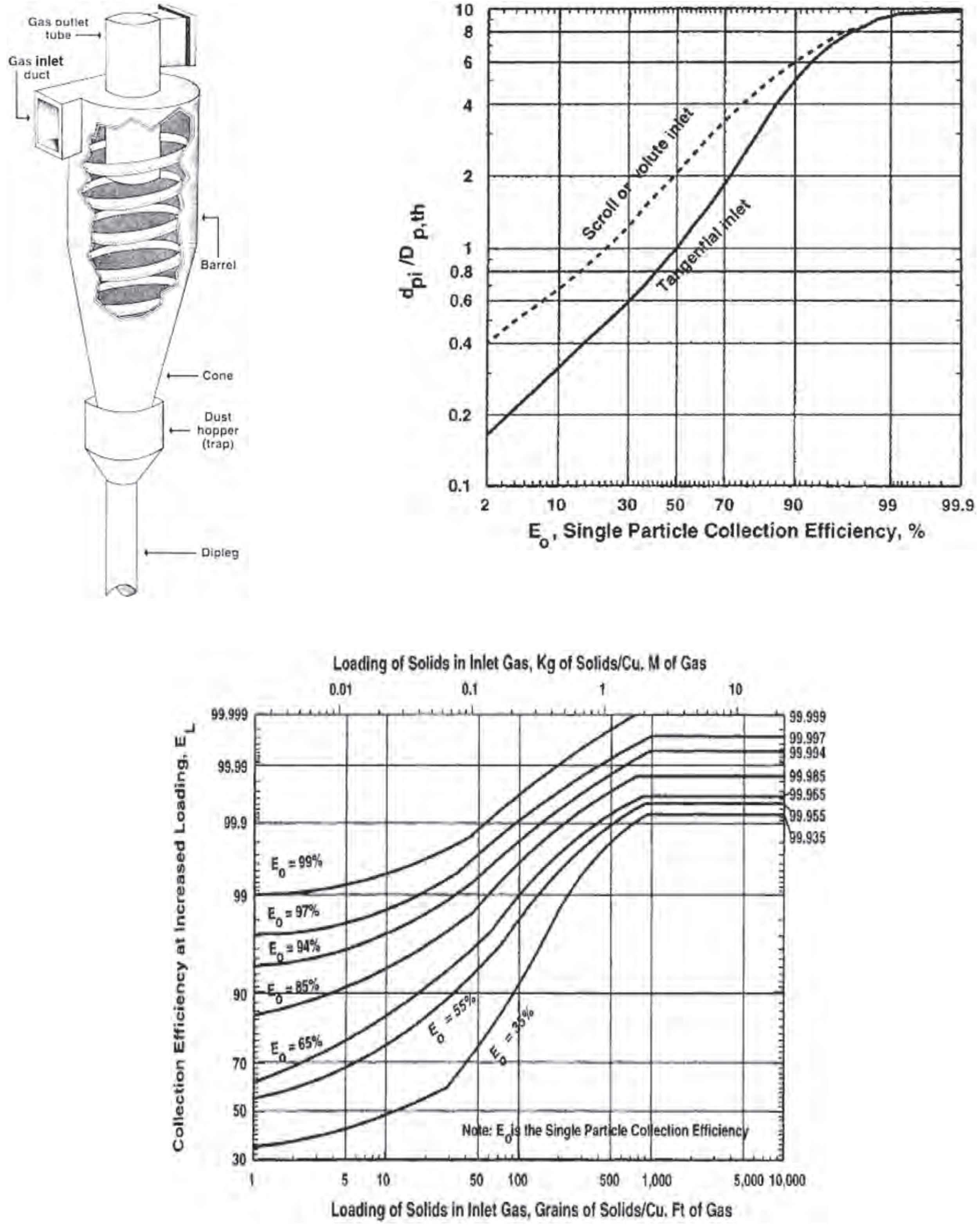


Figure 6.18—Cyclone performance curves. *Source:* Figure used with permission from [51].

sodium is detrimental to the catalyst because sodium neutralizes the zeolite acidity and reduces its hydrothermal stability. Both standard Y and USY can be treated with other cations, particularly with rare earth mixture (mainly cerium and lanthanum), to remove sodium to form REY and REUSY zeolites, respectively. Although sodium cannot be completely removed from zeolite, it can be reduced to as low as 0.2–0.3 wt % after steaming followed by ion exchanges. Rare earth exchange not only increases the activity of the zeolite but also enhances the resistance to deactivation. A richer rare earth content in zeolite improves the hydrothermal stability. A schematic

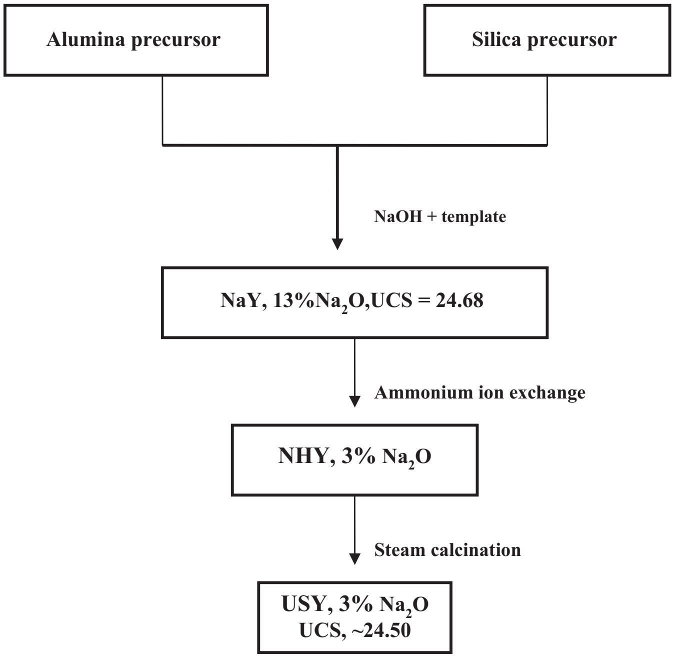


Figure 6.19—Schematic of synthesis of USY zeolite [41].

of commercial synthesis of the Y zeolite and exchanged zeolites is represented in Figure 6.19.

Higher zeolite acid site density favors increased hydrogen transfer, resulting in more paraffin formation. The presence of higher paraffins in gasoline leads to lower octane. Because paraffins are more stable than olefins, they undergo less consecutive cracking themselves. Hence, REY catalyst with higher acid site density (higher aluminum content) results in poor gasoline quality but a slight improvement in gasoline yields. However, coke yield also increases with such catalyst as a result of increased hydrogen transfer reactions. Loss of hydrogen from heavy aromatics increases their coke-forming tendency. The influence of rare earth content on zeolite unit cell parameter is explained in Figure 6.20.

6.8.1.3 STABILITY OF ZEOLITE

Zeolite is subjected to severe hydrothermal conditions in FCC units during catalyst regeneration. This leads to breakage of Al–O bonds, which are weaker than Si–O bonds, ultimately resulting in a collapse of zeolite structure. To improve the stability, manufacturers dealuminate the zeolites in a controlled manner by steam or chemical treatment. The dealumination process extracts aluminum from the framework. The vacancy thus created is filled with a silicon atom, preventing collapse of the framework structure. The resulting ultrastable zeolite Y (USY) is more resistant to deactivation in the FCC than its parent standard Y because the lower framework aluminum content in USY reduces the thermodynamic driving force for expelling additional aluminum at FCC unit operating conditions. Further, the sodium level in USY is generally lower because of the dealumination process, which also gives higher resistance to deactivation. Steaming or hydrothermal pretreatment is a preferred option over chemical treatment for the production of USY zeolite. During this process mesopores in the range of 30–60 Å are formed when a small portion of aluminum is not replaced by silicon. The increased porosity enhances hydrocarbon diffusion.

The catalyst activity mainly depends on the zeolite acidity, which in turn depends on the Si/Al ratio. The zeolite Si/Al ratio can be determined by measuring unit cell size (UCS) by X-ray powder diffraction. Because the Al atom is larger than the Si atom, the UCS decreases with an increase in the Si/Al atomic ratio. Hence, the lower the UCS, the lower is the aluminum content and acid density. The UCS of USY is always lower than that of standard zeolite because the former contains less aluminum atoms per unit cell. For example, a standard fresh zeolite Y with a UCS of 24.93 Å contains 85 Al atoms per unit cell, and a USY zeolite with a UCS of 24.25 Å contains 34 Al atoms per unit cell. Therefore, USY is less acidic than standard Y zeolite. The structure of Y zeolite and other FCC catalyst constituents are shown in Figure 6.21.

6.8.1.4 ACTIVE MATRIX

The active matrix is one of the most important constituents in FCC catalysts and possesses cracking activity, other than the zeolite. The main function of the matrix is to pre-crack the molecules that are too large to enter the micropores of zeolite, thereby contributing significantly to the overall performance of the FCC catalyst. However, matrices are not as selective as zeolites. Active matrix material such as

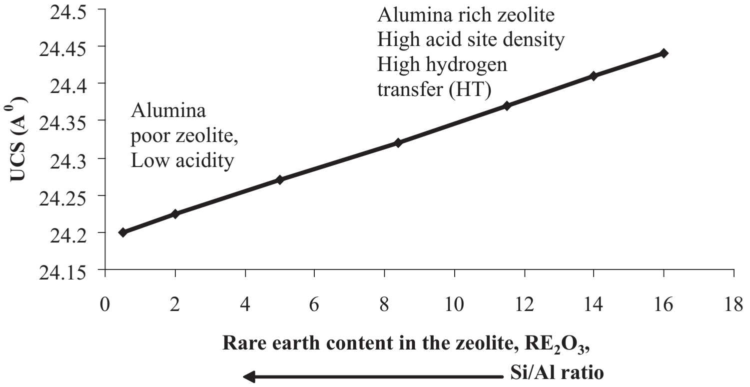


Figure 6.20—Influence of rare earth content on zeolite UCS parameter [52].

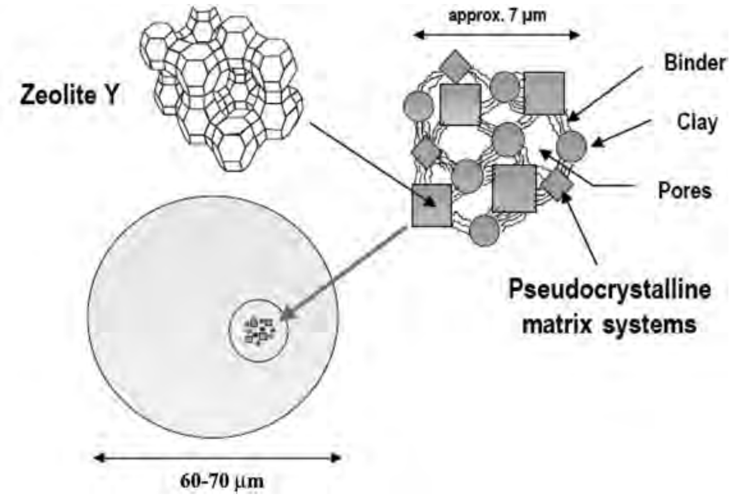


Figure 6.21—FCC catalyst constituents. *Source:* Figure used courtesy of Intercat, Inc.

alumina or silica-alumina used in FCC catalysts is mostly amorphous in nature. However, the active matrices consist of large pores in the mesopore (20–500 Å) and macropore (>500 Å) range. The large pores provide access to heavier hydrocarbons present in the FCC feed, resulting in higher bottoms cracking. The degree of bottoms conversion can be adjusted by varying the amounts of active matrix and zeolite in a catalyst. The active matrix activity and selectivity are affected by its acid site density, acid strength, and pore structure. All of these aspects can be varied by the specific type of active matrix selected and the physical and chemical treatment these materials are subjected to. Hence, different matrix materials can exhibit different cracking activity depending on their acid site density, acid strength, and pore structure. Matrix surface area is one of the measures of its activity. Reduction in active matrix surface area reduces its cracking activity. However, matrices are more resistant to deactivation than zeolite. Active matrix also acts as a trap for some of the vanadium and basic nitrogen present in the feed. Metals such as vanadium destroy the zeolite, but active matrix is less sensitive to their attack.

Although the active matrix is useful for bottoms cracking, its poor selectivity limits its quantity in an FCC catalyst. Therefore, a proper balance between matrix and zeolite activity needs to be maintained depending on feed type, unit operating conditions, and product demand. The ratio of surface area of zeolite to matrix (Z/M) is one of the measures of the expected performance of the catalyst. The Z/M of a given catalyst can be experimentally measured by nitrogen adsorption.

6.8.1.5 FILLER AND BINDER

Filler is a clay, mostly kaoline, added into an FCC catalyst to dilute its activity. It also acts as a heat sink and heat transfer medium. It can also act as a sink for sodium, thereby improving the resistance to sodium poisoning. Filler is mostly inert; if treated, then some acidity may be incorporated into it.

Binder is an important component of an FCC catalyst because it helps in holding together all of the constituents (i.e., zeolite, active matrix, and filler). Generally, binder may not have catalytic activity. However, some binders such as alumina polymers and clay-based binders may have bottoms cracking activity. The binder plays a predominant role in enhancing the mechanical strength, especially when FCC catalyst contains more zeolite [53].

The combined role of filler and binder is to provide physical strength, heat transfer media, and particle size distribution as well as to improve fluidization behavior. In summary, zeolite is the main component of FCC catalyst contributing to surface area, activity, and selectivity. The matrix takes care of large hydrocarbon molecules approaching the zeolite. Filler and binder ensure overall strength of the catalyst. The synergetic effect of all three constituents results in the desired performance of the FCC catalyst.

6.8.2 Catalyst Design

Each FCC unit is specific and needs, depending on feed quality, product requirement and process conditions, a specifically tailored catalyst. Designing of an optimal catalyst for a given situation requires a good understanding of the nature and proportions of various catalyst components. Scherzer [52] classified FCC catalysts into five main domains that are shown schematically by plotting zeolite UCS versus the Z/M ratio (Figure 6.22). This scheme gives a clear understanding of the requirement of different catalyst properties for a specific application.

While designing an FCC catalyst for resid feeds, the main parameters to be considered are catalyst pore structure, coke selectivity, and metal tolerance. Pore dimensions must be optimized for efficient diffusion of reactants and products by adjusting for the properties of the active matrix and the zeolite component. In addition, the resid cracking catalyst should also have additional properties such as metal tolerance. Use of metal traps can increase the metal tolerance level of catalysts. Coke selectivity is another important parameter. An improvement in catalyst coke selectivity helps in achieving higher conversion in the FCC unit. Coke yield increases with an increase in the degree of rare earth, whereas coke selectivity decreases with the increase in UCS [52]. Thus, when designing FCC catalysts for maximal coke selectivity, rare earth exchange in zeolite should be used to target moderate UCS (24.28–24.33 Å). In addition, rare-earth-based vanadium traps can be

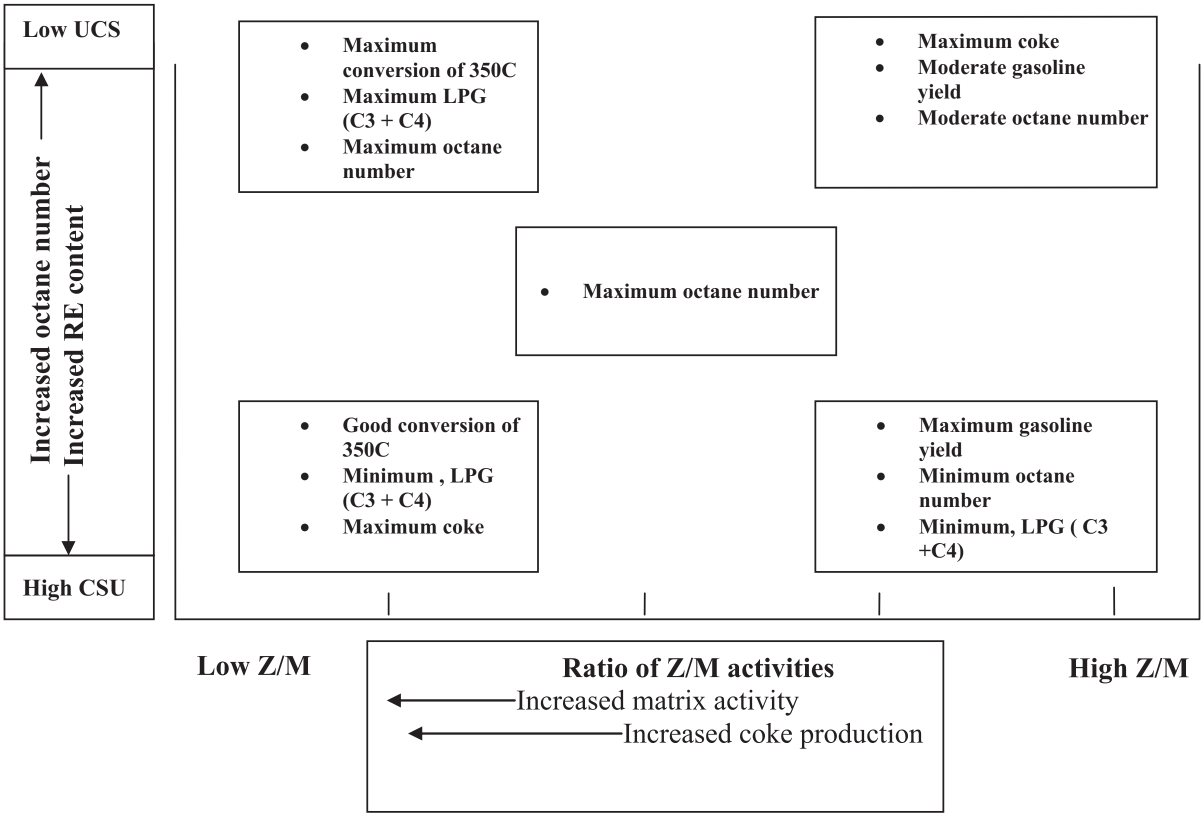


Figure 6.22—FCC catalyst composition corresponding to specific utilization [52].

formulated as a separate catalyst additive to improve coke selectivity by trapping metals and inhibiting undesirable hydrogen-forming reactions [54].

The FCC unit bottoms cracking mechanism involves three different reaction types: precracking of large molecules, dealkylation of alkyl aromatics, and conversion of naphtheno aromatics [55]. Designing catalyst pore structure for efficient diffusion is an important consideration when resid feed is processed. Molecular simulation studies have indicated that molecules boiling in the range of 371–570°C are approximately 10–30 Å in diameter. A diffusion simulation model suggests that the pore size must be 10–20 times bigger than the actual feed molecules to overcome diffusion limitations. Thus, the FCC catalyst must have pore diameters of 100–600 Å to allow for the active diffusion of resid molecules. Pores smaller than 100 Å result in coke and hydrogen; pores larger than 1000 Å result in high catalyst attrition.

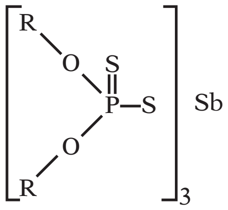
During the cracking process, metals in FCC feedstock are deposited on the catalyst surface leading to reduced activity. Vanadium and sodium cause permanent catalyst deactivation whereas nitrogen is a temporary poison. Nickel promotes dehydrogenation reactions, which result in higher dry gas and coke make.

Vanadium is harmful to the catalyst because in presence of steam it forms vanadic acid, which can destroy the zeolite by hydrolysis of its framework.

$$V_2O_5 + 3H_2O \longrightarrow 2H_3VO_4 \qquad (6.21)$$

The deleterious effects of metal can be countered to some extent by increasing the catalyst addition rates. However, use of a metal trap is a better approach when the feed metal concentration is high. Different metal oxides or mixed oxides such as Al_2O_3, TiO_2, $BaTiO_3$, Ca ZrO_3, and SnO_2 as well as natural clays have been used as metal traps. Metal traps are used in two ways. One way is to use a metal trap as an integral part of an FCC catalyst; the other way is to add separately as and when required.

Antimony- or bismuth-based additives are generally used as nickel passivators.



(6.22)

Antimony-based additives are typically liquid additives, and their general formula is represented in Eq 6.22, where R is a hydrocarbyl radical containing from 1 to approximately 18 carbon atoms. The overall number of carbon atoms per molecule is in the range of 6 to approximately 90, and the nickel is passivated by forming a nickel antimony alloy [56,57]. Addition of antimony solution depends on the concentration of nickel in the FCC equilibrium catalyst. An antimony-to-nickel ratio of 0.3–0.5 is considered to be optimum for effective nickel passivation [41].

While processing resids, iron is another metal poison. If present in feed, iron can cause a loss in unit conversion, poor catalyst circulation, lower gasoline research

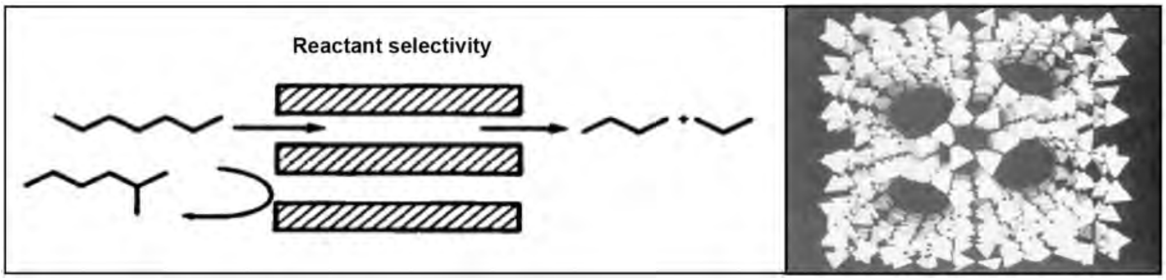


Figure 6.23—Shape selectivity of ZSM-5 [58].

octane number (RON), and SO_x emissions [59–61]. Iron contamination can lead to pore closure and nodule formation. The effect is attributed to the reaction of iron oxides with silica or other metals such as sodium and calcium, resulting in low temperature phases and collapse of the exterior surface of the catalyst particle, which decreases the apparent bulk density. Alumina is resistant to such effects by iron. Significant improvements can be achieved by switching to high-accessibility alumina-based catalysts while processing iron-containing feeds [60]. The alkali metals (sodium and potassium) and alkaline earths (calcium, magnesium, and barium) are harmful to a catalyst, especially under high regenerator severity. The activity is lost because of formation of eutectics with the catalyst. Catalysts with a balanced Z/M and a high zeolite content with moderate rare earth exchange (UCS ≥ 24.30 Å) resist deactivation. Active matrix is also suggested to act as a sodium sink and protect zeolite [62]. To counter the temporary deactivation due to nitrogen, the catalyst should be formulated with high zeolite content and with an active matrix. Also, high reactor temperature reduces nitrogen adsorption whereas an increased C/O ratio counters the nitrogen effect [41].

6.8.3 FCC Additives

FCC additives are specialty catalysts designed to achieve certain objectives such as gasoline quality improvement, enhancement of light olefin yields, higher conversions, reduced flue gas emissions, etc., without any modification in the plant hardware. The additive concentration typically ranges from 0.1 to 40 wt % of the base catalyst depending on the type of the reaction. The physicochemical properties of these additives closely match with the base catalyst. The most common FCC additives are ZSM-5, gasoline sulfur reduction additive, SO_x reduction additive, CO combustion promoter additive, metal passivator, and NO_x reduction additive.

6.8.3.1 ZSM-5

ZSM-5 belongs to the pentasil zeolite family and is primarily used for octane boosting or LPG maximization. It is a stable zeolite with an alumina content below 10 % and pores with diameters in the range of 5.5 Å. It has a distinctly different pore structure and pore arrangement than Y zeolite. Because of shape selectivity, only long-chain, low-octane-gasoline-range, normal paraffin molecules enter its pores and undergo rapid cracking (Figure 6.23) [58]. Because of its high Si/Al (>20) ratio, use of ZSM-5 results in a higher olefin yield with lower hydrogen transfer activity (Figure 6.24).

6.8.3.2 GASOLINE SULFUR REDUCTION ADDITIVE

A FCC unit generally contributes over 40 % to the refinery gasoline pool. FCC gasoline contains sulfur compounds such as mercaptans, sulfides, disulfides, thiophenes, and benzothiophenes that account for most of the gasoline sulfur. These compounds are formed in the riser either by cracking of heavier sulfur compounds or by

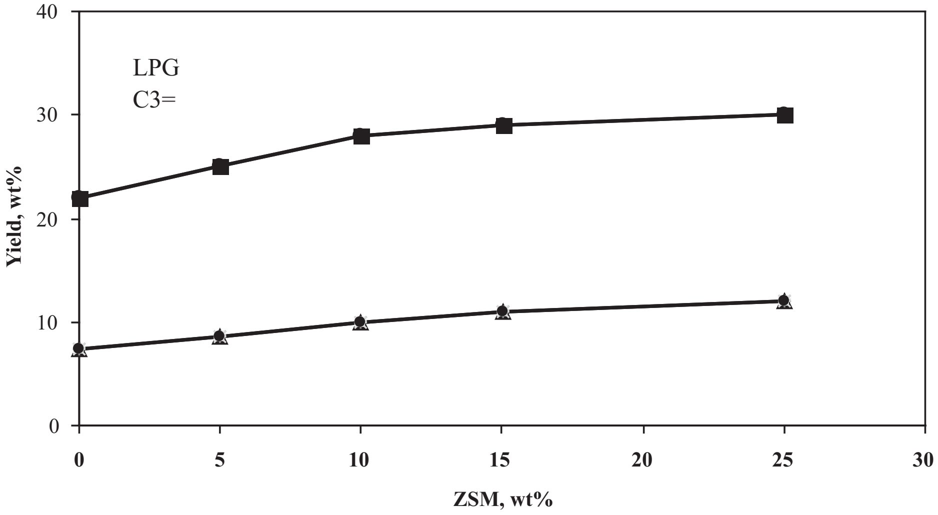


Figure 6.24—Effect of ZSM-5 concentration on product yields [63].

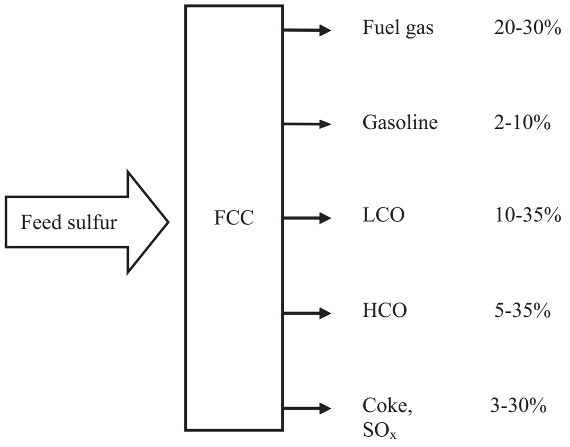
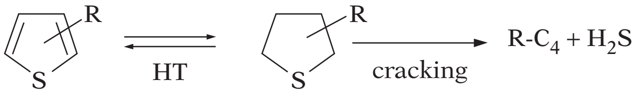


Figure 6.25—FCC feed sulfur distribution [64].

recombination of hydrogen sulfide (H_2S) with olefins. Typically, 2–10% of FCC feed sulfur ends up in gasoline. Figure 6.25 shows the typical distribution of feed sulfur in the FCC product.

Thiophenic compounds are the major constituents of gasoline. Benzothiophenes, which are present in the higher boiling range of gasoline, are difficult to crack. It is generally believed that thiophene conversion requires hydrogenation by hydrogen transfer (HT) from hydrogen-donor molecules before cracking (Scheme 1).

Scheme 1



(6.23)

To date, the gasoline sulfur reduction mechanism is not fully understood. However, it is believed that the reduction follows the cracking of sulfur species formed in the process to release H_2S or inhibition of the formation of sulfur compounds. Harding et al. [65] have proposed that gasoline sulfur reduction additives primarily enhance the rate of tetrahydrothiophene (THT) cracking to H_2S, thus preventing its conversion to thiophene by hydrogenation reactions. Alternatively, gasoline sulfur reduction could be due to improved HT to thiophenic species initiated by the increase of coke production [66,67]. Shan et al. [68] and Vargas-Tah et al. [69] have proposed that sulfur reduction occurs by strong adsorption of thiophenic species on the Lewis acid sites of the additive and further cracking.

The dosage of additive varies from 10 to 40 wt % of the total FCC catalyst inventory on the basis of the feed and product sulfur targets. Laboratory MAT or pilot plant tests have shown that these additives could decrease the sulfur content of FCC gasoline by as much as 40 % without significantly affecting other yields, excepting a slight increase of coke and hydrogen production. However, in some reports [70] gasoline sulfur reduction additive addition caused a substantial change in the yield pattern (Table 6.6). An Indian refinery processing 1.3-wt % sulfur feed achieved 28–40 % gasoline sulfur reduction with addition of 15-wt % GSR additive [71].

TABLE 6.6—Effect of GSR Additive on Yield Pattern [71]

Products	Delta Yields, wt % on Fresh Feed Basis	
GSR additive, 15 wt %	A	B
Dry gas	+0.01	+0.17
LPG	-2.49	-1.87
Gasoline	-0.84	-0.76
TCO	+2.73	+3.46
CLO	+0.57	-0.67
Coke	+0.02	-0.02
Sulfur reduction in gasoline, wt %	26	42

6.8.3.3 SO_X REDUCTION ADDITIVE

The source of SO_x (a mixture of SO_2 and SO_3) emissions from FCC is the sulfur present on the coke that was deposited on the catalyst during the reaction. SO_x emissions are hazardous because of the formation of acidic compounds in the environment. Typically, 10–30 wt % of sulfur in feed contributes to SO_x. SO_x reduction additives are more effective at adsorbing SO_3 than SO_2 under regenerator conditions. SO_x reduction additive contains mainly two components: one is an oxidizing agent that promotes SO_2 oxidation to SO_3 and the other one is a sulfur pick-up agent. The main reactions of the process are represented in Figure 6.26. Base catalyst or catalysts with high alumina can play the role of sulfur pick-up agent for SO_3 as shown in Eq 6.24.

$$Al_2O_3 + 3\ SO_3 \longrightarrow Al_2\ (SO_4)_3 \qquad (6.24)$$

The presence of excess oxygen or CO combustion promoter additive also oxidizes SO_2 to SO_3, thus reducing the load on the SO_x additive. Magnesium is the active metal in both of the additives. One is based on the spinel $MgAl_2O_4$ crystal structure with a cubic, close-packed array of oxides and the other one is based on hydrotalcite {$Mg_6\ Al_2\ (OH)_{18}$ 45 H_2O}, which also has a layered structure with easy access for SO_x species. Efficiency of SO_x removal varies from unit to unit and the type of additive being used. While processing 1.1-wt % sulfur feed with a throughput of 3125 t/day, approximately 11.5 Mt of SO_x per a day is emitted. By the addition of 10-wt % SO_x reduction additive, a decline of approximately 60 wt % SO_x level is observed [72].

6.8.3.4 CO COMBUSTION PROMOTER

A CO combustion promoter catalyst is used to enhance CO combustion in an FCC regenerator and to reduce the afterburn. Variation of ΔT (the temperature difference between the dense and dilute bed) and the concentration of CO are generally taken as measures for the performance of the additive in the FCC unit. Because of the higher heat of combustion, the dense bed temperature increases with CO promoter addition. The active ingredient in the CO combustion promoter is a noble metal, mainly platinum. The addition rate of a CO promoter is typically in the range of 0.2–1 wt % of the base catalyst or 1 ppm of noble metal on the overall catalyst inventory [73]. The active metal is also occasionally

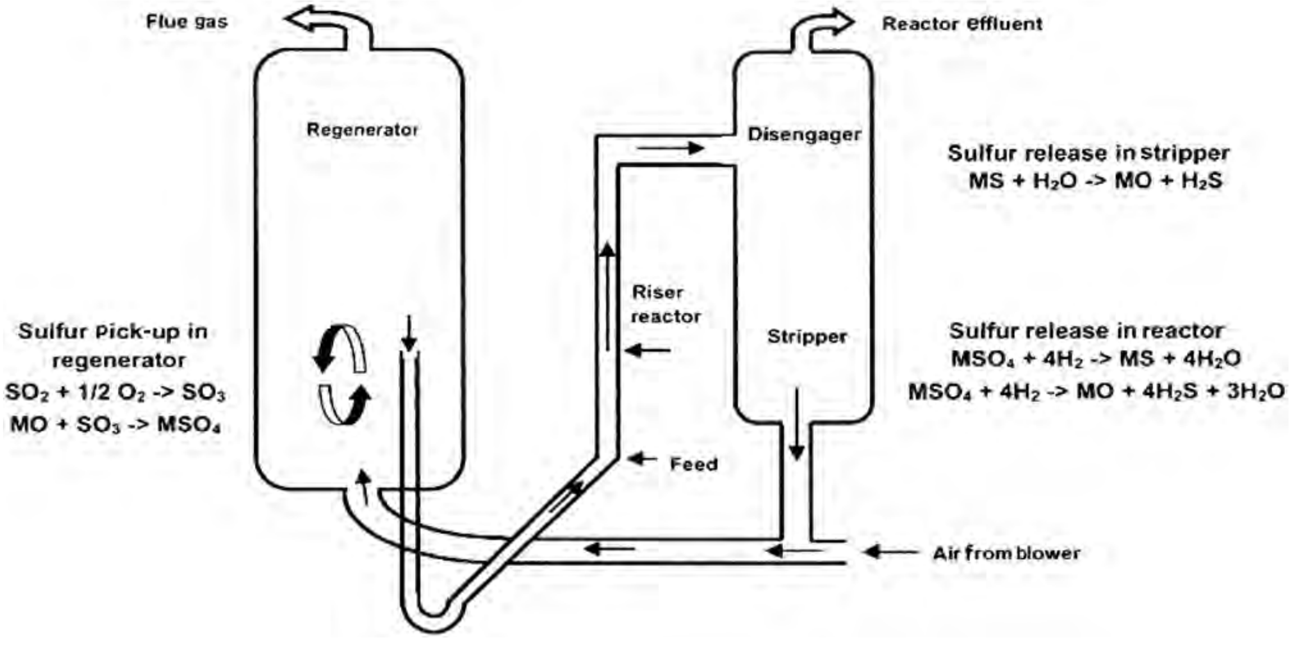


Figure 6.26—Typical FCC unit SO_x reduction chemistry [74]. *Source:* Figure used courtesy of Intercat, Inc.

incorporated along with the base catalyst. In the case of non-platinum-based additives such as palladium-based additives, higher addition rates are required because of lower activity. However, such additives also give the additional advantage of NO_x reduction.

6.8.3.5 NO_X REDUCTION ADDITIVE

FCC alone contributes 50 % of the total NO_x emitted in a refinery [75]. A partial-burn FCC regenerator without CO combustion promoter additive typically does not emit more than 50–150 ppm NO_x. However, units that are operated in full-burn mode may emit NO_x as high as 500 ppm. As per the Grace Davison studies, 50 % of the nitrogen in feed was found in the bottoms and LCO, 5 % was released as ammonia in the riser reactor, and the rest was deposited as coke on the catalyst. Nitrogen deposited on coke was mostly oxidized to molecular N_2. NO_x as the percentage of N_2 in coke varied from 10 to 25 wt % [62].

With the addition rate of 1–2 wt % additive, NO_x can be reduced by almost 70 wt %. Although additive plays significant role in NO_x reduction, FCC unit operating conditions greatly affect NO_x. A high-oxygen environment typically favors NO_x formation. The effect of oxygen concentration on NO_x content is presented in Figure 6.27. The addition

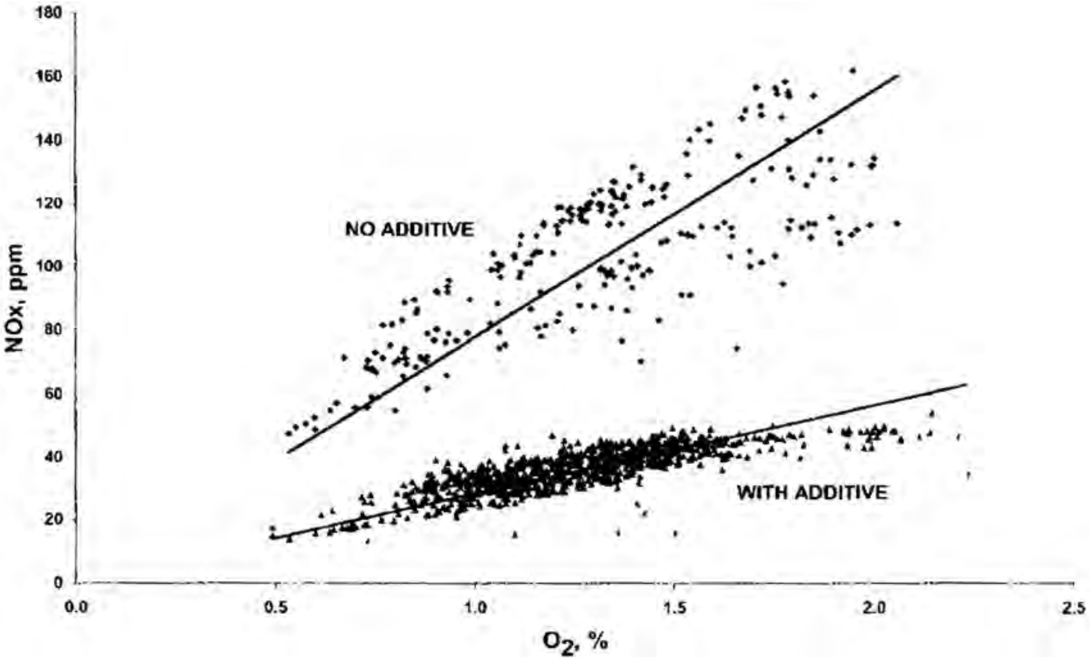


Figure 6.27—Variation of NO_x with respect to regenerator oxygen [74]. *Source:* Figure used courtesy of Intercat, Inc.

of CO combustion promoters increases the NO_x formation due to noble-metal-promoted oxidation. Likewise, the NO_x additive performance is influenced by the presence of other gases such as SO_2, SO_3, CO, and CO_2 [74]. NO_x is also reduced in the regenerator by reacting with coke.

The typical reactions that help for NO_x reduction are as follows:

$$2NO + CO \longrightarrow N_2 + CO_2 + \tfrac{1}{2} O_2 \qquad (6.25)$$

$$2NO + C \longrightarrow N_2 + CO_2 \qquad (6.26)$$

NO_x reduction additives contain noble metals dispersed on an inorganic support. The metals used are iridium and palladium. Irridium was found to be more selective because of its ability to dissociatively adsorb NO in the presence of excess O_2 [74,76,77].

6.8.4 Selection of Catalyst

Selection and use of improved catalyst or additive substantially enhances the profit margins and is one of the quickest ways for meeting refinery goals. Catalyst selection depends on several factors such as product yields and quality requirements, FCC unit constraints, the nature of the feed being processed, the metal content of the feed, etc. Hence, FCC catalyst selection is unit specific and may need to be tailor-made to meet the refiner's objectives.

A catalyst change should be considered whenever there has been a significant change in feed quality, product demand, or unit hardware constraints. The availability of better catalysts over a period of time is also a key reason for the refiner to look for an alternative catalyst. To gainfully exploit the new developments, a refiner should consider catalyst change once every 2 years or sooner.

6.8.4.1 CATALYST SELECTION PROCESS

Catalyst evaluation through laboratory microreactors or a pilot plant provides valuable inputs for selecting an optimal catalyst for the commercial plant. Major steps in the catalyst evaluation procedure are the laboratory deactivation of catalyst to mimic the plant equilibrium catalyst (e-cat), laboratory conversion studies on deactivated catalysts, and modeling and simulation to translate the laboratory conversion results to the commercial-scale unit. For the convenience of the reader, a few frequently used terms are explained:

- "Fresh" fluid cracking catalyst is catalyst, as manufactured and sold by catalyst vendors.
- "Equilibrium" fluid cracking catalyst (e-cat) is the inventory of circulating catalyst composition in an FCC unit once it has reached a steady state within the environment of the FCC unit.
- The coke-laid-down catalyst, which was taken out from the FCC, is referred to as "spent catalyst."

Because of hydrothermal aging in a commercial unit, a portion of zeolite and matrix loses its structural integrity, leading to surface area and activity loss [34]. To maintain the desired activity, fresh catalyst (~1–2 % of the inventory) is added in a day, and an equal amount of spent catalyst is withdrawn from the system. Thus, the catalyst inventory in the unit is a mixture of different aged particles. Therefore, the e-cat activity, which is an average activity of particles of different ages, is lower than the fresh catalyst activity. Table 6.7 gives the typical properties of FCC fresh and e-cat samples. When selecting a fresh catalyst, the equivalent e-cat activity of new catalyst is needed, and this can be simulated in the laboratory by following a suitable laboratory deactivation method. Laboratory deactivation procedures attempt to simulate the changes that occur commercially under accelerated deactivation conditions [78].

TABLE 6.7—Comparison of Physical Characteristics of Catalysts

Physical Property	Plant E-Cat	Fresh Cat
BET surface area, m^2/g	157	325
Microporous area, m^2/g	99	265
Matrix surface area, m^2/g	58	60
Micropore volume, cm^3/g	0.04	0.1
Unit cell, Å	24.24	24.61

6.8.4.2 SIMULATION OF CATALYST DEACTIVATION

Fresh catalyst is subjected to laboratory deactivation, which involves metal doping, reduction/oxidation, and hydrothermal deactivation to simulate plant e-cat. Metals are loaded on the base catalyst over several cycles of cracking using a metal-doped VGO feed followed by catalyst regeneration at conditions similar to those encountered in the commercial FCC unit [79]. Alternatively, metals can be doped directly by impregnation [80,81]. Metal species doped by an impregnation method are more active; hence, only a fraction of the e-cat metals (~33 %) are targeted for laboratory deactivation to match the properties of plant e-cat.

6.8.4.3 COMMERCIAL YIELD ESTIMATION

Catalyst activity studies can be performed by bench-scale units such as a MAT or a fluid bed simulation test (FST) Liquid and gaseous products are typically analyzed using standard analysis equipment such as a gas analyzer [gas chromatograph (GC)] and a simulated distillation (SIMDIS) GC, whereas coke is estimated through online or offline methods by burning the deposited coke. Microreactor yield data are the key input for mathematical models. The mathematical models help in estimating the commercial yields from the laboratory experimental data. The procedure involves estimating catalyst-dependent kinetic parameters from laboratory experiments and estimating yields after incorporating suitable hydrodynamic aspects of the FCC hardware. For this procedure to be accurate, one must validate the model with several cases of plant data and carefully planned catalyst activity data.

6.8.5 Equilibrium Catalyst Monitoring and Troubleshooting

Monitoring of an e-cat provides valuable information pertaining to operational, mechanical, and catalyst aspects, thus aiding in unit optimization and troubleshooting various unit problems. The data analysis sheet comprises catalytic activity, physical properties, and chemical analysis

TABLE 6.8—E-Cat Data Analysis Sheet

	Activity			Physical Properties							Chemical Properties							
							PSD (wt %)											
Sample Date	Micro Activity	Coke Factor	Gas Factor	Surface Area (m^2/g)	Pore Volume (ml/g)	ABD (g/ml)	0–20	0–40	0–60	0–90	Al_2O_3 (Wt%)	C (wt %)	Na (wt %)	Fe (wt %)	Ni (ppm)	V (ppm)	Cu (ppm)	Sb (ppm)
22.6.09	66	0.8	1	121	0.3	0.81	9	20	70	80	42	0.27	0.18	0.31	722	719	12	0
15.6.09	68	0.7.	1	125	0.28	0.83	10	19	69	82	42	0.23	0.17	0.29	519	733	7	0
18.5.09	71	0.9	1.2	122	0.26	0.81	7	22	73	84	42.7	0.22	0.19	0.29	464	854	7	0
11.5.09	70	0.8	1	118	0.34	0.78	8	22	68	80	43	0.35	0.18	0.32	625	740	14	0
27.4.09	71	0.7	1	119	0.33	0.80	11	18	65	88	43	0.27	0.17	0.31	600	720	22	0

Coke factor is relative number that is proportional to specific coke, defined as *specific coke = coke yield* × (100 – *conversion*)/*conversion*.
Gas factor is a relative number that is proportional to the specific hydrogen yield. Specific hydrogen is defined as *specific* H_2 = H_2 *yield* × (*function of FST conversion*).

(Table 6.8) [41]. The e-cat monitoring is generally performed on weekly basis.

6.8.5.1 CATALYTIC ACTIVITY

Catalytic activity includes the conversion of VGO to gas, liquid, and coke. These are measured in a MAT/FST unit using standard gas oil feed at standard conditions. However, the MAT values can differ because each testing laboratory has benchmarked their own testing conditions against their own feeds.

Activity is a measure of the catalyst's ability to crack heavy oils to lighter products. It is generally reported as second-order conversion, or *Conv*/(100 – *Conv*). The gas factor indicates the effect of metals or change in fresh catalyst formulation, which influences dehydrogenation activity of the metals. The gas factor is a measure of a yield of gas produced in the MAT/FST. The coke factor is a measure of the catalyst coking tendency. It is expressed as coke yield divided by the second-order conversion. Higher metals increase the coke factor and are influenced by fresh catalyst properties.

6.8.5.2 PHYSICAL PROPERTIES

The main physical properties are surface area, average bulk density, particle size distribution, and the attrition index measurement.

- *Surface area (SA):* Measurement of SA is an indirect measurement of catalyst activity. A decrease in SA is an indication of loss of activity. SA loss may be due to hydrothermal deactivation or metal deactivation of the catalyst.
- *Particle size distribution (PSD):* Monitoring PSD is helpful to identify the strength of catalyst and the unit condition. A decrease in catalyst fines or loss of catalyst indicates an imbalance in cyclone performance. An increase in fines content shows increased catalyst or additives attrition. Figure 6.28 shows the changes in e-cat PSD with different problems in the unit.
- *Attrition index (AI):* AI measurement gives valuable information about the strength of the catalyst. The ASTM method for AI measurement is widely practiced. However, different laboratories practice different test protocol. An attrition measurement helps to predict the attrition behavior of fresh catalysts and additives. E-cat

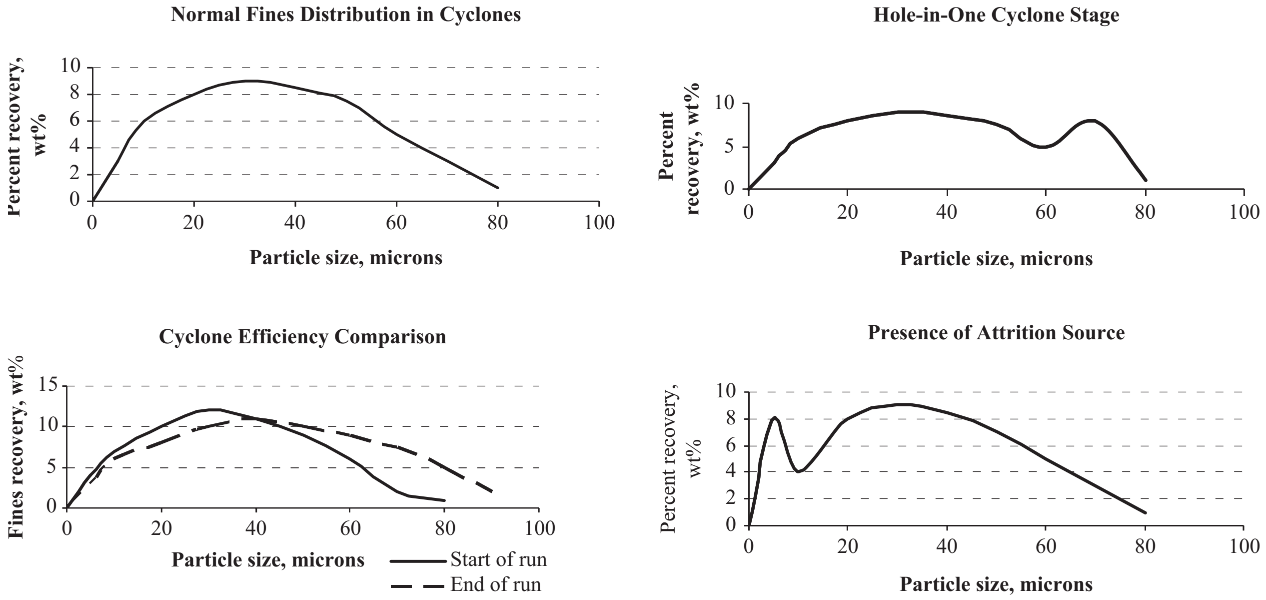


Figure 6.28—E-cat particle size as an indicator of regenerator problems [83].

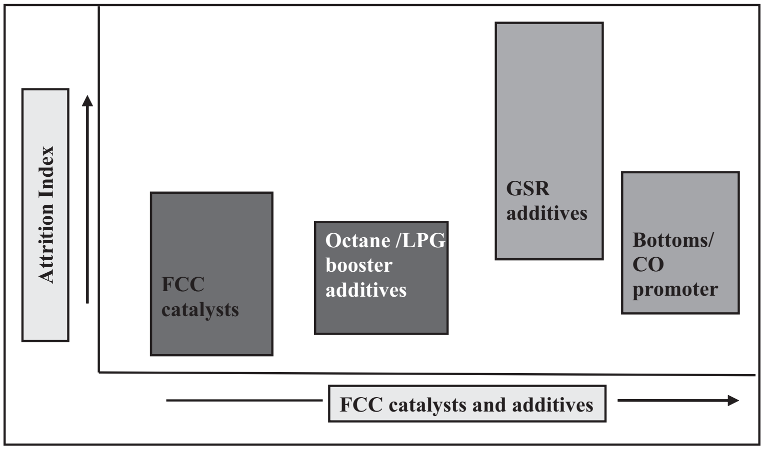


Figure 6.29—Attrition behavior of catalysts and additives.

attrition is performed only in the case of troubleshooting if there is excess generation of fines in the unit. There is always wide variation of attrition properties among the catalysts and additives. Figure 6.29 shows typical values of different catalysts and additives [53].

6.8.5.3 CHEMICAL PROPERTIES

Important chemical components include alumina, rare earth, sodium, carbon on the regenerated catalyst, and metals (nickel, vanadium, sodium, copper, and iron).

- *Alumina (Al_2O_3):* The regular measurement of alumina content indicates the catalyst inventory, fresh catalyst addition rate, or compositional changes in the catalyst or additives.
- *Rare earth content:* Rare earth content is an indirect indication of the zeolite type that was used for fresh catalyst preparation. The rare earth element forms bridges among acid sites and protects the leaching of acid sites from the framework. High rare earth content is an indication of high HT reactions, which are gasoline selective with low octane number.
- *Sodium (Na):* E-cat sodium content is a combination of fresh catalyst sodium and the sodium present in feed. Sodium is detrimental to the catalyst by deactivating the acid sites and causing the destruction of the zeolite crystal structure. Sodium inhibits HT reactions and increases the olefins in gasoline. The tolerance limit of commercial catalyst is approximately 4500 ppm without affecting the conversion and catalyst structures. Approximately 6 points of MAT activity are lost per weight percentage of sodium originating from the FCC feed. At high sodium levels the catalyst is also more sensitive to high regenerator temperature because of increased rates of sintering and SA destruction. High fresh catalyst addition rates are required to recover from sodium poisoning [83].
- *Nickel, vanadium, iron, and copper:* Catalyst coke- and gas-making tendencies increase when these heavy metals are deposited on the catalyst. Feed is the main source of nickel and vanadium. The monitoring of vanadium metal levels helps to predict the deactivation level of the catalyst. The loss in MAT activity with vanadium content on the catalyst is presented in Figure 6.28 [84]. It was also found that approximately 1000 ppm of vanadium on the e-cat reduces the sulfur species in the gasoline range. Nickel promotes dehydrogenation

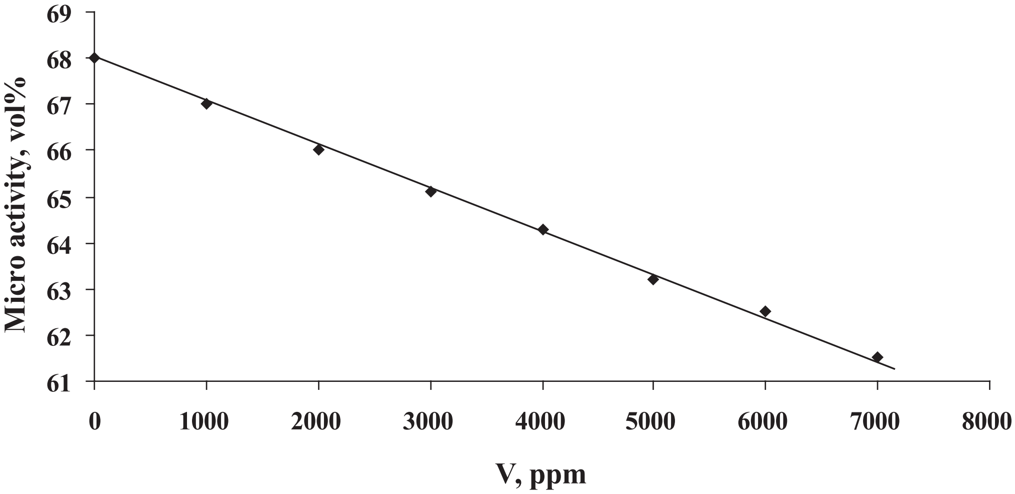


Figure 6.30—Variation in MAT activity with vanadium content [84].

reactions, leading to gas and coke make. The contribution to coke and gas make due to nickel, copper, vanadium, and other metals is commonly reported through indices that are in nickel-equivalent form (e.g., Davison index: $Ni + Cu + V/4$). The metals are active when deposited first and their activity reduces with continuous cycles of oxidation and reduction. On average, one-third of the nickel retains its dehydrogenation activity [41]. It is observed that iron, present in organic and inorganic forms, affects the activity of the main FCC catalyst. Iron changes the surface structure, blocks pores, reduces ABD, and increases slurry yield. A common cause of iron contamination is malfunctioning of the crude desalting unit. Grace Davison reported typical average e-cat iron levels to be 0.57 wt % [61].

- *Carbon:* The carbon level on the e-cat is an indicator of regenerator performance. FCC units operating in full combustion mode have carbon levels of 0.05 wt % or less on the e-cat, whereas partial combustion units have a carbon level of 0.1 wt % or higher. Any variation indicates a problem due to coke burning in the regenerator.

The typical e-cat evaluation datasheet is shown in Table 6.8. FCC units generally experience catalyst-related problems such as circulation, catalyst loss and activity decline, and hardware-related problems. Regular monitoring of the plant e-cat and fresh samples in terms of the physicochemical properties and activity in the MAT unit helps refiners to troubleshoot the unit problems in a more efficient manner and maintain the desired activity.

6.9 KEY PROCESS VARIABLES AND THEIR IMPACT ON OPERATIONS

The FCC process includes many variables; hence, the design or operating personnel must judiciously use them for meeting the process objectives. The important independent variables available for the refiner are riser temperature, feed flow rate, feed inlet temperature, catalyst activity and composition, and recycle rates, whereas the key dependent variables include catalyst circulation rates, regenerator temperature, and conversion [34].

Riser temperature and the catalyst-to-oil ratio are the key variables that decide the severity of FCC operation and hence are maximized for higher conversions. However, to maintain the heat balance between the riser and the regenerator, only riser temperature can be varied independently whereas the catalyst circulation rate and regenerator temperatures are bounded by the following heat balance relationships

- *Riser heat balance:* Enthalpy lost by the circulating catalyst = Heat of reaction + Enthalpy difference between feed and product + heat losses
- *Regenerator heat balance:* Heat of coke combustion = Enthalpy difference between flue gas and air + Enthalpy gain by the circulating catalyst + heat losses

A reduced feed temperature allows for higher catalyst circulation for a constant riser temperature. The increased catalyst circulation also decreases the regenerator bed temperatures because of higher heat removal as sensible heat. The net heat of reaction, although endothermic, is a strong function of the type of feed and the catalyst used. The HT reactions are exothermic; hence, the net heat of reaction with rare-earth-based catalysts is generally lower than the USY-based catalyst because of higher HT reactions with the former. The recycling of unconverted feed is typically practiced with low severity units and sometimes to balance the coke make or when catalyst fines loss is high. Recycling of unconverted feed increases coke on catalyst as well as regenerator temperature. The catalyst activity can be controlled through proper design and selection of optimal fresh catalyst as well as optimal catalyst addition rates [85]. Although there are several variables available in FCC, because of the heavy interdependence the refiner has a narrow range of options for process optimization, which needs to be exploited gainfully.

6.10 DIVERSE APPLICATIONS AND CONTINUOUS IMPROVEMENTS

The FCC process, which was originally invented for gasoline production, has evolved over the last 60 years. Figure 6.31 summarizes the key technological milestones and the

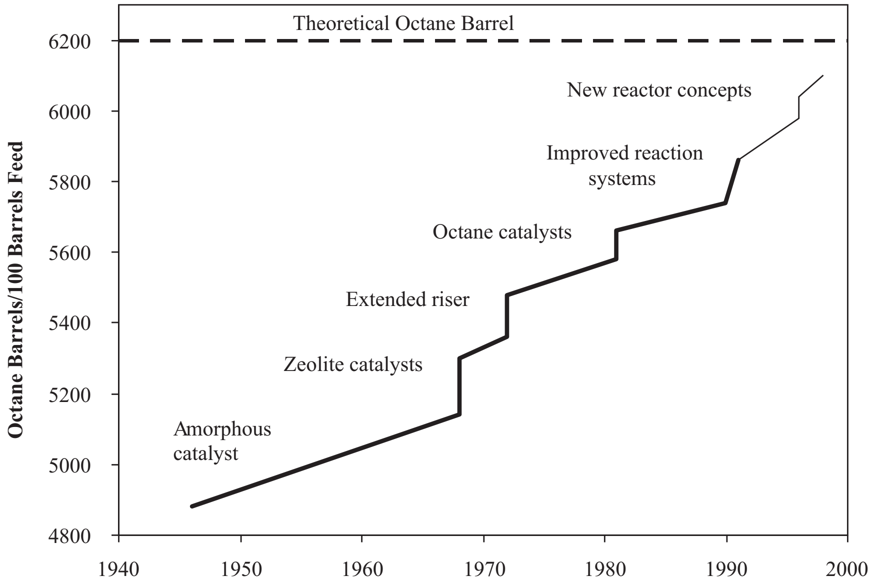


Figure 6.31—Summary of the key technological milestones and the progress with reference to theoretical targets over these years.

progress with reference to theoretical targets [86]. Over these years, the process has been successfully adapted to maximize diesel and LPG through changes in catalyst and operating conditions. The LPG mode of operation has been further improved to selectively maximize either propylene or butylene. Propylene production is attracting major attention because of huge demand, and it is estimated that nearly 30–40 % propylene would be produced through FCC. Propylene-selective DCC technologies are commercially available from licensors such as UOP, Stone and Webster/RIPP, etc., whereas new entrants such as IOCL also offer similar technologies (Indmax™) [87].

To further maximize the light olefin production, downer reactors are being advocated in recent developments. The key advantages envisaged are reduced HT reactions for lower coke make and more valuable olefins by exploiting the down-flowing high catalyst velocities with short residence times. Following this theme, UOP has set up the millisecond catalytic cracking unit, whereas the Nippon Oil and Saudi Aramco consortium are in an advanced stage of development [88]. New processes for upgrading olefin- or paraffin-rich naphtha along with VGO feed or on a standalone mode are also available for licensing. In this process, to maximize conversions, zeolite-rich catalyst formulations and high severity conditions are proposed in duel riser configurations (e.g., Maxofin™ of KBR) [89]. Exploiting these concepts further, several new engineering innovations aim to obtain better distillate yields, reduced gasoline olefins, and maximal iso-paraffins than conventional FCC [90,91]. The invention of new materials such as ITQ-33 with large-pore 18-membered rings opened new dimensions for oil cracking [92]. Synthesis of nano-sized zeolite-based FCC catalysts and their catalytic activity for cracking was recently reported [93]. In this synthesis, organic solvents such as formamide and toluene are used instead of water for zeolite crystallization to achieve nanoparticles. Likewise, with the shifting demand toward diesel, FCC catalyst manufacturers are coming up with improved catalyst solutions with controlled matrix dispersions and high stability. In another innovation, UOP reported application of an FCC-based technology for upgrading low-API, high-viscosity, pour-point crudes to pumpable specification [94]. Recently, with an increased availability of biomass, upgrading biofuels through an FCC route is being seriously considered as a co-processing option along with gas oil feeds [95]. A quick glance at such wide ranging applications from conventional downstream fuel and petrochemical processes to nonconventional crude upgrading in upstream reveals that more diverse applications are expected in the future in accordance with demand.

6.11 SUMMARY

The FCC process has witnessed continuous improvements since its genesis. Perhaps no other industrial process has received such extensive attention in a sustainable manner. New materials, catalysts, and improvement in hardware design contributed substantially to these developments. As a process, FCC has reached maturity for gasoline production, whereas the diverse applications continue to fuel its growth. In the coming years, higher value addition, tighter integration with other conversion processes, production of high-quality fuels from heavy feeds, and reduced emissions and reliability are other drivers that are likely to further catalyze the new innovations.

ACKNOWLEDGMENTS

The authors gratefully acknowledge generous inputs from M/s KBR, Inc., Axens/Shaw, Exxon Mobil, UOP, Albemarle, Grace Davison, Intercat, PSRI, and BPCL management for giving permission to publish this work.

REFERENCES

[1] Avidan, A.A., and Reuel, S., "Development of Catalytic Cracking Technology: A Lesson in Chemical Engineering Design," *Ind. Eng. Chem. Res.*, Vol. 29, 1990, pp. 931–942.

[2] Schnaith, M.W., Gilbert, A.T., Lomas, D.A., and Myers, D.N., "Advances in FCC Reactor Technology," Paper AM-95-36 presented at the NPRA Annual Meeting, San Francisco, CA, 1995.

[3] Grace Davison Guide to Fluid Catalytic Cracking, Parts I, II, and III, 1993–1999.

[4] Venuto, P.B., and Habib, E.T.J., "Fluid Catalytic Cracking with Zeolite Catalysts," Marcel Decker, New York, 1979.

[5] Bonifay, R., and Marcilly, C., "Catalytic Cracking," in P. Leprince (Ed.), *Conversion Processes*, Technip Editions, Paris, 1998.

[6] Blanding, F.H., "Reaction Rates in the Catalytic Cracking of Petroleum," *Ind. Eng. Chem. Res.*, Vol. 45, 1953, pp. 1186–1197.

[7] Bollas, G.M., Vasalos, I.A., Lappas, A.A., Iatridis, D.K., and Tsioni, G.K., "Bulk Molecular Characterization Approach for the Simulation of FCC Feed Stocks," *Ind. Eng. Chem. Res.*, Vol. 43, 2004, pp. 3270–3281.

[8] Voorhies, A., "Carbon Formation in Catalytic Cracking," *Ind. Eng. Chem. Res.*, Vol. 37, 1945, p. 318.

[9] Krambeck, F.J., "Continuous Mixtures in Fluid Catalytic Cracking and Extensions," Mobil Workshop on Chemical Reaction in Complex Mixtures, Van Nostrand Reinhold, New York, 1991, pp. 1–8.

[10] Arbel, A., Huang, Z., Rinard, I.H., Shinnar, R., and Sapre, A.V., "Dynamic and Control of Fluidized Catalytic Crackers. 1. Modeling of the Current Generation FCCs," *Ind. Eng. Chem. Res.*, Vol. 34, 1995, pp. 1228–1243.

[11] Ancheyta, J., and Murillo, J.A., "A Simple Method for Estimating Gasoline, Gas and Coke Yields in FCC Processes," *Energy & Fuels*, Vol. 14, 2000, pp. 373–379.

[12] Jacob, S.M, Gross, B., Voltz, S.E., and Weekman, V.M., Jr., "A Lumping Reaction Scheme for Catalytic Cracking," *AIChE J.*, Vol. 22, 1976, pp. 701–713.

[13] Weisz, P.B., "Combustion of Carbonaceous Deposits within Porous Catalyst Particles, III. The CO_2/CO Product Ratio," *J. Catal.*, Vol. 6, 1966, pp. 425–430.

[14] Wilson, J.W., *Fluid Catalytic Cracking Technology and Operation*, PennWell, Tulsa, OK, 1997.

[15] Albemarle, FCC manual 5.10, "FCC Unit Monitoring," p. 4.

[16] ASTM Standard D611-07: Standard Test Methods for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 2007.

[17] ASTM Standard D1218-02: "Standard Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 2007.

[18] Ackelson, D.B., Antos, G.J., Christolini, B.A., Krenze, L.D., and Wood B.M., "UOP's Hydroprocessing Experience—Customized Solutions for Improved Diesel Quality," Paper presented at the UOP Refining Technology Conference, 1995.

[19] Brierley, G.R., Gembicki, V.A., Cowan T.M., "Changing refinery configuration for heavy and synthetic crude processing,"paper AM-06-1, presented at the NPRA Annual Meeting, Salt Lake City, UT, 2006.

[20] Lomas, D.A., Cabrera, C.A., Cepla, D.M., Hemler, C.L., and Upson, L.L., "Controlled Catalytic Cracking," Paper presented at the UOP Technology Conference, 1990.

[21] Letzsch, W.S., “Deep Catalytic Cracking, the New Light Olefins Generator,” in R.A. Meyers (Ed.), *Handbook of Petroleum Refining Processes*, 3rd ed., McGraw Hill, New York, 2003a.

[22] Soni, D., Rama Rao, M., Saidulu, G., Bhattacharya, D., and Satheesh, V.K., “Catalytic Cracking Process Enhances Production of Olefins,” *Petrol. Technol. Quarter.*, Q4, 2009, pp. 95–100.

[23] Dharia, D., Kim, H., Letzsch, W.S., McCue, D., and Chapin, L., “Increase Light Olefins Production,” *Hydrocarbon Process.*, April, 2004.

[24] Hemler, C.L., and Smith, L.F., “UOP Fluid Catalytic Cracking Process,” in R.A. Meyers (Ed.), *Handbook of Petroleum Refining Processes*, 3rd ed., McGraw Hill, New York, 2003.

[25] Niccum, P.K., Santer C.R., “KBR Fluid Catalytic Cracking Process,” in R.A. Meyers (Ed.), *Handbook of Petroleum Refining Processes*, 3rd ed., McGraw Hill, New York, 2003.

[26] Chapin, L.E., and Letzsch, W.S., “Deep Catalytic Cracking,” *Petrol. Technol. Quarter.*, Winter, 1996/1997, pp. 57–66.

[27] Letzsch, W.S., “Commercial Performance of the Latest FCC Technology Advances,” Paper AM-00-07 presented at the NPRA Annual Meeting, San Antonio, TX, 2000.

[28] Chen, Y., “Recent Advances in FCC Technology,” *Powder Technol.*, Vol. 163, 2006, pp. 2–8.

[29] Letzsch, W.S., *Stone and Webster–Institut Français du Pétrole Fluid RFCC Process*, 3rd ed., R.A. Meyers (Ed.), McGraw Hill, New York, 2003b.

[30] Levenspiel, O., *Chemical Reaction Engineering*, 3rd ed., John Wiley & Sons, New York, 1999.

[31] Letzsch, W.S., Santner, C., and Tragesser, S., “FCC Reactor Design: Part I,” *Petrol. Technol. Quarter.*, Q4, 2008, pp. 63–67.

[32] Miller, R.B., Johnson, T.E., and Santner, C.R., “The Impact of State-of-the-Art FCC Reaction System Technology,” presented at the M.W. Kellogg Company Refining Technology Seminar, 1995.

[33] Gupta, A., and Subba Rao, A., “Model for the Performance of a Fluid Catalytic Cracking (FCC) Riser Reactor: Effect of Feed Atomization,” *Chem. Eng. Sci.*, Vol. 56, 2001, pp. 4489–4503.

[34] King, D., “Engineering of Fluidized Catalytic Crackers,” in H.I. de Lasa, G. Dogu, and A. Ravella (Eds.), *Chemical Reactor Technology for Environmentally Safe Reactors and Products*, Springer, New York, 1992.

[35] Kauff, D., and Hedrick, B.W., “FCC Process Technology for the 1990s,” Paper AM-92-06 presented at the NPRA Annual Meeting, New Orleans, LA, 1992.

[36] Avidan, A.A., Krambeck, F.J., Owen, H., and Schipper, P.H., “FCC Closed-Cyclone System Eliminates Post Riser Cracking,” *Oil & Gas J.*, March, 1990.

[37] Avidan, A.A., “Fluid Catalytic Cracking,” in J.R. Grace, A.A. Avidan, and T.M. Knowlton (Eds.), *Circulating Fluid Beds*, Blackie Academic & Professional, London, 1997, pp. 466–488.

[38] Papa, G., and Zenz, F.A., “Correlating Throughput and Back Mixing in Fluidized Beds,” *Hydrocarbon Process.*, January, 1995, pp. 81–87.

[39] York, J.L., Barberio, J.T., Samyn, M., Zenz, F.A., and Zenz, J.A., “Solve All Column Flows with One Equation,” *Chem. Eng. Prog.*, October, 1992, p. 93.

[40] Zenz, F.A., Othmer, D.F., “Fluidization and Fluid-Particle Systems,” Reinhold, 1960.

[41] Reza, S., *Fluid Catalytic Cracking Handbook: Design, Operation, and Troubleshooting of FCC Facilities*, 2nd Ed., Gulf Publishing: Houston, TX, 2000.

[42] Grace Davison Guide to Fluid Catalytic Cracking Part I, 1993, pp. 69–70.

[43] Knowlton, T.M., “Standpipes and Return Systems,” in J.R. Grace, A.A. Avidan, and T.M. Knowlton (Eds.), *Circulating Fluid Beds*, Blackie Academic & Professional, London, 1997, pp. 214–260.

[44] Karri, S.B.R., and Knowlton, T.M., “Comparison of Group A Solids Flow in Hybrid Angled and Vertical Stand Pipes,” in A. Avidan (Ed.), *Circulating Fluid Bed Technology IV*, AIChE, New York, 1993, pp. 253–259.

[45] Zenz, F.A., *Fluidization and Fluid Particle Systems, Vol. II Draft*, Pemm-Corp Publications, Cold Springs, NY, 1989.

[46] Geldart, D., and Radtke, A.L., “The Effect of Particle Properties on Behaviour of Equilibrium Cracking Catalysts in Standpipe Flow,” *Powder Technol.*, Vol. 47, 1986, pp. 157–165.

[47] Singh, H., Voolapalli, R.K., and Chopra, S.J., “Efficient Hardware Design Selection for Commercial FCC Regenerator Air Grids,” in J.R. Grace, J. Zhu, and H. de Lasa (Eds.), *Proceedings of the 7th International Conference on Circulating Fluidized Beds*, Niagara Falls, Ontario, Canada, 2002, pp. 857–864.

[48] Zenz, F.A., “Bubble Formation and Grid Design,” *I. Chem. E. Symp. Ser.*, Vol. 30, 1968, pp. 136–139.

[49] Zenz, F.A.,“Cyclone Design Tips,” *Chem. Eng.*, January, 2001, pp. 60–64.

[50] Wilson, J.W., “Modernize Older FCCUs,” Paper AM-00-09 presented at the NPRA Annual Meeting, San Antonio, TX, 2000.

[51] Karri, S.B.R., and Knowlton, T.M., “Cyclone Section,” in *PSRI Fluidization Seminar Handbook*, Particulate Solid Research, Inc., Chicago, 2010.

[52] Scherzer, J., “Correlation between Catalyst Formulation and Catalytic Properties,” in J.S. Magee and M.M. Mitchell (Eds.), *Stud. Surf. Sci. Catal.*, Vol. 76, 1993, pp. 145–183.

[53] Gokak, D.T., Chiranjeevi, T., Ravikumar, V., and Choudary, N.V., “Attrition Behaviour of Catalysts and Additives,” paper presented at the XIV Refinery Technology Meeting, Trivandrum, India, 2007, p. 47.

[54] Lim, T.F., Haryanto, A., Tallulembang, I., and Jaya, K.A., “Aurora-LC Demonstrates Superior Performance in Severe Resid Application,” *Davison Catalysts Catalagram News*, July 2002.

[55] Zhao, X., Cheng, W.C., and Rudesill, J.A., “FCC Bottoms Cracking Mechanisms and Implications for Catalyst Design for Resid Applications,” Paper AM-02-53 presented at the NPRA Annual Meeting, San Antonio, TX, 2002.

[56] Shuqin, S., “Additives Used in Catalytic Cracking of Hydrocarbons,” U.S. Patent 6723228, 2004.

[57] Dwayne, R.S., and Bartlesville, O., “Metals Passivation of Cracking Catalysts,” U.S. Patent 5389233, 1995.

[58] Majon, R.J., and Spielman, J., “Increasing Gasoline Octane and Light Olefin Yields with ZSM-5,” *Catalyst Report*, Vol. 5, 1990, pp. 45–57.

[59] Yaluris, G., Cheng, W.C., Peters, M., Hunt, L.J., and Boock, L.T., “The Effects of Fe Poisoning on FCC Catalysts,” Paper AM-01- presented at the NPRA Annual Meeting, New Orleans, LA, 2001.

[60] Rautainen, E., “Control Iron Contamination in Resid FCC,” *Hydrocarbon Process.*, January, 2001.

[61] Hunt D., Proceedings of NPRA 2010 Q&A and Technology Forum, Session on Refining and Petrochemical Technology, Baltimore, MD, 2010.

[62] Grace Davison Guide to Fluid Catalytic Cracking Part III, 1999, p. 133.

[63] Rao, M.R., Mandal, S., Das, A.K., Krishnan, V., Makhija, S., “Options for Maximizing Propylene/Light Olefins Production in Refineries,” Intercat-IOCL FCC Catalyst Additive Symposium, Mumbai, India., February, 2006.

[64] Michael, K.M., “Reducing Gasoline Sulphur with Additives,” *Petrol. Technol. Quarter.*, 2004, pp. 71–75.

[65] Harding, R.H., Peters A.W., and Nee J.R.D., “New Developments in FCC Technology,” *Appl. Catal. A*, Vol. 221, 2001, pp. 389–396.

[66] Anderson, P.-O.F., Pirjamali, M., Jaras, S.G., and Boutonnet-Kizling, M., “Cracking Catalyst Additives for Sulfur Removal from FCC Gasoline,” *Catal. Today*, Vol. 53, 1999, pp. 565–573.

[67] Myrstad, T., Engan, H., Seljestokken, B., and Rytter, E., “Sulphur Reduction of Fluid Catalytic Cracking Naphtha by an In Situ Zn/Mg (Al)OFCC Additive,” *Appl. Catal. A*, Vol. 187, 1999, pp. 207–212.

[68] Shan, H.H., Li, C.Y., Yang, C.H., Zhao, H., Zhao, B.Y., and Zhang, J.F., “Mechanistic Studies on Thiophene Species Cracking over USY Zeolite,” *Catal. Today*, Vol. 77, 2002, pp. 117–126.

[69] Vargas-Tah, A.A., Garcia, R.C., Archila, L.F.P., Solis, J.R, and Lopez, A.J.G., “A Study on Sulphur Reduction in FCC Gasoline Using Zn-Mg-Al Spinels,” *Catal. Today* Vol. 107–108, 2005, pp. 713–718.

[70] http://www.Intercatinc.com.

[71] Bharatan, S., "Maximization of HS Crude Processing Using FCC Additives," presented at the Environment and Profitability Challenges and Opportunities in FCC, IOC and Intercat Joint FCC Catalyst and Additives Seminar, New Delhi, India, January, 2008.

[72] Baruah, B.J., Jagannadha Rao, M., Bharathan, S., and Varaprasad, P.N., "Sulphur Dioxide Emission Reduction by Using DeSOx Additive in FCC Units at HPCL–Visakh Refinery,“ Presented at the XIV Refinery Technology Meeting, Trivandrum, India, 2007.

[73] Arthur, W.C, "CO Combustion of Promoters: Past and Present," in *Studies in Surface Science and Catalysis*, Vol. 166, 2007, pp. 67–76.

[74] Lliopoulou, E.A., Efthimiadis, L., Nalbandian, B., Vasalos, I.A., Barth, J.O., and Lercher, J.A., "Ir-Based Additives for NO Reduction and CO Oxidation in the FCC Regenerator: Evaluation, Characterization and Mechanistic Studies," *Appl. Catal. B*, Vol. 60, 2005, pp. 277–288.

[75] Gudio, W.A., "FCC Additive Demonstrations, Part 2," *Petrol. Technol. Quarter.,* Q4 2004, pp. 49–58.

[76] Zhao, X., Peters, A.W., and Weatherbee, G.W., "Nitrogen Chemistry and NO_x Control in FCC Regenerator," *Ind. Eng. Chem. Res.*, Vol. 36, 1997, pp. 4535–4542.

[77] Cheng, W.C., Kim, G., Peters, A.W., Zhao, X., Rajagopalan, K., Ziebarth, M.S., and Pereira, C.J., "Environmental Fluid Catalytic Cracking," *Catal. Rev. Sci. Eng.,* Vol. 40 1998, pp. 39–79.

[78] Ravichander, N., Chirajeevi, T., Gokak, D.T., Voolapalli R.K., and Choudary, N.V., "FCC Catalyst and Additive Evaluation—A Case Study," *Catal. Today,* Vol. 141, 2009, pp. 115–119.

[79] Gerritsen, L.A., Winjngaards, H.N.J., Verwoert, J., and Connor, P.O., "Cyclic Deactivation: A Novel Technique to Simulate the Deactivation of FCC Catalyst in Commercial Units," *Catal. Today,* Vol. 1, 1994, pp. 61–72.

[80] Bendiksen, M., Tangstad, E., and Myrstad, T., "A Comparison of Laboratory Deactivation Methods for FCC Catalysts," *Appl. Catal.,* Vol. 129, 1995, pp. 21–31.

[81] Chiranjeevi, T., Ravichander, N., Gokak, D.T., Ravikumar, V., and Choudary, N.V., "Development of Alternate Method for Simulation of FCC E Cat in the Laboratory," in Proceedings 7th International Oil & Gas Conference, New Delhi, India, 2007.

[82] Albemarle, FCC manual 5.5, "Troubleshooting Catalyst Losses on the FCC," http://www.albemarle.com/products_and_services/catalysts/fcc/Services/_Technical_papers.

[83] Albemarle, FCC manual 5.3, "FCC Catalyst Analysis," http://www.albemarle.com/products_and_services/catalysts/fcc/Services/_Technical_papers.

[84] Grace Davison Guide to Fluid Catalytic Cracking, Parts I, II, and III, 1993–1999.

[85] Voolapalli, R.K., Ravichander, N., Murali, C., Gokak, D.T., Choudary, N.V., and Siddiqui, M.A., "Fine-Tune Catalyst Addition Rates," *Hydrocarbon Processing*, August, 2007, pp. 109–112.

[86] Gembicki, S.A. "Innovation and Future Energy Challenges," presented at the Lovraj Kumar Memorial Presentation, New Delhi, India, 2006.

[87] Mandal, S., Kumarshah, S., Bhattacharya, D., Murthy, V.L.N., Das, A.K., Singh, S., Thakur, R.M., Sharma, S., Dixit, J.K., Ghosh, S., Das, S.K., Santra, M., Saroya, L.L., Rao, M.R., Mishra, G.S., and Makhija S., "Process for Catalytic Cracking of Petroleum Based Feed Stocks," U.S. Patent 5846402, 1998.

[88] Fujiyama, Y., Nakanishi, M., Dean, C., Al-Tayyar, M., Aitini, A., and Saeed, M., "High Severity FCC Operation," *Petrol. Technol. Quarter.,* Q1, 2007, pp. 101–105.

[89] Niccum, P.K., Gilbert, M.F., Tallman, M.J., and Santner, C.R., "Future Refinery—FCC Role in Refinery/Petrochemical Integration," Paper AM-01-61 presented at the NPRA Annual Meeting, New Orleans, LA, 2001.

[90] Han, W.D., Huang, R.K., and Gong, J.H., "Commercial Application of New FCC Process MIP-CGP," *Petrol. Refinery Eng.*, Vol. 36, 2006, pp. 1–4.

[91] Lan, X., Xu, C., Wang G, Wu, L., and Gao, J., "CFD Modeling of Gas–Solid Flow and Cracking Reaction in Two-Stage Riser FCC Reactors," *Chem. Eng. Sci.*, Vol. 64, 2009, pp. 3847–3858.

[92] Corma, A., Diaz-Cabanas, M., Luis Jorda, J., Martinez, C., and Moliner, M., "High Throughput Synthesis and Catalytic Properties of a Molecular Sieve with 18 and 10 Member Rings," *Nature*, Vol. 443, 2006, pp. 842–845.

[93] Vuong, G.-T., Hoang, V.-T., Nguyen, D.-T., and Do, T.-O., "Synthesis of Nanozeolites and Nanozeolite-Based FCC Catalysts, and Their Catalytic Activity in Gas Oil Cracking Reaction," *Appl. Catal. A*, Vol. 382, 2010, pp. 231–239.

[94] Hedrick, B.W, Seibert, K.D., and Crewe, C., "A New Approach to Heavy Oil and Bitumen Upgrading," Paper AM-06-29, presented at the NPRA Annual Meeting, Salt Lake City, UT, 2006.

[95] Lappas, A.A., Bezergianni, S., and Vasalo, I.A., "Production of Biofuels via Co-Processing in Conventional Refining Processes," *Catal. Today*, Vol. 145, 2009, pp. 55–62.

7

Hydroisomerization of Paraffins in Light Naphthas and Lube Oils for Quality Improvement

B.L. Newalkar[1], N.V. Choudary[1], and M.A. Siddiqui[1]

7.1 INTRODUCTION

With an increased worldwide environmental concern, the operation of the modern refinery is becoming more and more complex for meeting stringent transportation fuel specifications. For gasoline the challenge is to maintain high octane while meeting stricter requirements for Reid vapor pressure (RVP), removing lead-based antiknock agents such as tetraethyl lead, removing of benzene, aromatic control, lower sulfur content, and the impending ban of the gasoline oxygenate methyl tertiary butyl ether (MTBE) and other homologues with longer alkyl side chains. However, the reduction in high-octane possessing aromatics, olefins, and oxygenate components would result in the lowering of octane number of gasoline. Thus, to compensate for the RON loss, the highly branched alkanes are a desired alternative because of their high octane numbers (Table 7.1) to produce reformulated gasoline (RFG) [1,2].

Because of this, hydroisomerization of light naphtha, which produces isoparaffin-based high-octane gasoline blend stock from light- and mid-cut naphtha, has gained importance in recent time. Hydroisomerization (light naphtha for gasoline) accounts for approximately 2 % of the total crude processed, and naphtha hydroisomerization capacity has increased from 1.26 million barrels per day (mbpd) in 1995 to 1.51 mbpd in 2002. It is further estimated to increase at the rate of 5.8 % per year [2].

Similarly, futuristic demands for base oil in terms of higher purity, high viscosity index (VI), lower volatility, and longer life has led to emergence of a hydroisomerization-based dewaxing route in the early 1990s for the production of lube oil base stock (LOBS) [3]. Lube base oils produced by hydroisomerization-based dewaxing, coupled with hydrofinishing in conjunction with severe hydrocracking, offer the following attractive features:

- Very high VI (100 to 130),
- Low volatility,
- Superior oxidation resistance,
- High thermal stability,
- Excellent low-temperature fluidity, and
- Low toxicity.

These features in the lube oil are achieved by increasing the isoparaffins and maximizing saturates by means of the hydroisomerization and hydrofinishing step, respectively. This can be seen from Table 7.2, in which the effect of hydrocarbon types on the properties of lube oil is summarized. The aforementioned features give performance characteristics in finished lubricants very similar to synthetic ones such as poly-alpha-olefins (PAO).

On the basis of these features, the American Petroleum Institute (API) established a base oil classification as given in Table 7.3.

Most of the above developments were possible because of significant advances over the last 3 decades in the selective hydroconversion of n-alkanes into their branched isomers. Thus, this chapter is aimed at understanding the chemistry of catalyst developments in the evolution of hydroisomerization processes along with their salient features.

7.2 PROCESS THERMODYNAMICS AND CATALYST CHEMISTRY

The hydroisomerization of n-paraffin is a thermodynamic equilibrium-driven reaction with mild exothermicity on the order of –4 to –20 kJ/mol. It occurs without any variation in the number of moles and is therefore not influenced by variations in pressure [4].

The hydroisomerization reaction is always accompanied by a hydrocracking reaction that lowers more or less the yield for the isomerized hydrocarbons. The rates for the isomerization and cracking steps determine the product distribution. It may be noted that the rates of the hydroisomerization and hydrocracking of alkanes, as two competitive reactions, strongly depend on the carbon numbers in the feed molecules [5,6]. Light alkanes such as *n*-hexane can be cracked only slowly via the secondary carbenium ions as transition states, leading to a high selectivity to isomerization. On the other hand, multibranched isomers of long-chain n-paraffins are more prone to cracking because of their adsorption ability over the catalyst surface than those of the short-chain, multibranched isomers of C_5 and C_6 paraffins that constitute light naphtha [5,6]. Thus, to decrease cracking reactions, one must limit multibranching at its optimal level to have a successful hydroisomerization of long-chain n-paraffins [5,6]. On the basis of the aforementioned considerations, the best adapted catalysts to this

---

[1] Bharat Petroleum Corporation, Ltd., Greater Noida, India

TABLE 7.1—RON of Pure Paraffins

Paraffin	RON	Paraffin	RON
n-Butane	113	2,3-Dimethylbutane	96
Isobutane	122	*n*-Heptane	0
n-Pentane	62	2-Methylhexane	41
2-Methylbutane	99	3-Methylhexane	56
2,2-Dimethylpropane	100	3-Ethylpentane	64
n-Hexane	19	2,2-Dimethylpentane	89
2-Methylpentane	83	2,3-Dimethylpentane	87
3-Methylpentane	86	2,2,3-Trimethylbutane	113
2,2-Dimethylbutane	89		

TABLE 7.2—Lube Oil Components and Their Properties

Hydrocarbon Type	Viscosity	VI	Pour Point	Stability	Value in Lube Oil
n-Paraffins (wax)	High	High	High	Medium	Very low
i-Paraffins	Medium	High	Medium	Medium	High
Naphthenes	High	Low	Low	Medium	Medium
Aromatics	Low	Low	Low	Low	Very low

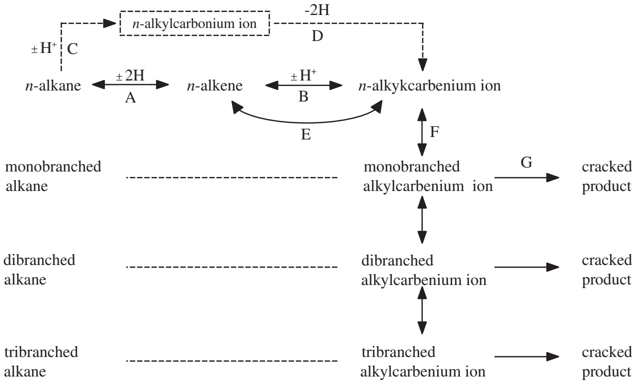
TABLE 7.3—API Classification of Base Oils

Group	Saturate wt %	Sulfur wt %	VI
I	<90	>0.03	>80 to <120
II	≥90	≤0.03	≥80 to ≤120
III	≥90	≤0.03	≥120
IV	All PAOs		
V	All base stocks not included in groups I–IV		

reaction must be tailored to favor hydroisomerization over hydrocracking reactions.

Hydroisomerization catalysts are bifunctional in nature and consist of a metal, such as platinum (Pt), dispersed on an acidic support. The metal function acts as a dehydrogenation/hydrogenation agent whereas the acidic support is responsible for the skeletal isomerization reaction of the olefinic intermediates formed over the metal sites and cracking. If the metal and acid functions on the catalyst are well balanced, the catalysts are referred to as ideal bifunctional catalysts. Over these ideal bifunctional catalysts, the hydrogenation and dehydrogenation reactions occur rapidly and the rearrangements of the hydrocarbon intermediates over the acid sites constitute the rate-determining steps. As a consequence, the hydroisomerization and hydrocracking reactions appear to occur consecutively, with the sequence of products being monobranched isomers, dibranched isomers, and then cracked products [5,6].

The pictorial representation of the aforementioned steps is illustrated as follows:



where:

A = hydrogenation-dehydrogenation on metal sites,
B = protonation-deprotonation on acid sites,
C = addition of proton to form alkyl carbenium ion on acid sites,
D = dehydrogenation to form alkyl carbenium ion,
E = competitive adsorption-desorption of alkene and carbenium ion on acid sites,
F = rearrangement of alkyl carbenium ion, and
G = cracking of alkyl carbenium ion.

In view of the above, the preferred consecutive steps for successful isomerization are summarized as follows:

- Dehydrogenation on the metal,
- Protonation of olefins on the Brönsted acid sites with formation of a secondary alkyl carbenium,
- Rearrangement of the alkyl carbenium ion via formation of cyclic alkyl carbenium-type transition state,
- Deprotonation, and
- Hydrogenation on the metal.

Thus, it is imperative that the ideal hydroisomerization catalyst must have an optimal balance between metal and acid functions to favor isomerization. The degree of isomerization in terms of branching usually depends on the targeted application. For example, multibranched paraffin isomers are desired to achieve the RON (Table 7.1) whereas mono- and dibranched paraffins are more preferred as lube oil components (Table 7.2) to meet the VI parameter for lube oil. Therefore, it is but obvious that catalyst requirements differ for light naphtha and lube-range paraffin isomerization, respectively. Thus, catalysts for light naphtha isomerization are designed to produce multibranched paraffin isomers whereas those of wax isomerization are tailored to favor mono- and dibranched long-chain paraffin isomers. Typical features of such catalysts are described in the following section.

7.3 HYDROISOMERIZATION CATALYSTS

7.3.1 Catalyst for Light Naphtha Isomerization

Light naphtha isomerization suffers from thermodynamic limitations (Figure 7.1) and equilibrium shifts toward low-octane isomers at higher reaction temperature (e.g., from dimethylbutanes via methylpentanes to *n*-hexane) [6]. On the other hand, the rate of reaction can become a limiting factor at lower temperatures for achieving the desired RON. Therefore, it is desirable to use very active catalyst to perform this reaction at a lower temperature. The catalysts used for the

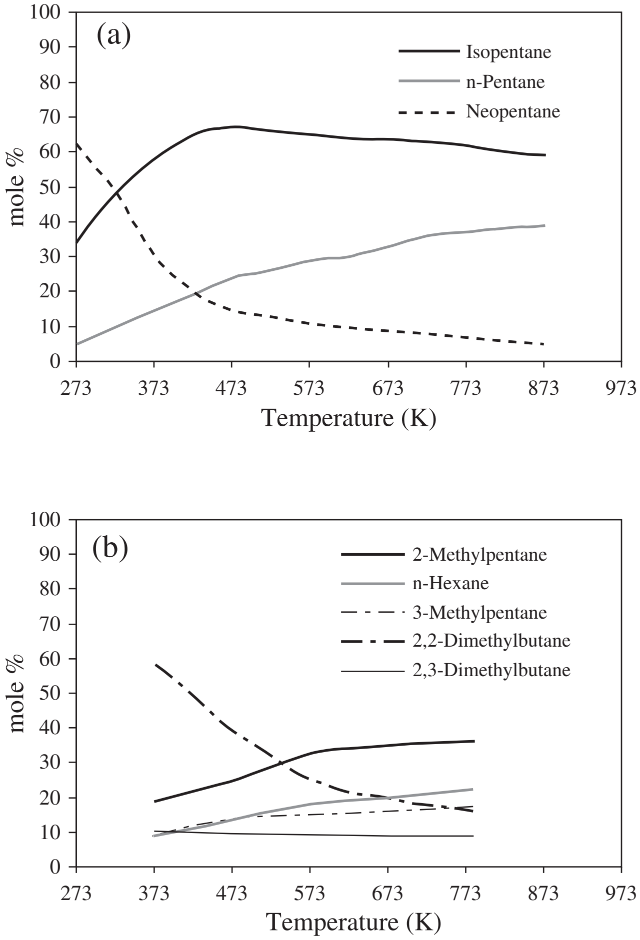


Figure 7.1—Thermodynamic distribution of (a) C_5 and (b) C_6 paraffins.

earlier industrial isomerization of light n-paraffins (n-C_4-n-C_8) were Friedel–Crafts catalysts such as $AlCl_3$ with additives such as $SbCl_3$ and HCl. These catalysts were strongly acidic and very active even at 353–390 K [4]. However, the processes using these catalysts do not exist anymore because of the problems of corrosion of the reactor and the disposal of the spent catalysts. Moreover, they were very sensitive to poisons such as water, aromatics, and sulfur [4]. These disadvantages have added impetus to the development of new/improved catalysts in this field.

The second-generation catalysts introduced were similar to reforming catalyst having a bifunctional role. Typically, Pt/alumina was used. However, these catalysts were found to be effective in the high temperature range wherein significant cracked products were formed. Thus, such catalysts are prone to rapid deactivation and thermodynamic limitations on conversion per pass [4].

To overcome these problems, bifunctional catalysts having increased acidity, via halogenation, to operate at lower temperature are introduced. Thus, Pt-loaded chlorided alumina is used. In the case of Pt/Al_2O_3 catalysts, Al_2O_3 is chlorinated to improve acidic character by a chlorine-containing organic compound, which is continuously supplied during operation to compensate for the loss of chlorine on the surface. This catalyst is very active and can operate at lower temperatures (370–470 K), thereby yielding a greater proportion of branched alkanes by taking advantage of the thermodynamic equilibrium as illustrated in Figure 7.1 [5,6].

However, such catalysts demand feed pretreatment because they are sensitive to poisons such as feed sulfur and in particular water [4]. The feed sulfur acts as a poison for metal function whereas water reacts with the catalyst chloride leading to formation of HCl. Thus, the continuous injection of chlorine compounds during operation are often found to pose handling and corrosion problems with such catalysts. Therefore, the necessity to develop an alternative catalyst in terms of acidic supports was clearly evident. This has led to the development of molecular sieve zeolite-based catalyst supports.

In view of the above, numerous studies have been performed over the last 3 decades using various zeolite structures, metal oxide frameworks, and sulfated zirconia to develop new catalyst recipes for light naphtha isomerization. In this context, excellent reviews and monographs have been published [7–10].

Solid acids such as zeolites are active for alkane isomerization although the higher temperature is required compared with Pt/Al_2O_3-based catalyst. In the case of Pt-supported zeolite catalysts, the chlorination (and feed of chlorine-containing compounds) is not required because of the higher acidity of zeolites. However, they are found to be highly tolerant for feed contaminant, especially water. In fact, Pt-supported mordenite zeolite was commercially used in early 1970s by Shell in a process called Hysomer for C_5-C_6 isomerization.

7.3.1.1 ZEOLITE-BASED CATALYST (E.G., Y, BETA, MORDENITE, ZSM-5)

Crystalline aluminosilicates, commonly known as zeolites, are microporous in nature. They are generally classified into three categories: small-, medium-, and large-pore crystalline materials [11,12]. The acidity of the zeolite framework is dependent on the framework silicon (Si)/aluminum (Al) ratio. The framework acidity is found to increase with an increase in the framework Al content. The unique pore size of approximately 5–7 Å for medium-pore zeolites offers shape selectivity in terms of reactant, product, and transition-state selectivity, as displayed in Figure 7.2 [11–13].

The fine tuning of the characteristic framework properties of zeolite offer a platform to develop a catalyst having

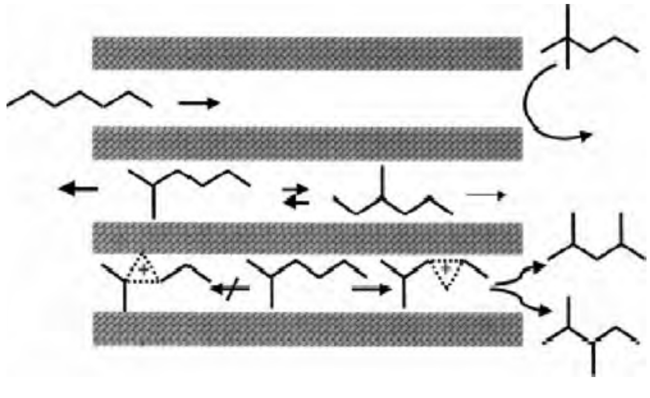


Figure 7.2—Shape selectivity concepts valid for n-C_7 hydroconversion: (top) reactant selectivity (RS), (middle) product shape selectivity (PS), and (bottom) transition state selectivity (TS).

controlled acidity levels by tuning the Si/Al ratio and ion exchange of the extra framework of cations, thereby leading to low coke tendency; high hydrophobicity with an increase in the Si/Al ratio; high aromatic, organic nitrogen, and sulfur resistance; and easy regeneration ability for light alkane isomerization. Zeolites such as Y, ZSM-5, mordenite, and beta-based catalyst have particularly been exploited. Typical pore dimensions of these zeolites are listed in Table 7.4.

Since the introduction of the Hysomer process, mordenite-type zeolite has been extensively investigated for light alkane isomerization. Thus, the activity and selectivity of hydroisomerization of n-C_5-C_6 alkanes over Pt/mordenite is reported to be influenced by acid leaching [13]. Activity and selectivity are found to favor primary products, namely branched isomers. Such improvements are ascribed to the modification of pore structure because of mesopore formation during the acid leaching process [13]. These mesopores in turn are responsible for providing accessibility for more reactive sites and help in faster diffusion of formed products, thereby reducing the chances of coke formation and the subsequent deactivation of catalyst.

In view of the thermodynamic limitation for n-C_5 and n-C_6 isomerization, particularly at high temperature, increasing efforts are made to develop a zeolite-based catalyst for n-C_7 and n-C_8 isomerization. This is primarily because (1) 2-methylhexane, 2,3-dimethylpentane, and *iso*octane have research octane ratings of 53, 93 and 100, respectively; and (2) no effective catalyst for C_7 or C_8 paraffins is currently in use because of the high tendency of their multibranched isomers to crack. A brief overview of such investigations is given below.

On the basis of the open literature, zeolites with different pore sizes and topologies and different crystallite sizes such as mordenite, ZSM-5, ZSM-12, ZSM-22, beta zeolites, and Y zeolites have been investigated for this purpose [14–29]. Pt/mordenite is found to be less selective when dealing with longer paraffins such as n-C_7 and n-C_8 because of their high acid strength. However, the selectivity of reaction on Pt/mordenite catalysts could be significantly improved by increasing the reaction pressure and by increasing the Si/Al ratio [28]. On the other hand, Pt/UY catalysts are reported to be active and selective in n-C_7 isomerization with up to 94 % selectivity at 72 % conversion [46]. On similar lines, ZSM-5 and zeolite Y-based catalysts have been evaluated [10]. However, such catalysts are found to favor hydrocracking over hydroisomerization because of their strong acidity. Attempts have been made to modify the acidity and acid site density for these zeolites for optimizing their performance for hydroisomerization of n-C_7-C_8 paraffins [10]. Furthermore, ion exchange of metals such as zinc, nickel, and cadmium in zeolite Y has resulted in significant enhancement of n-C_7 isomerization compared with cracking. Such a system is usually termed a trifunctional catalyst in which to the usual bifunctional catalytic site configuration a new cationic site is added for which the main role is to speed up the desorption of olefinic species from the acid site and its transfer to the metallic Pt site [29]. In such a way, the residence time of the branched carbocation on the zeolite acid site is much shorter than the conventional bifunctional catalyst, thus avoiding further undesired cracking. For this purpose, zinc species are found to be ideal and are reported to behave as a Lewis acid site during reaction [28].

TABLE 7.4—Zeolite Pore Dimension Data

Zeolite	Zeolite Type Index	Pore opening (Å)
Beta	BEA	5.7 × 7.5, 5.6 × 6.5
Mordenite	MOR	6.5 × 7
Y	FAU	7.4 × 7.4
USY	FAU	7.4 × 7.4

USY = Ultrastable Y

Pt/HBEA catalysts also show higher activity and selectivity (exceeding 86 %) in the hydroisomerization of *n*-heptane [28,29]. It has recently been demonstrated that a large-pore tridimensional zeolite Beta, especially when synthesized with smaller crystallite sizes, can be better than mordenite to isomerize n-C_7 paraffin, which is one of the major constituents of the gasoline pool [5,6].

Selective isomerization of *n*-heptane has also been investigated over one-dimensional zeolites. On the basis of the reported studies, ITQ-4, a unidirectional zeolite, is found to be more selective for the isomerization of *n*-heptane than mordenite [30]. Selectivity and kinetic parameters observed in the hydroconversion of n-C_5-n-C_7 on 12MR unidirectional zeolite (ITQ-4) indicate that differences in pore topology are more important than acidity for determining isomerization selectivity [30]. Likewise, one-dimensional zeolite ZSM-12-based catalyst is found to be active for isomerization of *n*-heptane [31].

The hydroconversion of C_8-alkanes has also been studied extensively [31–41]. The hydrocracking and hydroisomerization of *n*-octane, 2,5-dimethylhexane, and 2,2,4-trimethylpentane on Ni/ZSM-5, mordenite, and Beta-zeolite was investigated at 533 K and 20 atm total pressure [36]. On the basis of the obtained results, the activity decreased in the sequence ZSM-5 >> Beta ~ Mordenite for the *n*-octane conversion and increased in this sequence for the conversion of 2,5-dimethylhexane and 2,2,4-trimethylpentane. The selectivity for *n*-octane and 2,5-dimethylhexane isomerization was the highest on Ni/Beta and lowest on Ni/HZSM-5.

The activity, product selectivity, and stability of several Pt- and Pd-loaded zeolite catalysts (ZSM-5, ZSM-12, mordenite, USY, and Beta) with different Si/Al ratios have been compared for the hydroisomerization of *n*-octane [38,39]. Accordingly, the catalytic activity is reported to decrease in the following order: ZSM-12 > Beta > MOR > USY and ZSM-5 >> Beta > MOR [38]. The branched product selectivity is found to increase with the increase in Brønsted acid strength. Among the investigated zeolites, ZSM-12, which has a one-dimensional channel (5.6 × 6.0A°), demonstrated superior stability even under accelerated coking conditions [37]. On the other hand, USY and Beta-zeolites, because of their relatively large pore sizes, allow to a higher extent the branching of *n*-octane at the same level of conversion in comparison with ZSM-12. According to the results of these works, the zeolite acidity (number and strength distribution) and the pore structure are inferred to play very important roles in the conversion and product selectivity for the hydroconversion of *n*-octane.

Attempts have also been made to explore the zeolite membrane reactor concept for the hydroisomerization of *n*-hexane and *n*-heptane, respectively, using silicalite-1 membrane [42,41]. The results obtained indicate separation selectivities with factors close to 20 for n-, mono-, and dibranched components in a gas mixture as well as *n*-hexane conversions up to equilibrium values over zeolite membrane. The research octane number (RON) calculated for the product stream of the different experiments indicates numbers as high as 85. For the hydroisomerization of C_7 alkanes, a concept of two reactors and a zeolite membrane has been proposed and an industrial-scale process is simulated. Although the calculated product yield is found to be approximately 24 % of the process feed, an improvement in a RON from 57 for the feed to 92 for the product has been noticed. Both processes show that the application of zeolite membranes in the hydroisomerization of light alkanes can result in an octane number higher than in the "state-of-the-art" processes [43].

Attempts are also been made to exploit the composite zeolite system to improve the isomerization selectivity. Such a system consists of a combination of catalyst component, which converts the n-alkanes into monobranched isomers, and a large-pore catalyst system. This in turn is reported to enhance the yield of multibranched isomers. [5,6] Thus, a varied combination of acid form of zeolite Y and H-ZSM-5 has been investigated on hydroconversion of light alkanes (n-C_6-C_8) in the literature. The overall conversions observed for the aforementioned zeolite mixtures are found to be in line with those predicted by the additive criteria, but the selectivities are found to be clearly different for the reaction products. Likewise, Pt/Beta-zeolite catalyst also improved the catalytic activity in the hydroconversion of *n*-octane when it is mixed with bentonite because of the synergetic effect between extra-framework Al species and the acid sites [5,6]. Similarly, a catalyst composed of the sulfated zirconia (SZ) and zeolite has showed enhanced activity in the hydroconversion of *n*-octane [5,6].

Extending the mixed catalyst system, attempts have been made to explore the catalytic potential of a system consisting of bimodal pore size distribution. Thus, the composite catalysts containing the acidic zeolitic component (Pt-MCM-22, Pt-Beta) and an inert mesoporous material (MCM-41) have been prepared. These composites showed higher activity and higher selectivity in the hydroisomerization of *n*-heptane because of improved diffusion properties of the catalytic system. This trend has led to the discovery of a new composite family of materials known as "TUD-1" with significantly broader catalytic utility as well as enhanced structural, thermal, and hydrothermal stability compared with MCM-41 [44,45]. It has been shown that zeolite/TUD-1 composites can have a significant synergistic catalytic effect [5,6].

7.3.1.2 AMORPHOUS OXIDES OR MIXTURE OF OXIDES (SiO_2–Al_2O_3, SO_4^{2-}/ZrO_2)

The first alternative commercial catalysts used for hydroconversion of light n-paraffins were based on amorphous inorganic oxides, such as mixed silica-alumina (MSA). Successful attempts have been made to synthesize MSA supports with mild Brönsted acidity, a very high surface area, and a narrow pore size distribution in the mesopore region. The supports so obtained are reported to demonstrate the best selectivity for light n-paraffins. However, similar to traditional alumina-based catalyst, MSA-based catalyst demands constant chlorination to maintain acidity and acid density, because of which they are prone to feed contaminants such as water and sulfur [5,6,10].

Attempts have been made to use strong solid acid-based anion-modified zirconium oxide as a support to prepare catalysts for the hydroisomerization of n-paraffins. It is found that SO_4^{2-}/ZrO_2, commonly known as SZ when used as a support for Pt loading, exhibits high activity and selectivity in C_4-C_6 n-paraffin isomerization [10]. In this context, the role of zirconia crystal structure in determining isomerization selectivity is investigated. Accordingly, the monoclinic zirconia phase is found to favor the isomerization of light n-paraffins [46]. Later, the joint research of Cosmo Oil Ltd. and Mitsubishi Heavy Industries led to the development of the process for the isomerization of light naphtha using such catalyst. The process was commercialized by UOP LLC [47]. On similar lines, M/s Sud-Chemie has developed a catalyst system that is based on a modified SZ (super acid), called HYSOPAR catalyst, which has been claimed to be tolerant up to approximately 100 ppm feed sulfur [48]. This catalyst is successfully used in the Par-Isom process as described in Section 7.4.

7.3.1.3 HETEROPOLY ACIDS AND THEIR METAL SALTS

Heteropoly acids, such as $H_3PW_{12}O_{40}$ (WPA), are known to be highly acidic and catalyze many kinds of reactions as a solid-acid [49–54]. Palladium salts of WPA supported on silica are highly active for the isomerization of *n*-hexane under hydrogen. WPA supported on commercial Pd/C is even more active. This catalyst shows 96.4 % selectivity for *n*-hexane isomers at the conversion of 77.9 % at 523 K. On the basis of such selectivity, the unique role of Pd and heteropoly anions has been proposed [52–54]. The metal dissociates H_2 to form H atoms, which in turn react with heteropoly anion to form proton and the reduced form of the anion as shown below:

$$H_2 \overset{Pd}{\leftrightarrow} 2H$$
$$H + PW_{12}O_{40}^{3-} \leftrightarrow H^+ + PW_{12}O_{40}^{4-}$$

The catalytic activity is reported to change reversibly with hydrogen pressure, indicating that reactions are reversible. Likewise, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was active for *n*-alkane isomerization and the activity was more stable under hydrogen when the material was loaded with Pt [54].

7.3.1.4 MOLYBDENUM/TUNGSTEN OXYCARBIDE AND PARTIALLY REDUCED MoO_3

The possible replacement of noble metal-based catalysts for the isomerization of alkanes has been one of the prime focuses to develop cost-effective hydroisomerization catalyst. In contrast to noble metal-supported catalysts, the use of transition metals is found to be ineffective in the hydroconversion of alkanes because of their strong affinity for intermediate reaction species. However, lattice substitution with nonmetals such as S, C, O, and N atoms in transition metals such as Mo and W deeply modifies the electronic structure of the parent metals, thereby boosting its activity comparable to that of noble metals. Therefore, in recent times, the use of transition metal carbides of tungsten carbide (WC) and Mo_2O as catalysts has received significant attention because of their comparable catalytic properties with noble metals [55–58]. Thus, WC treated with oxygen at 800 K is active for isomerization of *n*-hexanes and *n*-heptanes. The dehydrogenation–hydrogenation function is offered by the patches of carbide, whereas the acidic function is offered by patches of tungsten oxide. The product distribution using this catalyst system showed the formation of 3,3-dimethylpentane during the isomerization on *n*-heptane [56–57]. The large improvement in isomerization selectivity is observed when the surface of molybdenum carbide (Mo_2C) is oxidized [55]. The molybdenum oxycarbide (MoO_xC_y) thus prepared is reported to be highly selective even for the isomerization of *n*-heptane and *n*-octane [58].

Partially reduced MoO_3 at 623 K is reported to give a high surface area and demonstrates a high catalytic activity and selectivity for *n*-heptane isomerization. However, the activity is found to be very much dependent on the degree of reduction (on time and temperature of exposure to hydrogen). Interestingly, the catalyst is most active when the Mo oxidation number is between 2.5 and 3.5. On the other hand, MoO_3 loaded with transition metals is more active than MoO_3 without metal loading for *n*-heptane isomerization under hydrogen after it was reduced with hydrogen [57,58]. Among transition metals, Pt is found to be the most effective metal. The role of Pt is suggested to enhance the formation of the H_xMoO_3 phase, which is the precursor to the active MoO_xH_y phase.

The catalytic activity and selectivity for *n*-octane, *n*-heptane isomerization over MoO_xC_y at 563 K demonstrated high selectivity of 95 % even at high conversion of 75 % for C_8 isomers and approximately 90 % even at 78 % conversion for C_7 isomers, respectively [57]. However, the mechanism of isomerization is yet to be established, but it is worthy to note that these groups of catalysts are very selective for *n*-heptane isomerization.

7.3.1.5 COMMERCIAL CATALYSTS FOR LIGHT NAPHTHA ISOMERIZATION

Although, numerous attempts have been made for catalyst development for light naphtha including C_7 and C_8 isomerization, commercial exploitation of the aforementioned catalysts is limited. The commercial utilization is typically governed by

- Selectivity for isomerization,
- Cost of catalyst (support),
- Isomer yields,
- Operation parameters,
- Efficiency for benzene saturation,
- Lower fill cost,
- Minimum noble metal content,
- Tolerance for naphthene content, and
- Catalyst and cycle life.

Before naphtha isomerization, feed is hydrotreated to remove feed contaminants such as sulfur. The obtained hydrotreated naphtha undergoes distillation to obtain light naphtha (IBP-303 K–FBP 363 K) and heavy naphtha (IBP-363 K-FBP 473 K), respectively. The light naphtha cut is routed to the isomerization unit whereas heavy naphtha is routed through the reformer unit. Today, with stringent gasoline specifications, especially with reference to benzene limits, refiners are restrained to process benzene precursors through the reformer unit; hence, isomerate feed typically contains benzene and its precursors (cyclohexane and methyl cyclohexane). Therefore, it is of utmost importance to use a catalyst that can

- Saturate benzene present in the feed (it may be noted that benzene saturation is a highly exothermic process);
- Handle naphthenes (it may be noted that naphthene limit isomerate yields as they preferentially adsorb over catalyst surface) and produce less coke than naphthenes under hydrodecyclization, thereby allowing formation of coke precursors at higher temperature; and
- Isomerize cyclohexane (RON 83) to methylcyclopentane (RON 91) to gain advantage of RON despite the presence of feed naphthenes.

In this context, Pt/alumina has been extensively practiced because of its mild operation severity (373–423 K), its high selectivity for C_5 and C_6 isomers, and its ability to saturate benzene. Thus, it has undergone significant improvements at the commercial level. Today, the bulk density of alumina support used in the catalyst preparation can be tailored, and low-bulk density alumina offers not only high volume activity but also lower fill costs and Pt requirements associated with low density. The reduction in Pt content is possible because the Pt function in the catalytic reaction does not limit the rate of isomerization. Furthermore, advances in the chlorination step offer higher site density over the alumina surface, which allows low-temperature operation of the Pt/alumina system to favor the formation of more branched compounds for achieving RONs higher than 87.5. However, performance of the Pt/alumina system is prone to feed containing high naphthene content as well as water. Generally, naphthenes are adsorbed strongly, thereby inhibiting adsorption of n-paraffins over the alumina surface, whereas water leaches out surface chloride. Thus, the feed naphthene content needs to be controlled to the optimal level for achieving the desired RON over the Pt/Alumina system. In view of the commercial requirements, catalyst manufacturers M/s Axen (ATS-2L) and M/s AkzoNoble-Total (AT-2G) have introduced advanced Pt/alumina-based catalyst with increased water tolerance to meet the aforementioned requirements of refiners.

On the other hand, commercial catalyst systems based on Pt/mordenite are less prone to feed naphthene content but demand energy-intensive conditions vis-à-vis Pt/alumina catalyst because of their lower activity at lower temperature. The higher operating conditions (Table 7.5) for such catalyst often limit the RON boost per pass because of the thermodynamic limitations of the process. However, such a catalyst system does offer the benefit of capital saving in terms of feed pretreatment because of its high tolerance for water. Unlike alumina, flexibility in tailoring the bulk density is limited with zeolite-based catalyst, which limits the possibilities of lowering the Pt content, thereby making

TABLE 7.5—Comparison of Operating Conditions for Pt/Al_2O_3 and Pt/Zeolite Systems

Operating Conditions	Pt/Al_2O_3	Pt/Zeolite
Temperature (K)	373–463	523–543
Pressure (Psi)	20–30	15–30
Space velocity (h^{-1})	1–2	1–2
H_2/HC (mol/mol)	0.1–2	2–4
RON per pass	83–84	78–80

it costly compared with alumina catalyst. Typical operating conditions used for both of the catalyst systems are listed in Table 7.5.

In view of the aforementioned advances in alumina science, Pt/alumina catalyst has gained commercial edge and sometimes even outweighs the zeolite-based catalyst from techno-commercial aspects.

7.3.2 Catalysts Long-Chain Paraffin Isomerization

The demand for improved lube oil with respect to VI, pour point, oxidation stability, and need for gross refinery margin (GRM) improvement has added impetus for the development of a new catalyst chemistry since the late 1980s. Accordingly, lube oil dewaxing processes have also undergone step change from a solvent dewaxing to catalytic-cracking-based dewaxing to hydroisomerization-assisted dewaxing processes with increased yields vis-à-vis solvent and catalytic cracking dewaxing processes. The catalyst used for this process differs significantly from those practiced for isomerization of light naphtha. Unlike light naphtha isomerization, long-chain paraffin isomerization needs to be controlled to an optimal level to achieve the desired VI and pour point, respectively. Furthermore, the position of branching and the branching index are found to be key for the production of lube oil with high viscosity index and the desired pour point, respectively. The branching at the near-terminal position of long-chain paraffins vis-à-vis at near-center positions is reported to have significant effect, especially on VI [59].

Thus, to meet such stringent criteria, it is of the utmost importance to use a catalyst having fine-tuned balance between metal-acid functions to achieve the highest isomer selectivity and yield at the lowest possible reaction temperature. To develop such a catalyst system, focused attempts have been made to understand zeolite, SZ, and mesoporous materials in terms of their structure and acidity level for improving the isomerization selectivity with an increase in conversion. Excellent reviews covering the aforementioned aspects are available in the literature. The following subsections present a brief overview of such efforts.

7.3.2.1 ZEOLITES (E.G., ZSM-23, ZSM-22, AND ZSM-48)

Among the various zeolite frameworks, medium-pore zeolites have gained considerable attention for isomerization of long-chain paraffins. This is primarily because medium-pore zeolites favor the formation of methyl branchings in the linear aliphatic hydrocarbon chains because of their restricted pore geometry. In other words, if the pore opening of zeolite is small enough to restrict the larger isoparaffins from reacting at the acidic sites inside of the pore, the catalyst will show good selectivity for converting n-paraffins. The unique selectivity of medium-pore zeolite is ascribed to the pore mouth/key-lock catalysis mechanism [60,61]. In general, methyl branching increases with the decreasing pore width of the zeolite, whereas ethyl and propyl branched isomers that are more susceptible to hydrocracking are obtained from wide pore openings and large cavities [62].

On the basis of the pore mouth/key-lock catalysis mechanism, it is apparent that the potential medium-pore zeolite should have following characteristics for selective hydroisomerization:

- Optimal acid site distribution on the surface,
- Increased external surface area, and
- Submicron zeolite crystallite size.

In view of this, Al framework distribution as a function of the Si/Al ratio can be judged as an important parameter to control optimal acid strength at the pore mouth. Likewise, particle size in the submicron region is envisaged to offer an increased platform to favor a pore mouth/key-lock-type mechanism. These aspects for potential zeolites, namely ZSM-22, ZSM-23, ZSM-48, and SSZ-32, have been addressed in the patent literature.

On the basis of the open literature, medium-pore zeolites viz. ZSM-22 (TON) and ZSM-23 (MTT) are found to be highly selective for hydroisomerization of long-chain paraffins [60–64]. With ZSM-22/ZSM-23 zeolite catalysts, the branchings are generated at very specific carbon positions along the alkane chains as revealed in the conversions model for n-alkanes with carbon numbers up to n-C_{24} [62]. On the basis of the developed model, monobranched isomers with branching at the C_2 carbon position are found to be favored over the ZSM-22-type zeolite whereas branching at center positions are favored over the ZSM-23 type of zeolite [65]. Such a trend is noticed over Pt (0.3 wt %)/ZSM-22 in the hydroisomerization of long-chain n-paraffins in the range of *n*-decane to *n*-tetracosane. The maximum yield of total isomers (monobranched and multibranched isomers) between 77 and 90 wt % is noticed over ZSM-22 zeolite with a maximum yield of monobranched isomers obtained with the different n-paraffins in the range of 55–80 wt %. Skeletal isomerization has been investigated on Pt/ZSM-23. Attempts have also been made to fine-tune the acidity level of such zeolites. Accordingly, the acidity level is fine-tuned by means of steam deactivation for Pt (0.6 wt %)/ZSM-48, ZSM-22, and ZSM-23 catalysts for the hydroisomerization of *n*-decane. The tests showed that by steaming, the maximum isomerization yield of Pt/ZSM-48, ZSM-22, and ZSM-23 catalyst can be increased from 78 to 90, 50 to 68, and 50 to 72 wt %, respectively [64].

It is interesting to note that Pt/ZSM-23 is reported to favor monobranching near the center of the molecule. Such a branching pattern is reported to favor an increase in VI [59]. In view of this, MTT zeolite can be judged to have an edge over TON-type zeolite for production of lube oil with high VI.

In view of this, patent literature extensively covers MTT- and TON-type zeolite-based catalysts for lube oil production. It also covers small-crystal MTT and the TON-MTT intergrowth topology framework for such application [66,67]. The small zeolite crystals, on the basis of the pore mouth catalysis concept, are expected to offer higher external surface area and are anticipated to favor isomerization with increased yield and selectivity. On similar lines, the morphology of potential zeolite crystals is anticipated to play a critical role in improving the catalyst performance in the isomerization process. It is noteworthy that patent literature indicates the improved performance of zeolite crystals with slab morphology with respect to conversion and selectivity under isomerization conditions.

7.3.2.2 SILICOALUMINOPHOSPHATE MOLECULAR SIEVES (E.G., SAPO-11, SAPO-31, AND SAPO-41)

Silicoaluminophosphate (SAPO) molecular sieves generally have a lower acidity than zeolites. Among SAPO molecular sieves, medium-pore SAPOs (SAPO-11, SAPO-31, and

SAPO-41) have been envisaged to be suitable for constituting catalysts that manifest better performance for long-chain hydrocarbon isomerization [68]. The main SAPO feature is that it results in relatively low-branched isoparaffins [69]. The SAPO framework is created by Si substitution into the $AlPO_4$ framework. There are two mechanisms for this substitution:

1. *SM2:* One Si substitutes for one P, and
2. *SM3*: Two Si substitute for one P and one Al.

When Si substitutes P, Brönsted acid sites are formed, whereas if P and Al are simultaneously replaced by two Si atoms, the tetrahedral framework remains neutral [11,12].

Among the potential SAPO frameworks, SAPO-11 with AEL-type topology is selective for producing monobranched alkanes during the hydroisomerization of long-chain normal paraffins. Medium-pore SAPO-11 was initially used by M/s Chevron in their isodewaxing process for the selective isomerization process of high-boiling waxes for the production of high-viscosity lube oils.

The hydroisomerization of n-C_{14} over Pt (0.4 wt. %)/SAPO-11 catalyst in a fixed-bed reactor shows high isomerization selectivity. Over this catalyst, conversion of *n*-heptane presented a similar trend, but the values were lower than those of *n*-tetradecane hydroisomerization at the same experimental conditions. As for the isomerization products, the maximum yield of feed isomers was 55 % for *n*-heptane hydroconversion. A maximum yield of more than 80 % was obtained for n-C_{14} hydroconversion. Also, SAPO-11-based catalyst when evaluated for hydroisomerization of *n*-hexane, *n*-octane, and *n*-hexadecane showed the least activity for *n*-hexane conversion and is the most reactive for *n*-hexadecane. This result shows that the SAPO catalysts are adequate only for long-chain n-paraffins [70–73]. The performance of Pt/SAPO-11 is enhanced with doping of tin. Isomerization of *n*-dodecane over Pt-Sn/SAPO-11 catalysts showed more than 90 % *n*-dodecane conversion but only 85 % isomerization selectivity at 87 % *n*-dodecane conversion over Pt/SAPO-11 has been obtained. The results indicate that, on SAPO-11 base catalysts, *n*-dodecane (a long-chain n-paraffin) can intensively isomerize with very limited cracking. The better hydroisomerization performance of the former catalyst has been attributed to the addition of tin to the metallic catalyst composition [70–73]. Like other zeolite catalysts, the performance of SAPO-based catalysts is reported to be influenced by metal dispersion and the surface area of the catalyst. To achieve higher acidity, attempts have been made to incorporate Si by the SM2 mechanism. Such mechanism prevails when SAPO-11 is prepared using the water-cetyltrimehtlammonium bromide-butanol phase [74]. The crystallized SAPO-11 framework is reported to have more Brönsted acid sites and smaller crystallite size. Such SAPO-11 support is found to be more active than the conventionally prepared framework [74]. SAPO-11 with small crystal size is expected to decrease the effect of diffusion; carbenium intermediates thus easily desorb from acid sites so that further isomerization and cracking are expected to decrease.

Among SAPO-11, SAPO-31, and SAPO-41 with identical acid strength, the hydroconversion activity for *n*-octane is found to decrease in the order SAPO-41 > SAPO-11 > SAPO-31. The low activity of SAPO-31 is ascribed to its framework structure (i.e., it has 12-membered ring one-dimensional circular channel). On the other hand, SAPO-41 and SAPO-11 have 10-membered ring one-dimensional elliptical channels that are effective for hydroconversion because of their shape selectivity, as described earlier. However, SAPO-41 is reported to be more active than SAPO-11 because of its slightly larger pore size, which in turn is expected to offer less diffusion constraints for reacting molecules as compared with SAPO-11 [70–73].

7.3.2.3 MESOPOROUS MATERIALS (MCM-41, ALMCM-41)

Since the discovery of the new class of mesoporous materials such as MCM-41 in 1992, there has been a growing interest in their potential catalytic applications [75]. Because of their relatively mild acid sites and the possibility to vary the Si/Al ratio over a wide range without significant changes in pore structure, these materials are very attractive model catalysts for the transformation of bulky compounds, especially for the hydroisomerization of long-chain n-paraffins [76–78]. Thus, *n*-decane hydroconversion on bifunctional catalysts comprising Pt, Pd, and bimetallic Pt–Pd supported on an Al-MCM-41 (Si/Al = 23) has been investigated [76–78]. The results of this investigation are shown in Table 7.6. Accordingly, the catalytic activity of all catalysts containing bimetallic clusters is increased in comparison with the values of monometallic catalysts [77].

On the other hand, Pd (0.35 wt %)/AlMCM-41 catalyst at 623 K in the hydroisomerization of *n*-tridecane is found to have good selectivity with a lowering framework Si/Al ratio (Table 7.7).

The observed trend suggests more critical balance between the acid function of MCM-41 and the metal function for simultaneous increase in isomer selectivity and selectivity at the lowest possible temperature.

7.3.2.4 TUNGSTATE-PROMOTED ZIRCONIA (WO_x-ZrO_2)

Anion-modified metal oxides, such as SZ (SO_4/ZrO_2) and tungstated zirconia (WO_3/ZrO_2), have been found to catalyze

TABLE 7.6—Maximum Isomer Yields of Pt, Pd, and Pt-Pd/AlMCM-41 Catalysts in the Hydroisomerization of *n*-Decane

Metal Compound	T_{max} (K)	Conversion (wt %)	Maximum Isomer Yield (wt %)
0.5 wt % Pt	628	81	53.8
0.27 wt % Pd	653	74.3	54.5
0.375 wt % Pt–0.068 wt % Pd	593	77.4	44
0.25 wt % Pt–0.135 wt % Pd	573	58.6	38.2
0.125 wt % Pt–0.203 wt % Pd	583	69.6	37.3
0.125 wt % Pt–0.068 wt % Pd	603	82.4	32.4
0.5 wt % Pt–0.27 wt % Pd	583	73.3	48.9

Reaction conditions: P_{H2} = 1 MPa, $P_{n\text{-}C10}$ = 10 kPa, H_2/n-C_{10} mole ratio = 100, W/F = 400 g×h/mol.

TABLE 7.7—The Results of Hydroisomerization of n-C_{13} over Different Pd/AlMCM-41 Catalysts [78]

Total Acid Amount (mmol/g)	Si/Al Ratio	n-C_{13} Conversion (wt %)	i-C_{13} Selectivity (wt %)
0.135	100	59.3	86.4
0.161	75	59.8	88.7
0.164	50	60.2	86.5
0.198	25	59.5	91.8
Reaction conditions: T = 623 K, Pt = 3.5 MPa, H_2/n-C_{13} = 600, WHSV = 1.5 h^{-1}			

hydrocarbon conversions under mild conditions. These strong solid acids are environmentally benign and regenerable. Butane isomerization over SZ has attracted considerable attention because isobutane is the precursor to methyl-*t*-butyl ether. Metal-promoted SZ is effective for isomerization of short-chain paraffins and for hydrocracking of long-chain paraffins including waxes and polyolefins [9]. However, loss of activity due to coke formation and sulfur loss, especially under reducing conditions, is an obstacle to certain practical uses of SZ. Moreover, high isomerization selectivity is difficult to achieve over SZ because the chain length increases, even at low conversions. Studies of tungstate-modified zirconia indicate that it is more stable than SZ and is promising for hydroisomerization of high-molecular-weight linear paraffins [79–84].

The performance of Pt (0.5 wt %)/WO_3/ZrO_2 catalyst for the hydroisomerization of *n*-hexadecane in a trickle-bed continuous reactor demonstrated high activity and selectivity for hydroisomerization of long-chain n-paraffins [79]. The optimal range of tungsten loading to achieve high isomerization selectivity at high *n*-hexadecane conversion is found to be between 6.5 and 8 wt % [79]. The comparison between Pt (0.5 wt %)-/SO_4/ZrO_2 and /WO_3/ZrO_2 (Table 7.8) shows that Pt (0.5 wt %)/SO_4/ZrO_2 catalyst converts 80 % of converted *n*-hexadecane to short-chain paraffins when operated at 423 K because it was very active and was not stable at high temperatures in the presence of hydrogen. On the other hand, Pt (0.5 wt %)/WO_3/ZrO_2 with a comparable n-C_{16} conversion to that of Pt/SO_4/ZrO_2 favored the formation of many more C_{16} isomer products [85].

In view of the observed trend, the combination of sulfate and tungstate species is expected to play a vital role in controlling the surface acidity and acid density for zirconia surface. However, metal function for Pt/WZR is found to be dependent on treatment conditions. The oxidation step during catalyst preparation is found to prevent the formation of tungsten-Pt species, which commonly leads to low dispersion of Pt and in turn demonstrates low activity for the isomerization reaction.

7.3.2.5 COMMERCIAL CATALYSTS FOR HYDROISOMERIZATION OF LUBE OIL

The advances made in understanding the role of medium-pore molecular sieve support in controlling the bulk properties of lube oil (i.e., VI and pour point) have added impetus for commercial catalyst development. On the basis of the reported literature data, commercial catalyst could be derived based on AEL (SAPO-11), TON (ZSM-22), and MTT (ZSM-23) molecular sieve. It is worthwhile to note that ease of zeolite scale-up in terms of cost of its synthesis with desired crystal morphology, fine tuning of textural properties, and crystallite size drives the commercial utilization of molecular sieve in lube oil production. On the basis of the patent literature, the cost of the structure-directing agent (viz. diquat-n type) for synthesis of the slab-shaped morphology of zeolite crystals can be envisaged to be a bottleneck in determining the cost of zeolite for catalyst development.

The first-generation catalyst based on SAPO-11 was developed by M/s Chevron in the early 1990s. However, it was soon phased out because of its poor activity, higher operation temperature, high hydrogen/feed ratio, and lower isomerization selectivity, especially to meet VI demand. Today, the commercial hydroisomerization-assisted lube oil production process uses a catalyst that offers the following main features:

- High selectivity for isomerization,
- Selective branching positions to meet the VI demand,
- Comparable isomer yields vis-à-vis conversion level,
- Increased catalyst life,
- Minimum hydrogen/feed ratio, and
- Minimum VI drop between feed and product to produce premium lube oil.

In view of this, M/s Chevron has reported high potential for SSZ-32 zeolite in patent literature. Likewise, M/s ExxonMobil has extensively covered ZSM-23, ZSM-22, and ZSM-48 in their patents.

On the basis of the progress made on the aforementioned catalyst front, commercial processes have been developed for the hydroisomerization of gasoline and lube dewaxing to improve product quality. In the following sections, these commercial hydroisomerization processes are discussed.

7.4 PROCESS FOR GASOLINE OCTANE BOOSTING

The isomerization of low-molecular-weight paraffins has been commercially practiced for many years. During the 1930s, World War II prompted the development of the laboratory processes into full-scale commercial units to meet the demand for isobutene, which was necessary for

TABLE 7.8—Hydroisomerization of n-C_{16} on Pt (0.5 wt %)/SO_4/ZrO_2 and Pt (0.5 wt %)/WO_3/ZrO_2 (6.5 wt % W)

Catalyst	Reaction Temperature (K)	n-C_{16} Conversion (wt %)	i-C_{16} Selectivity (wt %)	i-C_{16} Yield (wt %)
Pt (0.5 wt %)/SO_4/ZrO_2	423	76.7	19.8	15.2
Pt (0.5 wt %)/WO_3/ZrO_2	503	85.9	83.1	71.4
Reaction conditions: Pt = 300 psig, WHSV = 1 h^{-1}, H_2/n-C_{16} mole ratio = 2				

the manufacturing of large amounts of alkylate. Today, the interest in isomerization is especially focused on the upgrading of fractions of light naphtha for their use as motor gasoline components because of stringent environmental norms.

The first hydroisomerisation unit was introduced in 1953 by UOP, followed in 1965 by the first BP unit. In 1970, the first Shell hydroisomerisation (HYSOMER) unit was started up. The following major hydroisomerization processes are presently commercially available for C_5/C_6 isomerization [4]:

- SHELL HYSOMER;
- Axens ISOSORB and HEXSORB; and
- UOP PENEX, Par-Isom, and TIP.

The catalysts used in these processes are listed in Table 7.9 [4].

The typical product RONs obtained in a once-through process using these catalysts are depicted in Figure 7.3 [48].

All of these processes take place in the vapor phase on a fixed-bed catalyst containing Pt on a solid carrier. These processes are performed in the presence of hydrogen to suppress dehydrogenation and coking so as to improve catalyst life and its deactivation. The process temperature usually governs the cycle life for such catalysts. High process temperature generally increases the processing severity, which could lead to hydrocracking. On the other hand, low temperature, moderate hydrogen partial pressure, and low space velocity are found to promote long cycle lengths. Furthermore, increased naphthene and moisture content in the feed often impart an irreversible inhibitor effect. Thus, feed pretreatment is performed before isomerization to remove naphthenes and moisture, especially when Pt/Cl-alumina-based catalyst is used for isomerization. On the other hand, Pt/zeolite catalyst is more tolerant to such feed impurities [4]. Typical process flow diagrams that are based on alumina and zeolite catalysts are shown in Figure 7.4.

TABLE 7.9—Commercial Catalysts Used for Light Naphtha Isomerization

Catalyst	Catalyst Type	Licensor
IFP IS 612, 614A, ATIS-2L	Pt/Al_2O_3	IFP
IFP–IS 632, IP-632	Pt-mordenite	IFP
UOP I-7	Pt-zeolite	UOP
UOP I-8	Pt/Al_2O_3	UOP
Hysopar	Sulfated zirconia	Süd-Chemie

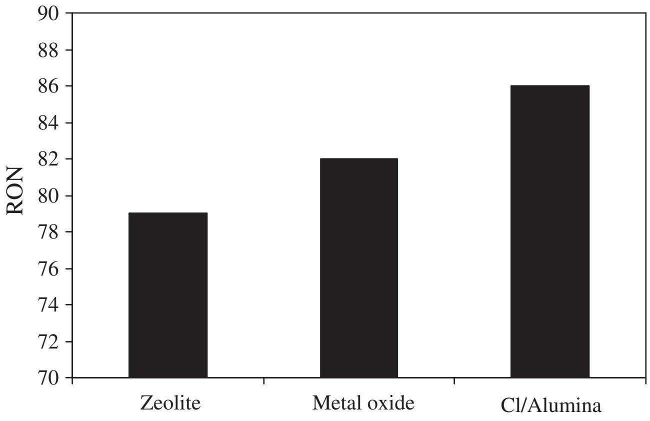


Figure 7.3—Typical product RONs obtained with various catalysts.

Such processes can be performed either in once-through or recycle mode. A typical once-through mode of operation minimizes hydrogen consumption, suppresses coking, and often limits product RONs up to 84, whereas recycle-mode operation helps to achieve RONs up to 92 (Table 7.10). The once-through process is generally performed at low temperatures by taking advantage of thermodynamics (Section 7.3) in the presence of Pt/Cl-alumina catalyst to achieve the desired product RON [4]. The recycle mode of operation can be performed using fractionation- and adsorptive-separation-based recycling options to improve the isomerate yields.

The recycle-mode operation with adsorptive separation uses a molecular sieve to separate isoparaffins from n-paraffins on the basis of a shape-selective separation principle. Thus, the separated fraction of n-paraffins (C_5 and C_6) is again recycled back to the isomerization reactor along with feed to improve the isomerate yield. Likewise, the recycle option by fractionation is performed by means of distillation to improve the product RON.

The molecular sieve recycle option was commercialized by M/s UOP in 1975 with the introduction of the total isomerization process (TIP), in which the isomerization is completely integrated with a molecular sieve separation process or the naphtha IsoSiv process. Recently, both of the recycle options were coupled by M/s IFP, which has led to the development of two processes: IPSORB and HEXSORB. IPSORB typically integrates the distillation and molecular sieve adsorption section: a deisopentanizer and molecular sieve desorption with isopentane for IPSORB. On similar lines, a deisohexanizer with methyl pentane desorption is coupled with distillation for HEXSORB.

In view of the above, the important features of the aforementioned light naphtha isomerization processes are

HYSOMER process:

- *Process temperature:* 505–558 K
- *Pressure:* 13–30 bar
- *Isomerate content in product relative to feed:* 97 % or better
- *Catalyst:* Pt/zeolite (mordenite), stable and regenerable
- *RON upgrade:* Between 8 and 10 points, depending on feedstock quality.

The HYSOMER process can be integrated with a catalytic reformer, resulting in substantial equipment savings, or with iso/normal separation processes, which allows for a complete conversion of pentane/hexane mixtures into isoparaffin mixtures.

TIP process [4]: This process uses

- Molecular sieve adsorbent-based recycle option to upgrade product RON;
- Zeolite catalyst with improved sulfur or water tolerance, or both, which allows in situ regeneration with extended life up to 10 years or more; and
- Similar operating conditions in isomerization and the molecular sieve separation section, thereby eliminating the costs associated with cooling, purifying, and reheating the recycled normal paraffins.

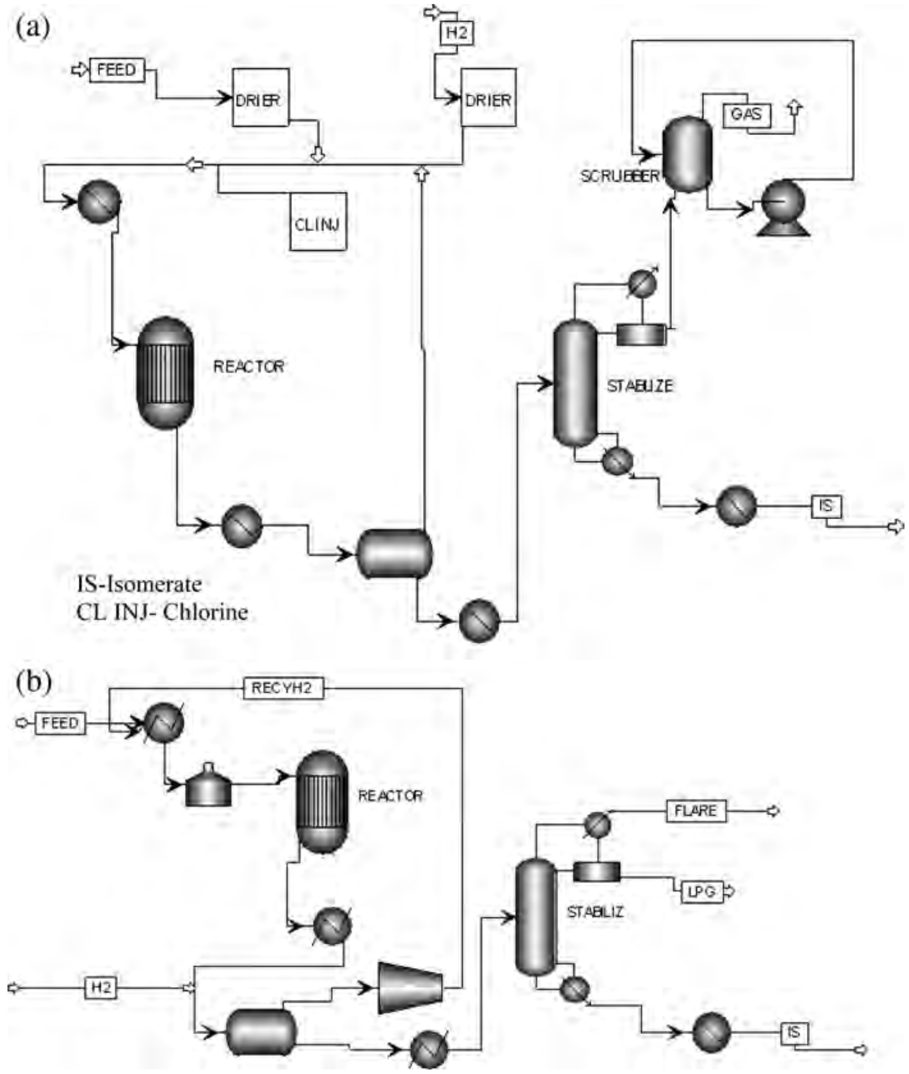


Figure 7.4—Flow diagram for an isomerization process based on (a) Pt/Cl$^-$-alumina and (b) Pt/zeolite catalysts.

A typical process flow diagram for TIP is provided in Figure 7.5.

IPSORB and HEXSORB processes [4]: The combination of distillation and molecular-sieve-based separation offers the following important and unique features:

- To lower the n-paraffin content in the isomerate, and
- To offer efficient separation and better efficiency in the unconverted n-paraffin recycle.

TABLE 7.10—RONs Achieved with Different Processes

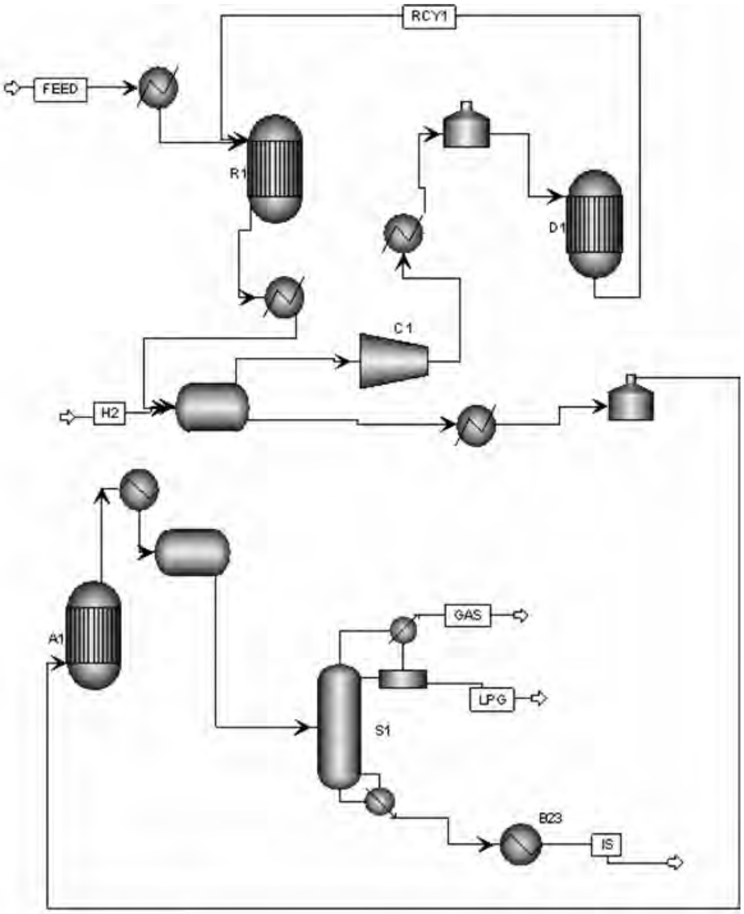
Process	Catalyst	
	Cl/alumina	Zeolite
Once-through	84	79
IPSORB (IFP)	90	88
HEXSORB (IFP)	92	90
TIP (UOP)	–	89

Continuous efforts are being made to improve the hydroisomerization catalyst and processes based on it so as to meet the challenges to handle feed variation. One of these efforts led to the development of a successful process called Par-Isom by M/s UOP in 1996 [48]. This process uses Pt/SZ catalyst.

The flow diagram of the Par-Isom process is depicted in Figure 7.6 [47]. A proprietary catalyst LPI-100 composed of Pt/SO_4^{2-}/ZrO_2 with excellent sulfur- and water-tolerant limits is used in this process. The LPI-100 catalyst is fully regenerable using the simple oxidation procedure. It also allows for lower reaction temperature operation and higher space velocity than the zeolitic catalyst process. This characteristic has been claimed to reduce the capital investment and lower the operation cost.

R1 = Isomerization reactor
D1 = Desorption unit
A1 = Adsorption unit
S1 = stabilization
RCY1 = Recycle: unconverted hydrogen and n-paraffins

The important features for various isomerization processes licensed by leading technology licensors that



R1-Isomerization reactor
D1- Desorption unit
A1- Adsorption unit
S1-stabilization
RCY1- Recycle: unconverted hydrogen and n-paraffins

Figure 7.5—Process flow diagram for TIP.

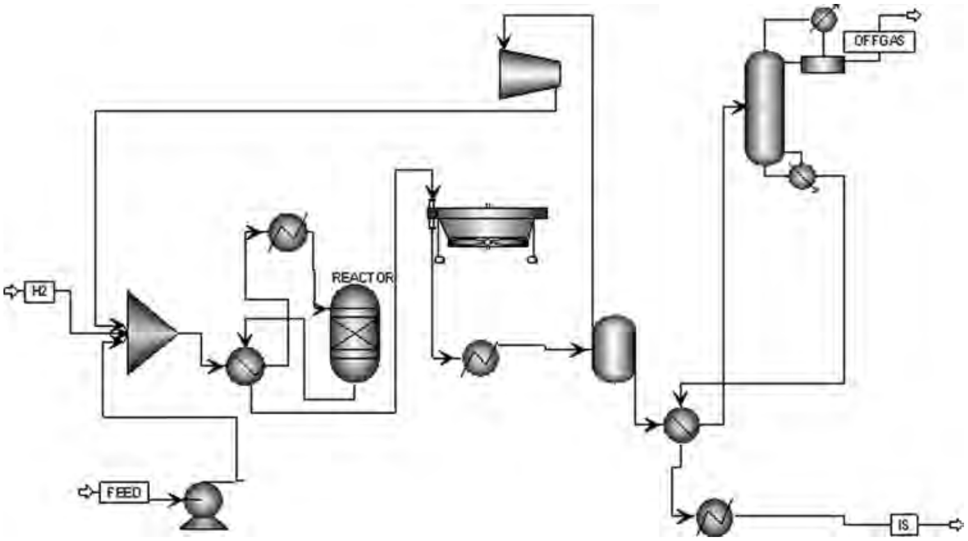


Figure 7.6—Process flow diagram for Par-Isom process.

TABLE 7.11—Isomerization Process Features

Catalyst—Process	Chlorinated Alumina (Penex Process)	Metal Oxide (Zirconia) (Par-Isom Process)	Common Zeolite (HYSOMER Process)	Modern Zeolite
Process licensor	**M/s UOP**	**M/s UOP**	**M/s Shell**	**M/s Axens (IFP)**
Feedstock conditions				
Feedstock type	C_5/C_6	C_5/C_6	C_5/C_6	C_5/C_6
Sulfur (ppm)	None	<20	<20	<200
Water (ppm)	None	<20	<20	<200
Aromatics/benzene (%)	<2	<2	<2	<10
C_7+ (%)	<2	<2	<2	<5
Feed-product treatment				
HDS	Yes	Yes	Yes	Optional
Sulfur guard	Yes	Optional	Optional	No
Feed dryer	Yes	Optional	Optional	No
Hydrogen dryer	Yes	Optional	Optional	No
Effluent guard system	Yes	No	No	No
Typical process conditions				
Temperature (K)	403–423	453–483	533–553	523–553
Pressure (barg)	15–35	15–35	15–35	15–35
Liquid hourly space velocity: (h^{-1})	1–3	1–3	1–3	1–3
H_2/HC molar ratio	1–2	1–2	1–2	1–1.5
Typical isomerate properties				
i-C_5/C_5-ratio[a]	68–72	65–71	60–65	63–67
2,2-DMB/C_6-ratio[a]	21	20.5	16	19
Isomerate yield[b] (%)	96+	96+	95+	96+
Isomerate octane[b]	Up to 94	Up to 94	Up to 94	Up to 94

[a] Reactor outlet.
[b] Unit outlet.

are based on different catalyst systems are summarized in the Table 7.11 [48].

7.5 PROCESS FOR BASE OIL PRODUCTION

Since 1890, petroleum-based lubricants are used at the automotive and industrial level [1,2]. However, as the demand for automobiles grew, so did the demand for better lubricants. This has led to process improvement in base oil production. The typical process developmental steps involved in lube oil production are depicted and described below.

Three popular processing routes that were used in early times (Figure 7.7) were solvent extraction/dewaxing, clay treating, and acid treating. These processes were primarily aimed at removing asphaltenes and wax by means of the solvent extraction route using solvents such as pentane followed by removal of aromatics by means of solvents viz. furfural, *n*-methyl pyrrolidone (NMP), or pyridine and other impurities such as oxygenates, nitrogen compounds, and color bodies via clay and acid treatment of base oil feedstock to obtain the desired lube oils. However, such a route often led to yield loss and was more suited for the production of Group I lube oil base stocks. Moreover, this route posed a serious problem for the disposal of waste clay/acid.

A major breakthrough in base oil production was achieved in the 1950s by introducing the hydroprocessing route [3]. Such a route was introduced to remove impurities, mainly unsaturated and aromatic hydrocarbons, via the hydrofinishing route (Figure 7.8).

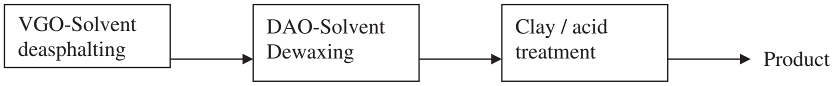


Figure 7.7—Typical process block diagram used during pre-1950s period for lube oil production.

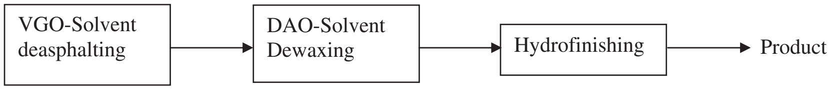


Figure 7.8—Typical process block diagram used during the 1950s for lube oil production.

With an increased demand for high-performance lube oil with high VI, the lube oil manufacturing process was revolutionized by replacing the solvent dewaxing route with the catalytic dewaxing route that is based on catalytic cracking (Figure 7.9). This technology was commercialized in the 1970s by M/s Shell to manufacture extra high-VI base oils in Europe. M/s Exxon and others built similar plants in the 1990s. Likewise, M/s Mobil used catalytic dewaxing in place of solvent dewaxing, but they still coupled it with solvent extraction to manufacture conventional neutral oils [20].

In the early 1990s, the need for higher quality lubricating oils prompted many lubricant producers to look to hydroprocessing as a means to upgrade marginal feeds to quality lube stocks and to further upgrade stocks to near-synthetic quality. Within this area, the primary focus was to obtain product yield and quality that exceed those obtained via solvent dewaxing and catalytic dewaxing. This has been the principal motivation for the development of several bifunctional, metal-loaded, molecular-sieve-based hydroisomerization catalysts that led to the evolution of all-hydroprocessing lube dewaxing technologies (Figure 7.10), including Chevron's isodewaxing and Exxon-Mobil's selective dewaxing (MSDW) and wax isomerization (MWI) processes.

In 1993, this modern wax hydroisomerization process was commercialized by M/s Chevron. This was an improvement over earlier catalytic dewaxing because the pour point of the base oil was lowered by isomerizing (reshaping) the n-paraffins and other molecules with waxy long chains into very desirable branched compounds (isoparaffins) with superior lubricating qualities rather than cracking them away. Hydroisomerization was also an improvement over the earlier wax hydroisomerization technology because it eliminated the subsequent solvent dewaxing step, which was a requirement for earlier generation wax isomerization technologies to achieve adequate yield at standard pour points. Modern wax hydroisomerization makes products with exceptional purity and stability because of the extremely high degree of saturation. They are very distinctive because, unlike other base oils, they typically have no color [86,87]. In view of the above, it is imperative to note that process improvement in lube oil production has changed over from physical separation to chemical transformation.

The modern hydroisomerization process licensed by M/s Chevron under the name ISODEWAXING® gained rapid acceptance since its introduction in 1993. In fact, approximately one third of all base oils manufactured in North America are now manufactured using this process. A similar trend can also be seen in the rest of the world. M/s Chevron has integrated the all-hydroprocessing routes (i.e., isocracking, isodewaxing, and hydrofinishing) for making high-purity Group II and Group III base oils—base oils that are as clear as water (Figure 7.11).

The general operating conditions for ISODEWAXING® are summarized as follows [3,86–90]:

- *Hydrogen partial pressure (psi):* 500–2500
- *Liquid hourly space velocity:* 0.3–1.5
- *Temperature (K):* 588–644
- *Hydrogen rate (SCF/barrel feed):* Not disclosed
- *Hydrogen consumption (SCFB):* 100–500

M/s ExxonMobil also added to this trend by commercializing an all-hydroprocessed route for Group II base oil production MSDW™, which they installed in their Jurong refinery in Singapore in 1997. MSDW™ converts waxy oils and raffinates to conventional or ultra-low pour-point (≤233 K) base oils and provides a serious jump in oil VI over hydroprocessed feed stocks. Base oils made from catalytic dewaxing exhibit improved cold-cranking performance compared with solvent dewaxed oils of similar viscosity. This is because of the unique effect of the shape-selective catalyst, which isomerizes n-paraffins rather than physically removing the wider spectrum high-melting-point waxes. The MSDW™ process also uses propriety zeolites and is claimed to be superior to Mobil's MLDW™ process, which uses ZSM-5-based catalyst, which selectively cracks paraffins leading to lower yields [89]. The improvement in product quality with the MSDW process as compared to solvent dewaxing for hydrocracked light-neutral lube oil feedstock is shown in Figures 7.12 and 7.13 [90].

Thus, advantages claimed with MSDW™ are as follows:

- High yields on all viscosity grades,
- Better cold-cranking in base oils, and
- Highly flexible process.

On similar lines, M/s ExxonMobil introduced a process called MWI for converting wax-rich streams, such as slack wax, into very high-VI lubes. This process uses a

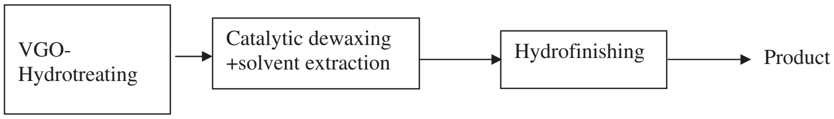


Figure 7.9—Typical process block diagram used during the 1970s for lube oil production.

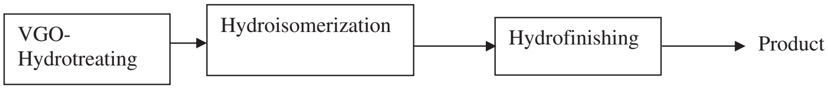


Figure 7.10—Typical process block diagram used during the 1990s for lube oil production.

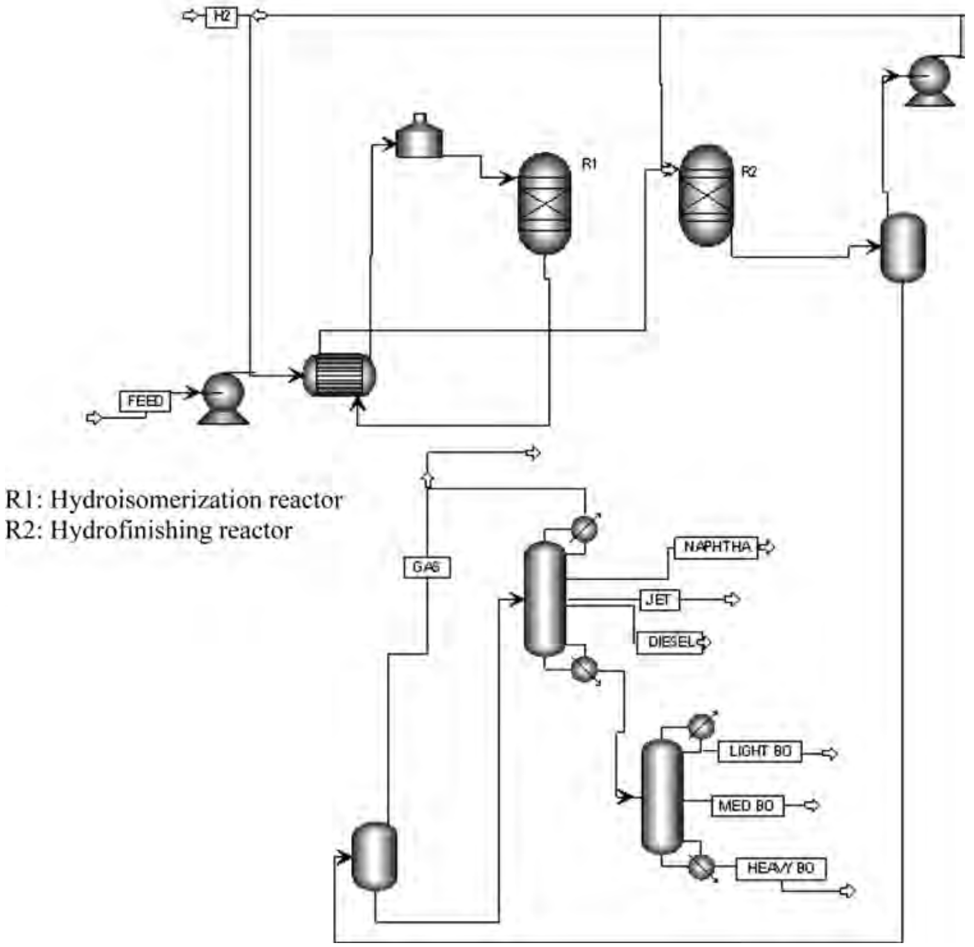


Figure 7.11—Process flow diagram for the ISODEWAXING® process.

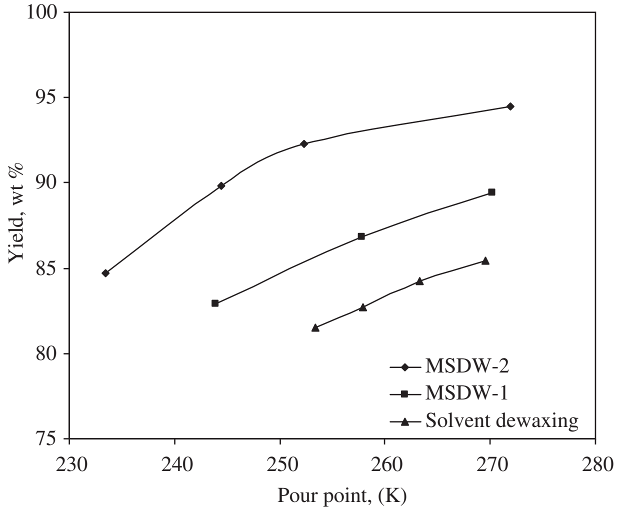


Figure 7.12—Variation for Lube oil yield as a function of pour point.

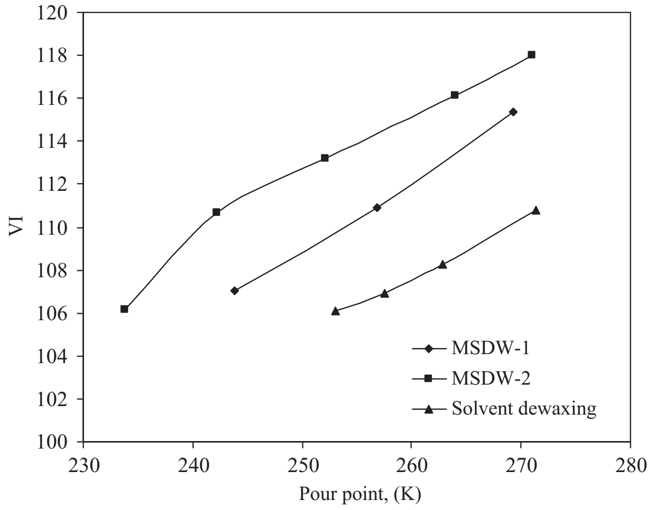


Figure 7.13—Variation for Lube oil Viscosity Index (VI) as a function of pour point.

bifunctional metal-zeolite catalyst to saturate residual aromatics, isomerizes paraffins, and opens some naphthene rings. A solvent dewaxing is used downstream of the MWI unit to remove residual wax in the product. M/s ExxonMobil recently announced an improved version of MWI in which very selective catalytic isomerization is used in place of the solvent dewaxing step to obtain high-quality lubes with very low pour points and high VIs. The MWI catalyst system can process a wide range of feedstock [89,90].

7.6 FUTURE CHALLENGES AND OPPORTUNITIES

In view of the significant aforementioned improvements in catalyst and process developments, it is important to note the major concerns and future challenges of the hydroisomerization catalyst and conversion processes.

As illustrated in Section 7.3, catalyst performance for light alkane isomerization is susceptible to the naphthene content in the feed. The processes practiced commercially in once-through mode often operate with restriction on the naphthene content in the feedstock. Therefore, a catalyst system to handle higher naphthene content needs to be developed. In this context, zeolite membrane reactors could offer clear advantages in terms of the handling of feed quality, improved yield, and energy savings due to the exceptional properties of zeolite membranes, which include their (1) size- and shape-selective separation behavior, (2) their thermal and chemical stability, and (3) the ability to couple the discrimination between molecules to catalytic conversion. However, it is clear that to capitalize on these benefits, a substantial reduction in membrane module cost and further improvements on the integrity (selectivity and permeability) of the molecular sieve films to facilitate a reduction in surface area requirements are mandatory for further commercial development.

On the other hand, the performance of the current lube oil catalyst is often limited because of isomerization selectivity, throughput, and feed impurities. Thus, it is important to further fine-tune lube oil dewaxing catalysts in terms of

- Increased conversion level,
- Increased isomer selectivity, and
- Feedstock flexibility and throughput (expansion of LHSV operation).

This can be achieved through catalyst design by developing the structures with certain distribution of active sites on the surface of the crystallites. Advances in nanoscience could open up the promising possibilities to realize this goal for catalyst synthesis that promote certain orientations of reacting molecules, thereby facilitating their highly selective rearrangements. The crystallite size of the support (zeolite) is also seen to be of paramount importance for improving the activity and selectivity in the hydroconversion of alkanes. Control of pore or surface structure at the nanolevel is envisaged to alter hydrocarbon diffusion efficiency, which in turn could significantly modify the activity, isomerization selectivity, and cycle life of catalysts. Few attempts have been made in this regard in which nanocrystals of MTT (ZSM-23 type) with enhanced activity and isomerization selectivity for *n*-octane, *n*-hexadecane, and wax hydroconversion have been achieved. In view of this, sustained efforts are essential to scale up such a catalyst system.

CONCLUSIONS

In view of the stringent fuel and base oil specifications, the isomerization of light and long-chain paraffins has gained considerable importance in recent times. Such a process is generally performed over bifunctional catalysts consisting of metallic and acidic function, respectively. The metal function promotes the dehydrogenation of n-paraffin followed by hydrogenation of formed olefin to isoparaffin, whereas the skeletal isomerization of formed olefin via a carbenium ion mechanism occurs by the acidic function of the catalyst. Catalysts that have a high degree of hydrogenation activity and a low degree of acidity are the best suited for light naphtha and lube oil isomerization. In this context, Pt/Al_2O_3, Pt/zeolite, and Pt/ Pt/SO_4^{2-}/ZrO_2 have been commercially exploited for light naphtha isomerization whereas medium-pore zeolites with TON/MTT topology are found to be an ideal choice for lube oil isomerization.

On the basis of the aforementioned catalyst systems, hydroisomerization processes have evolved. All of these processes are performed in a fixed-bed reactor. The processes for light naphtha isomerization have seen operational changeover from once-through to recycle mode to achieve RONs over 90. In the recycle mode, unconverted n-paraffins in the single pass are separated either through distillation or molecular sieve separation from isomerized products. Likewise, process steps for lube oil production have changed over from physical wax separation to its chemical transformation, thereby leading to the production of improved yields and better quality lubricant base stocks. Such step change has offered a platform to either integrate or replace the solvent dewaxing processes for production of Grade II/III base oils. However, catalyst limitations in terms of its conversion, isomerization selectivity, and maximization of throughput still demand the search for new catalysts and process improvements to produce high-quality fuels and lubricants.

ACKNOWLEDGMENTS

The authors are thankful to the management of Bharat Petroleum Corporation Limited for granting permission to publish this chapter.

REFERENCES

[1] Speight, J.G., *The Chemistry and Technology of Petroleum*, 3rd ed., Marcel Dekker, New York, 1999.

[2] Silvy, R.P., “Future Trends in the Refining Catalyst Market,” *Appl. Catal. A*, Vol. 261, 2004, pp. 247–252.

[3] Sequeira, A., Jr., *Lubricant Base Oil and Wax Processing*, Marcel Dekker, New York, Chemical Industries Series, 1994.

[4] Travers, C., and Leprince, P., Petroleum Refining, in *Conversion Processes*, Editions Technip, Paris, Vol. 3, 2001 pp. 229–256.

[5] Deldari, H., “Suitable Catalysts for Hydroisomerization of Long-Chain Normal Paraffins,” *Appl. Catal. A*, Vol. 293, 2005, pp. 1–10.

[6] Akhmedov, V.M., and Al-Khowaiter, S.H., “Recent Advances and Future Aspects in the Selective Isomerization of High n-Alkanes,” *Catal. Rev.*, Vol. 49, 2007, pp. 33–139.

[7] Condon, F.E., “Catalytic Isomerization of Hydrocarbons,” in P.H. Emmet, Ed., *Catalysis*, Reinhold, New York, 1958, Vol. 6, p. 43.

[8] Sie, S.T., “Isomerization Reactions,” in G. Ertl, H. Knozinger, and J. Weitkamp, Eds., *Handbook of Heterogeneous Catalysis*, Wiley VCH, Weinheim, Germany, 1997, Vol. 4, pp. 1998–2017.

[9] Yadav, G.D., and Nair, J.J., “Sulfated Zirconia and Its Modified Versions As Promising Catalysts for Industrial Processes,” *Micro. Meso. Mater.*, Vol. 33, 1999, pp. 1–48.

[10] Ono, Y., “A Survey of the Mechanism in Catalytic Isomerization of Alkanes,” *Catal. Today,* Vol. 81, 2003, pp. 3–16.

[11] Szostak, R., *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York, 1989.

[12] Szostak, R., *Handbook of Molecular Sieves*, Van Nostrand Reinhold, New York, 1997.

[13] Tromp, M., van Bokhovan, J.A., Garriga Oostenbrink, M.T., Bitter, J.H., de Jong, K.P., and Koningsberger, D.C., “Influence of the Generation of Mesopores on the Hydroisomeriztion Activity and Selectivity of *n*-Hexane over Pt/Mordenite,” *J. Catal.*, Vol. 190, 2000, p. 209.

[14] Guisnet, M., Alvarez, G., Gianetto, G., and Perot, G., “Hydromisomerization and Hydrocracking of n-Heptane on PtH Zeolites. Effect of the Porosity and of the Distribution of Metallic and Acid Sites,” *Catal. Today,* Vol. 1, 1987, 415.

[15] Henriques, C., Dufresne, P., Marcilly, C., and F. Ramoa-Ribeiro, "Influence of Tin on the Stability of Sn/Pd Hy Zeolites in the Hydrocracking and Hydroisomerization of n-Heptane," *Appl. Catal.*, Vol. 21, 1986, pp. 169–177.

[16] Akhmedov, V.M., and Klabunde, K.J., "High-Activity Re-Pt/MO Catalysts for C–C Bond Cleavage Reactions: Preparation by Solvated Metal Atom Dispersion," *J. Mol. Catal.*, Vol. 45, 1988, pp. 193–206.

[17] Martens, J.A., Jacobs, P.A., and Weitkamp, J., "Attempts to Rationalize the Distribution of Hydrocracked Products. I. Qualitative Description of the Primary Hydrocracking Modes of Long Chain Paraffins in Open Zeolites," *Appl. Catal.*, Vol. 20, 1986, pp. 239–281.

[18] Carvill, B.T., Lerner, B.A., Adelman, B.J., Tomczak, D.C., and Sachtler, W.M., "Increased Catalytic Activity Caused by Local Destruction of Linear Zeolite Channels: Effect of Reduction Temperature on Heptane Conversion over Platinum Supported in H-Mordenite," *J. Catal.*, Vol. 144, 1993, pp. 1–8.

[19] Blomsma, E., Martens, J.A., and Jacobs, P.A., "Reaction Mechanisms of Isomerization and Cracking of Heptane on Pd/H-Beta Zeolite," *J. Catal.*, Vol. 155, 1995, pp. 141–147.

[20] Blomsma, E., Martens, J.A., and Jacobs, P.A., "Mechanisms of Heptane Isomerization on Bifunctional Pd/H-Beta Zeolites," *J. Catal.*, Vol. 159, 1996, pp. 323–331.

[21] Remy, M.J., Stanica, D., Poncelet, G., Feijen, E.J.P., Grobet, P.J., Martens, J.A., and Jacobs, P.A., "Dealuminated H-Y Zeolites: Relation between Physicochemical Properties and Catalytic Activity in Heptane and Decane Isomerization," *J. Phys. Chem.*, Vol. 100, 1996, pp. 12440–12447.

[22] Chao, K.J., Wu, H.C., and Leu, L.J., "Hydroisomerization of Light Normal Paraffins over Series of Platinum-Loaded Mordenite and Beta Catalysts," *Appl. Catal. A*, Vol. 143, 1996, pp. 223–243.

[23] Wang, Z.B., Kamo, A., Yoneda, T., Komatsu, T., and Yashima, T., "Isomerization of n-Heptane over Pt-Loaded Zeolite β Catalysts," *Appl. Catal. A*, Vol. 159, 1997, pp. 119–132.

[24] Mao Le Van, R., and Saberi, M.A., "Catalysts for the Hydroisomerization of n-Heptane, Prepared According to the Concept of 'Triangular' Site Configuration (Acid/Metal/Desorption-Transfer Promoting Sites," *Appl. Catal. A*, Vol. 199, 2000, pp. 99–107.

[25] Meloni, D., Martin, D., and Guisnet, M., "Acidic and Catalytic Properties of H-MCM-22 Zeolites: 2. n-Heptane Cracking: Activity, Selectivity and Deactivation by Coking," *Appl. Catal. A*, Vol. 215, 2001, pp. 67–79.

[26] Pope, T.D., Kriz, J.F., Stanciulescu, M., and Monnier, J., "Study of Catalyst Formulations for Isomerization of C_7 Hydrocarbons," *Appl. Catal. A*, Vol. 233, 2002, pp. 45–62.

[27] Chao, K., Lin, C.-C., Lin, C.-H., Wu, H., Tseng, C., and Chen, S., "n-Heptane Hydroconversion on Platinum-Loaded Mordenite and Beta Zeolites: The Effect of Reaction Pressure," *Appl. Catal. A*, Vol. 203, 2000, pp. 211–220.

[28] Chica, A., Corma, A., and Miguel, P.J., "Isomerization of C_5-C_7 n-Alkanes on Unidirectional Large Pore Zeolites: Activity, Selectivity and Adsorption Features," *Catal. Today*, Vol. 65, 2001, pp. 101–110.

[29] Saberi, M.A., Le Van Mao, R., Martin, M., and Mak, A.W.H., "Effect of Zn Loading of the Pt-Zn-HY Trifunctional Catalysts on the Hydroisomeriztion of n-Heptane," *Appl. Catal. A*, Vol. 214, 2001, pp. 229–236.

[30] Gopal, S., and Smirniotis, P.G., "Pt/H-ZSM-12 As a Catalyst for the Hydroisomeriztion of C5-C7 n-Alkanes and Simultaneous Saturation of Benzene," *Appl. Catal. A*, Vol. 247, 2003, pp. 113–123.

[31] Akhmedov, V.M., Al-Khowaiter, S.H., Akhmedov, E., and Sadikhov, A., "Low Temperature Hydrocracking of Hydrocarbons on Ni-Supported Catalysts," *Appl. Catal. A*, Vol. 181, 1999, pp. 51–61.

[32] Akhmedov, V.M., and Al-Khowaiter, S.H., "Hydroconversion of Hydrocarbons over Ru-Containing Supported Catalysts Prepared by Metal Vapor Method," *Appl. Catal. A*, Vol. 197, 2000, pp. 201–212.

[33] Akhmedov, V.M., Al-Khowaiter, S.H., and Al-Refai, J.K., "Hydroconversion of C_4-C_8 Alkanes over Zr-Containing Supported Catalysts Prepared by Metal Vapor Method," *Appl. Catal. A*, Vol. 252, 2003, pp. 353–361.

[34] Lugstein, A., Jentys, A., and Vinek, H., "Hydroisomerization and Cracking of n-Octane and C_8 Isomers on Ni-Containing Zeolites," *Appl. Catal. A*, Vol. 176, 1999, pp. 119–128.

[35] Zhang, W., and Smirniotis, P.G., "Effect of Zeolite Structure and Acidity on the Product Selectivity and Reaction Mechanism for n-Octane Hydroisomerization and Hydrocracking," *J. Catal.*, Vol. 182, 1999, pp. 400–416.

[36] De Lucas, A., Valverde, J.L., Sánchez, P., Dorado, F., and Ramos, M.J., "Hydroisomerization of n-Octane over Platinum Catalysts with or without Binder," *Appl. Catal. A*, Vol. 282, 2005, pp. 15–24.

[37] De Lucas, A., Sánchez, P., Dorado, F., Ramos, M.J., and Valverde, J.L., "Effect of the Metal Loading in the Hydroisomerization of n-Octane over Beta Agglomerated Zeolite Based Catalysts," *Appl. Catal. A*, Vol. 294, 2005, pp. 215–225.

[38] Kuznetsov, P.N., "Study of n-Octane Hydrocracking and Hydroisomerization over Pt/HY Zeolites Using the Reactors of Different Configurations," *J. Catal.*, Vol. 218, 2003, pp. 12–23.

[39] Kinger, G., and Vinek, H.,"n-Nonane Hydroconversion on Ni and Pt Containing HMFI, HMOR, and HBEA," *Appl. Catal. A*, Vol. 218, 2001, pp. 139–149.

[40] Gora, L, and Jansen, J.C., "Hydroisomerization of C_6 with a Zeolite Membrane Reactor," *J. Catal.*, Vol. 230, 2005, pp. 269–281.

[41] Maloncy, M.L., Gora, L., Jansen, J.C., and Maschmeyer Th., "Conceptual Processes for Zeolite Membrane Based Hydroisomerization of Light Alkanes," *Ars Separatoria Acta*, Vol. 2, 2003, pp. 18–28.

[42] Shan, Z., Giannoti, E., Jansen, J.C., Peters, J.A., Marchese, L., and Maschmeyer, Th., "One-Step Synthesis of a Highly Active, Mesoporous, Titanium-Containing Silica by Using Bifunctional Templating," *Chem. Eur. J.*, Vol. 7, 2001, pp. 1437–1573.

[43] Jansen, J.C., Shan, Z., Marchese, L., Zhou, W.V., Puil, N., and Maschmeyer, Th., "A New Templating Method for Three-Dimensional Mesopore Networks," *Chem. Commun.*, 2001 pp. 713–714.

[44] Grau, J.M., Yori, C. J., Vera, C.R., Lovey, F.C., Condóc, A.M., and Parera, A.M., "Crystal Phase Dependent Metal-Support Interactions in Pt/SO_4^{2-}-ZrO_2 Catalysts for Hydroconversion of n-Alkanes," *Appl. Catal. A*, Vol. 265, 2004, pp. 141–152.

[45] Kimura, T., "Development of Pt/SO_4^{2-}/ZrO_2 Catalyst for Isomerization of Light Naphtha," *Catal. Today*, Vol. 81, 2003, pp. 57–63.

[46] Weyda, H., and Köhler, E., "Modern Refining Concepts—An Update on Naptha-Isomeriztion to Modern Gasoline Manufacture," *Catal. Today*, Vol. 81, 2003, pp. 51–55.

[47] Ono, Y., "Heteropoly Acid Catalysis—A Unique Blend of Acid-Base Redox Properties," in J.M. Thomas and K.I. Zamaraev, Eds., *Perspectives in Catalysis*, Blackwell, London, 1992, pp. 431–464.

[48] Okuhara, T., Mizuno, N., and Misono, M., "Catalytic Chemistry of Heteropoly Compounds," *Adv. Catal.*, Vol. 41, 1996, pp. 113–252.

[49] Misono, M., "Heterogeneous Catalysis by Heteropoly Compounds of Molybdenum and Tungsten," *Catal. Rev.*, Vol. 29, 1987, pp. 269.

[50] Misono, M., "Unique Acid Catalysis of Heteropoly Compounds (Heteropolyoxometalates) in the Solid State," *Chem. Commun.*, 2001, pp. 1141–1227.

[51] Suzuki, S., Kogai, M., and Ono, Y., "Isomerization of Alkanes over a Palladium Salt of Heteropolacid," *Chem. Lett.*, 1984, pp. 699–702.

[52] Ono, Y., Taguchi, M., Gerille, M., Suzuki, S., and Baba, T., "Heteropolyacids As Solid-Acid Catalysts," *Stud. Surf. Sci. Catal.*, Vol. 20, 1985, pp. 167–176.

[53] Ledoux, M.J., Pham-Huu, C., Dunlop, H., and Guille, J., "n-Hexane Isomerization on High Specific Surface Mo2C Activated by an Oxidative Treatment," *Stud. Surf. Sci. Catal.*, Vol. 75, 1993, pp. 955–967.

[54] Blekkan, E., Pham-Huu, C., Ledoux, M.J., and Guille, J., "Isomerization of n-Heptane on an Oxygen-Modified Molybdenum Carbide Catalyst," *Ind. Eng. Chem. Res*., Vol. 33, 1994, pp. 1657–1664.

[55] Ledoux, M.J., Pham-Huu, C., Delporte, P., Blekkan, E.A., York, A.P.E., Derouane, E.G., and Fonseca, A., "Evidence for a New, Very Active and Selective Catalyst for Hydrocarbon Isomerization: Molybdenum Oxicarbide," *Stud. Surf. Sci. Catal*., Vol. 92, 1994, p. 81.

[56] York, A.P.E., Pham-Huu, C., Gallo, P.D., and Ledoux, M.J., "Molybdenum Oxycarbide Hydrocarbon Isomerization Catalysts: Cleaner Fuels for the Future," *Catal. Today*, Vol. 35, 1997, pp. 51–57.

[57] Miller, S.J., U.S. Patent application 0 077 209, 2005.

[58] Martens, J.A., Souverijns, W., Verrelst, W., Parton, R., Froment, G.F., and Jacobs, P.A., "Selective Isomerization of Hydrocarbon Chains on External Surfaces of Zeolite Crystals," *Angew. Chem. Int. Ed. Engl*., Vol. 34, 1995, pp. 2528–2530.

[59] Claude, M.C., and Martens, J.A., "Monomethyl-Branching of Long n-Alkanes in the Range from Decane to Tetracosane on Pt/H-ZSM-22 Bifunctional Catalyst," *J. Catal*., Vol. 190, 2000, pp. 39–48.

[60] Claude, M.C., Vanbutsele, G., and Martens, J.A., "Dimethyl Branching of Long n-Alkanes in the Range from Decane to Tetracosane on Pt/H-ZSM-22 Bifunctional Catalyst," *J. Catal*., Vol. 203, 2001, pp. 213–231.

[61] Souverijns, W., Martens, J.A., Froment, G.F., and Jacobs, P.A., 'Hydrocracking of Isoheptadecanes on Pt/H-ZSM-22: An Example of Pore Mouth Catalysis,' *J. Catal*., Vol. 174, 1998, Vol. 177–184.

[62] Acharya, M., and Stern, D.L., WO 74,221A1, 2004.

[63] Huybrechts, W., Vanbutsele, G., Houthoofd, K.J., Bertinchamps, F., Laxmi Narasimhan, C. S., Gaigneaux, E.M., Thybaut, J.W., Marin, G.B., Denayer, J.F.M., Baron, G.V., Jacobs, P.A., and Martens, J.A., "Skeletal Isomerization of Octadecane on Bifunctional ZSM-23 Zeolite Catalyst," *Catal. Lett*., Vol. 100, 2005, pp. 235–.

[64] Zones, S., Jr., and Burton, W.A., U.S. Patent 6,676,923.

[65] Burton, A.W., Zones, S.I., Rea, T., and Chan, I.Y., "Preparation and Characterization of SSZ-54: A Family of MTT/TON Intergrowth Materials," *Micro. Meso. Mater*., Vol. 132, 2010, pp. 54–59.

[66] Maesen, Th.L.M., Schenk, M., Vlugt, T.J.H., de Jonge, J.P., and Smit, B., "The Shape Selectivity of Paraffin Hydroconversion on TON-, MTT-, and AEL-Type Sieves," *J. Catal*., Vol. 188, 1999, pp. 403–412.

[67] Geng, C.-H., Zhang, F., Gao, Z.-X., Zhao, L.-F., and Zhou, J.-L., "Hydroisomerization of *n*-Tetradecane over Pt/SAPO-11 Catalyst," *Catal. Today*, Vol. 93–95, 2004, pp. 485–491.

[68] Ernst, S., Weitkamp, J., Martens, J.A., and Jacobs, P.A., "Synthesis and Shape-Selective Properties of ZSM-22," *Appl. Catal.*, Vol. 48, 1989, pp. 137–148.

[69] Weitkamp, J., Ernst, S., and Kumar, R., "Zeolith ZSM-123: Hydrothermale Synthese und Katalytische Eigenschaften," *Chem. Ing. Tech*., Vol. 59, 1987, pp. 135–137.

[70] Huang, X., Wang, L., Kong, L., and Li, Q., "Improvement of Catalytic Properties of SAPO-11 Molecular Sieves Synthesized in H_2O-CTAB-Butanol System," *Appl. Catal. A*, Vol. 253, 2003, pp. 461–467.

[71] Sinha, A.K., Sivasanker, S., and Ratnasamy, P., "Hydroisomerization of n-Alkanes over Pt-SAPO-11 and Pt-SAPO-31 Synthesized from Aqueous and Nonaqueous Media," *Ind. Eng. Chem. Res*., Vol. 37, 1998, pp. 2208–2214.

[72] Blasco, T., Chica, A., Corma, A., Murphy, W.J., Rodriguez, A.-J., Pérez-Pariente, A., "Changing the Si Distribution in SAPO-11 by Synthesis with Surfactants Improves the Hydroisomerization/Dewaxing Properties," *J. Catal*., Vol. 242, 2006, pp. 153–161.

[73] Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C., and Beck, J.S., "Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism," *Nature*, Vol. 359, 1992, pp. 710–712.

[74] Fang, K., Wei, W., Ren, J., and Sun, Y., "n-Dodecane Hydroconversion over Ni/AlMCM-41 Catalysts," *Catal. Lett*., Vol. 93, 2004, pp. 235–242.

[75] Elangovan, S.P., Bischof, C., and Hartmann, M., "Isomerization and Hydrocracking of n-Decane over Bimetallic Pt-Pd Clusters Supported on Mesoporous MCM-41 Catalysts," *Catal. Lett*., Vol. 80, 2002, pp. 35–40.

[76] Lin, S., Ning, H., Wan-Fu, S., Wei-Min, L., and Qun-Ji, X., "Preparation of Pd/Al-MCM-41 Catalyst and Its Hydroisomerization Properties for Long Chain Alkane Compounds," *Stud. Surf. Sci. Catal*., Vol. 141, 2002, pp. 517–524.

[77] Barton, D.G., Soled, S.L., Meitzner, G.D., Fuentes, G.A., and Iglesia, E., "Structural and Catalytic Characterization of Solid Acids Based on Zirconia Modified by Tungsten Oxide," *J. Catal*., Vol. 181, 1999, pp. 57–72.

[78] Hino, M., and Arata, K., "Synthesis of Solid Superacid Catalyst with Acid Strength of H0 ≤ –16.04," *Chem. Commun*., 1980, pp. 851–852.

[79] Zhang, S., Zhang, Y., Tierney, J.W., and Wender, I., "Hydroisomerization of Normal Hexadecane with Platinum-Promoted Tungstate-Modified Zirconia Catalysts," *Appl. Catal. A*, Vol. 193, 2000, pp. 155–171.

[80] Wen, M.Y., Wender, I., Tierney, J.W., "Hydroisomerization and Hydrocracking of n-Heptane and n-Hexadecane on Solid Superacids," *Energy Fuels*, Vol. 4, 1990, pp. 372–379.

[81] Keogh, R.A., Sparks, D., Hu, J., Wender, I., and Tierney, J.W., "Hydroisomerization and Hydrocracking of n-Hexadecane over a Platinum-Promoted Sulfated Zirconia Catalyst," *Energy Fuels*, Vol. 8, 1994, pp. 755–762.

[82] Keogh, R.A., and Davis, B.H., "Hydroconversion of n-Hexadecane with Pt-Promoted Monoclinic and/or Tetragonal Sulfated Zirconia Catalysts," *Catal. Lett*., Vol. 57, 1999, pp. 33–35.

[83] Kramer, D.C., Lok, B.K., and Krug, R.R., "The Evolution of Base Oil Technology," in W.R. Herguth and T.M. Warne, Eds., *Turbine Lubrication in the 21st Century*, ASTM STP #1407, ASTM International, West Conshohocken, PA, 2001.

[84] Krishna, K.R., Rainis, A., Marcantonio, P.J., Mayer, J.F., Biscardi, J.A., and Zones, S.I., "Next Generation Isodewaxing® and Hydrofinishing Technology for Production of High Quality Base Oils," in *Proceedings of NPRA Meeting on Lubricants and Waxes*, 2002.

[85] Zones, S.I., Zhang, G., Krishna, K., Biscardi, J.A., Marcantonio, P., and Vittoratos, E., U.S. Patent 7468126, 2008.

[86] Maesen, T.L.M., and Krishna, K.R., U.S. Patent Application 2007/0029230 A1, 2006.

[87] Maesen, T.L.M., Smit, B., and Beerdsen, E., U.S. Patent Application 2007/0029229 A1, 2006.

[88] Zones, S., and Burton, A.W., Jr., U.S. Patent 6,676,923, 2004.

[89] Degnan, T.F., Jr., "Applications of Zeolites in Petroleum Refining," *Top. Catalysis*, Vol. 13, 2000, pp. 349–356.

[90] Kerby, M.C., Degnan, T.F., Jr., Marler, D.O., and Beck, J.S., "Advanced Catalyst Technology and Applications for High Quality Fuels and Lubricants," *Catal. Today*, Vol. 104, 2005, pp. 55–63.

8

Heavy-Oil Processing

Semih Eser[1] and Jose Guitian[2]

8.1 DEFINITIONS AND SOURCES OF HEAVY OILS

8.1.1 Definition of Heavy Oils

There are various ways to characterize crude oil. Most of them are based on API gravity and viscosity at field conditions. Table 8.1 gives a classification that is used for the purposes of this chapter.

Oils with an API gravity between 22° and 10° API are considered as heavy crude. Extra-heavy crudes are defined as oils with an API gravity of <10°API and a viscosity of <10,000 cSt and that are mobile at initial reservoir conditions. These types of crude can be found in the Orinoco Oil Belt in Venezuela, Colombia, Argentina, Peru, and California in the United States. Bitumens are characterized by an API gravity of <10°API that are immobile at reservoir conditions. These types of crude are also called "oil sands" or "tar sands" such as the Canadian oil sands. More information and data on different kinds of heavy oils can be found in the literature [1,2].

8.1.2 Sources of Heavy Crudes

Heavy oil and bitumen are widely distributed worldwide. They have been found in every continent except Antarctica, as indicated in Figure 8.1. The total estimated resources of heavy crude and bitumen are 3.3 trillion barrels, and 2.6 trillion barrels, respectively. According to the U.S. Department of Energy's (DOE) Energy Information Administration (EIA) [3] and the U.S. Geological Survey (USGS) [4], the potential recoverable reserves are on the order of 1 trillion barrels that are in the same order of magnitude as the proven reserves of the world's conventional (medium and light) crude oils.

Most of the heavy crude and bitumen produced today come mainly from North and South America: Canada, Venezuela, Mexico, the United States, Brazil, and Ecuador. The Canadian oil sands (bitumen) and the Venezuela Orinoco Oil Belt (heavy crude) are the largest accumulations of nonconventional oil reserves in the world. The Western Hemisphere has 69 % of the world's heavy-oil reserves and 63 % of the natural bitumen resources. In contrast, the Eastern Hemisphere has approximately 85 % of the world's light oil reserves.

Most heavy-oil reserves have not been massively extracted until recent times because of higher production, transport, and processing costs of this type of crude. Declining availability of conventional crude reserves has sparked recent interest in processing and converting the heavier crudes and bitumen. Major oil companies have considered the heavier crudes as replacement for light and medium crudes. The projections for estimated heavy-oil and bitumen production are shown in Figure 8.2.

According to the EIA, total oil consumption will increase from 85 million bbl/day in 2006 to 107 million bbl/day to in 2030, whereas the total heavy-oil production will increase from 8 million bbl/day in 2006 to 16 million bbl/day, and the extra-heavy-oil + bitumen production will increase from 2 million bbl/day in 2006 to 6 million bbl/day in 2030.

Currently, a large part of the heavy oil produced in Venezuela and Canada is upgraded to produce a light synthetic crude oil (SCO) of high quality or diluents to mix with the untreated heavy crude for transportation to the markets because of the lack of light crudes or naphtha for dilution. This type of crude is called "Synbit" because it consists of a mixture of synthetic distillates produced by upgrading the virgin heavy crude. In the future, the scarcity of the diluents will grow much larger. Therefore, most of the heavy crude will need to be commercialized as SCO.

8.2 ANALYSIS OF HEAVY OIL

As the crude oil base for worldwide refining gets heavier, the analysis of the heavy oils or the heavy (or high-boiling) components of crude oil stocks has become increasingly important. To optimize the selection of upgrading processes, processing conditions, and distribution to lighter products, it has become crucial to obtain analytical data on heavy oils beyond the conventional characterization techniques, such as API gravity, sulfur content, viscosity, and simple fractionation by distillation and/or solvent extraction. Several publications [5–9] have clearly articulated this need along with the associated challenges and reviewed the use of different methods for the analysis of heavy oils. Because of the extremely complex constitution of heavy oils, it is often necessary to separate the oil samples into fractions that can be more easily analyzed. The recent advances in the analysis of heavy oils stem from the improvements of instrumental techniques that enable better fractionation into compound groups and increased resolution of the molecular species in the separated fractions. This section provides an overview of analytical techniques that are commonly used to characterize heavy oils.

Because the volatility of the heavy-oil samples is low, gas chromatography applies only to analyze the components separated and concentrated using various preparative fractionation techniques. However, liquid chromatography is commonly used in a preparative scheme for initial fractionation of the samples for further analysis or in an analytical mode for speciation of the separated fractions. Barman et al. [10] and Sharma et al. [11] have reviewed the chromatographic techniques used for analyzing petroleum and related products.

---

[1] Pennsylvania State University, University Park, PA, USA

[2] Repsol S. A., Madrid, Spain

TABLE 8.1—Classification of Oils and Definition of Heavy Oil, Extra-Heavy Oil, and Bitumen

Type of Oil	API Gravity	Viscosity in the Reservoir	Definition of Oil
Conventional Oil	>45°		Condensate
	22–45°		Medium-light crude
Nonconventional Oil	10–22°	<10,000 cSt Mobile at reservoir conditions	Heavy crude
	<10°	<10,000 cSt Mobile at reservoir conditions	Extra-heavy crude
	<10°	>10,000 cSt Immobile at reservoir conditions	Bitumen

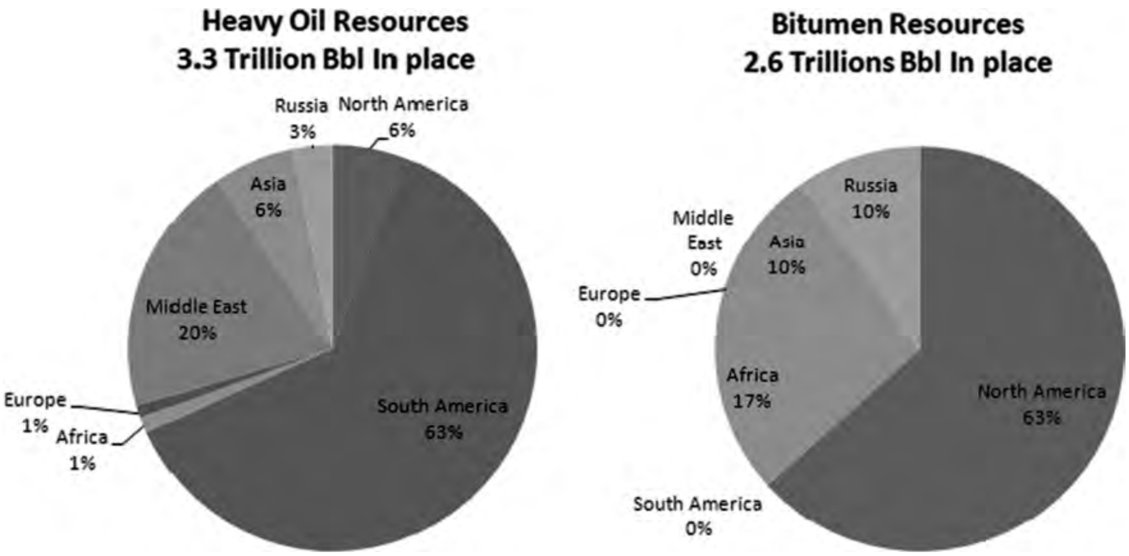


Figure 8.1—Heavy-oil and bitumen resources and their worldwide distribution [3].

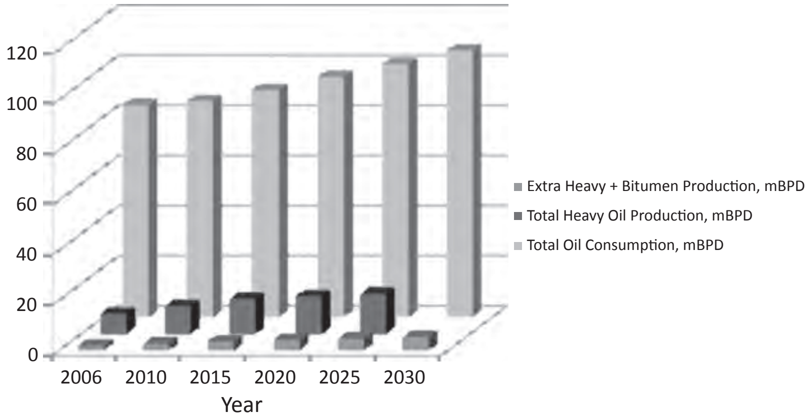


Figure 8.2—Projections of total oil consumption and total production of heavy-oil and extra-heavy-oil/bitumen production [3,4].

8.2.1 SARA Analysis

One prominent application of liquid chromatography is found in a frequently used SARA analysis that separates an oil sample into four fractions: saturates, aromatics, resins, and asphaltenes with respect to hydrocarbon types and the solubility/adsorption behavior of the constituent species [12]. Figure 8.3 shows a schematic diagram of the separation scheme used in SARA analysis. In the first step, the oil sample is mixed with an abundant quantity (typically a 1:40 ratio) of light n-paraffin solvent (e.g., *n*-heptane) to precipitate the insoluble materials (asphaltenes) that are filtered and exhaustively washed with the same solvent to make sure that all of the soluble material is recovered and added to the soluble (maltene) fraction for further

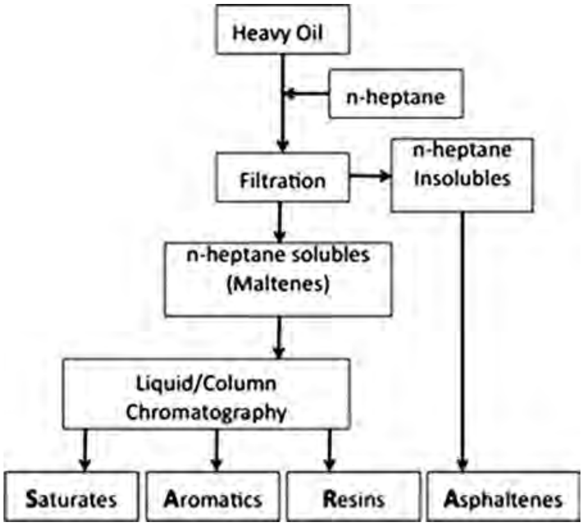


Figure 8.3—A schematic diagram of SARA analysis.

separation of the saturate, aromatic, and resin fraction using chromatography. In the chromatographic separation, one or two columns are used with a sequence of solvents to elute the adsorbed saturates, aromatics, and resins, respectively. The saturate fraction consists of (n-, i-, and cyclo-) alkanes (i.e., paraffins and naphthenes) and the aromatic fraction contains aromatic hydrocarbons. The concept of SARA analysis was introduced in 1972 [12] and adopted as a standard method (ASTM D2007) [13] and has gone through many modifications. A principal driving force for introducing these modifications has been to reduce the long time period and large quantities of samples and solvents needed for the ASTM procedure. The variations of SARA analysis have included using different n-paraffin solvents (*n*-pentane, *n*-hexane, and *n*-heptane), different oil-to-solvent ratios, different columns (e.g., clay-gel, silica, alumina, and lately bonded phase columns), and different liquid chromatography methods [e.g., open column, high-pressure liquid chromatography (HPLC), thin layer chromatography (TLC), and supercritical fluid chromatography (SFC)]. The variations used in SARA analysis lead to different results, including the differences in mass yields of the four fractions and their composition. Therefore, it is important to be cognizant of all of the experimental parameters used for the analysis when comparing the reported results. Kaminski et al. have reviewed the chromatic methods developed and validated for SARA analysis [13]. Several authors [14-18] have reported and compared results using different methodologies for SARA analysis of heavy oils. Hannisdal et al. [19] used near-infrared (NIR) and infrared (IR) spectroscopy and Sastry et al. [20] used Fourier transform infrared spectroscopy (FTIR) for analyzing the SARA fractions and provide a group-type analysis for heavy oils.

The results from SARA analysis can relate to important properties of heavy oils such as thermal reactivity, the stability of asphaltenes during processing, tendency to form coke on catalysts, and the expected yields and composition of the products from the upgrading processes. These relationships can help select the most beneficial upgrading process for a heavy-oil stock and the optimum processing conditions to achieve the desired product yields and composition.

8.2.2 Hydrocarbon Group Analysis and Molecular Speciation Techniques

In addition to being used as an effective separation technique in SARA analysis, HPLC has frequently been used as an analytical tool to provide molecular speciation of heavy oils or their maltene fractions [21–23]. More recently, Saravanabhavan et al. [24] and Pasadakis et al. [25] reported results on polycyclic aromatic hydrocarbon (PAH) composition of a heavy gas oil sample using HPLC with a photodiode array detector (PAD) to identify PAHs on the basis of the ultraviolet (UV) spectra. The HPLC/PAD results of Saravanabhavan et al. [24] compared well with the gas chromatography (GC)/mass spectrometry (MS) results on the same samples. Wang and Eser [26] reported analysis of the PAH composition of fluid catalytic cracking (FCC) decant oils by HPLC/PAD, HPLC in tandem mass detectors (HPLC/MS/MS), and laser desorption mass spectrometry (LDMS) to complement the GC/MS analysis to extend to higher-boiling compounds in the decant oils. Figure 8.4 shows their HPLC/PAD (top) and HPLC/MS/MS (bottom) chromatograms identifying the PAH ring systems and their alkyl-substituted analogs present in a decant oil. In heavy crude oil samples, longer alkyl chains are associated with the PAH ring systems. Hinkle et al. [27] reported results from pyrolysis–molecular beam mass spectroscopy (Py-MBMS) analysis of heavy-oil samples and correlations between MBMS data and the viscosity of heavy oils.

TLC has been advocated as a preferred method to HPLC to simultaneously separate the heavy oils into SARA fractions [12,28,29]. A coupled use of TLC with a flame ionization detector (FID) has enabled quantitative analysis of the TLC fractions. Figure 8.5 shows the TLC/FID chromatograms of a crude oil and its fractions separated by column chromatography to validate the TLC/FID technique. Rudzinski and Aminabhavi [30] reviewed the use of supercritical fluid extraction (SFE), SFC, and liquid chromatography (LC) for fractionation and analysis of crude oil samples. Recently, Dutriez et al. [31] reported on extending the use of high-temperature two-dimensional GC to analyze heavy-oil samples. The method they have proposed was successful in analyzing a vacuum gas oil (VGO) sample, but it needed improvement for analyzing deasphalted oils (DAOs).

8.2.3 Characterization and Structure of Asphaltenes

Simply defined as a solubility fraction of crude oil and related materials (soluble in aromatic, or other strong solvents but insoluble in light liquid n-paraffins such as *n*-pentane, *n*-hexane, or *n*-heptane), the structure and properties of asphaltenes still pose controversies after more than a century of research. Including the heaviest and possibly the highest molecular weight compounds in crude oils and related materials and richest in heteroatom species (e.g., sulfur and nitrogen) and organometallic compounds containing nickel, vanadium, and other metals, the composition, structure, and properties of asphaltenes differ depending on the source and separation methods used to isolate asphaltenes. A particular challenge for molecular analysis of asphaltenes is the tendency of self-association, or aggregation of the constituent molecules and their colloidal properties. Still, much progress has been made recently in understanding the structure and properties of asphaltenes

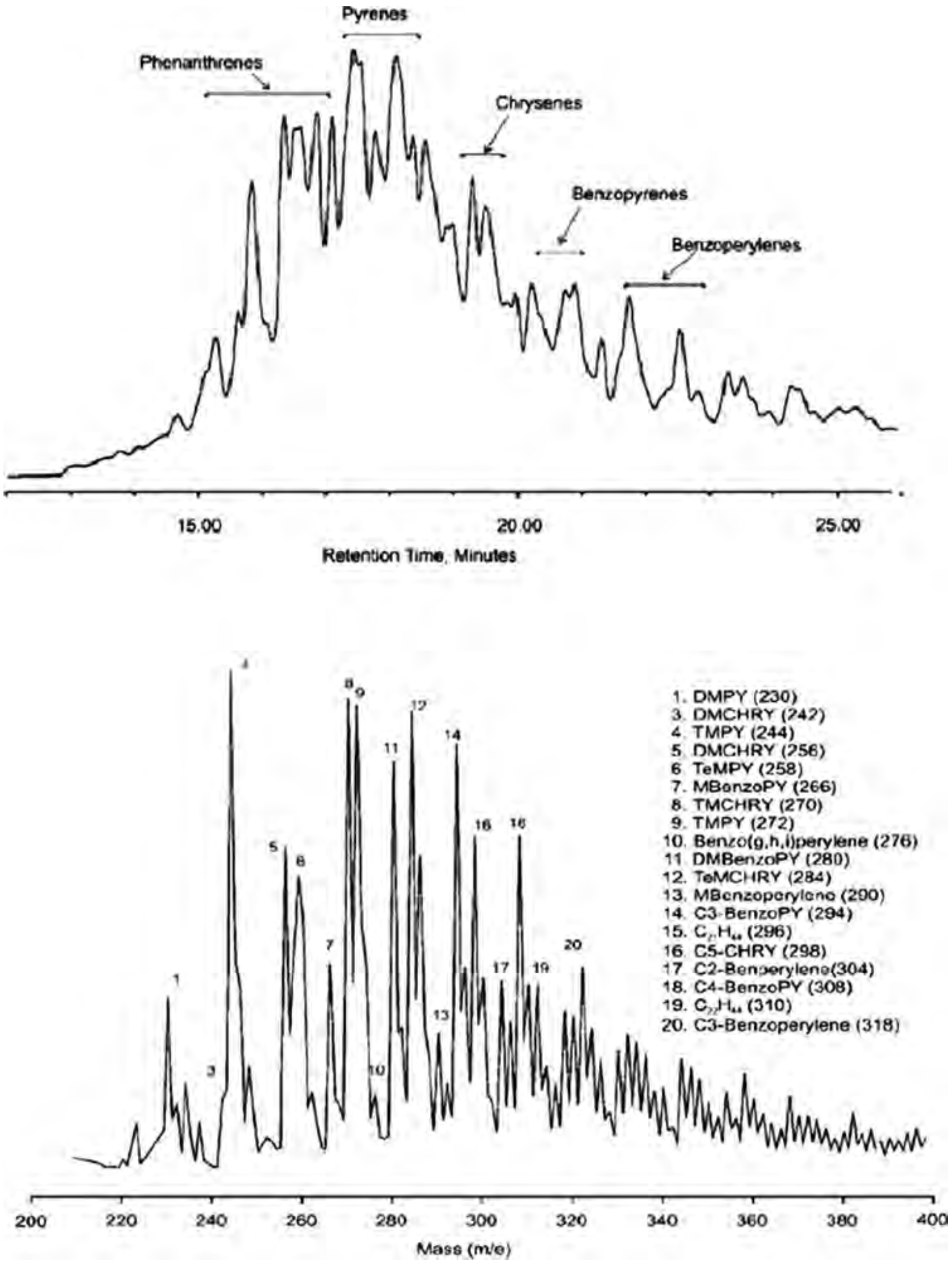


Figure 8.4—HPLC/DAD (top) and HPLC/MS/MS chromatograms of an FCC decant oil sample, indicating the PAHs pyrene (PY), chrysene (CHRY), and their alkylated analogs, including methyl (M), dimethyl (DM), trimethyl (T), and tetramethyl (Te) substituents on the PAH ring systems [26].

as reviewed in recent publications [7,9,32,33]. In upgrading heavy oils, the asphaltene fraction clearly poses the most challenging issues because it represents the most refractory compounds with a high tendency to produce coke, which not only reduces the yields of light distillate products but also causes operational problems with catalyst deactivation and coke deposition on reactor surfaces. Therefore, information on the structure and properties of the asphaltene fraction of heavy oils is critically important in optimizing and controlling the heavy-oil upgrading processes [9].

8.2.4 Using Analytical Data for Feedstock Evaluation and Process Selection

As mentioned at the beginning of this section and discussed throughout, an ultimate purpose of heavy-oil analysis is to select the best feedstock for a given upgrading process, or select the best upgrading process for a given feedstock and to select the optimum processing conditions. Some specific examples are referenced here on how to use analytical data for process and feedstock evaluation. Sánchez et al. [34] proposed an application of size exclusion chromatography (SEC) for evaluating the processes for upgrading heavy crudes. They compared the elution curves for heavy crude oil with those of the resulting products from catalytic hydrogenation and developed an algorithm to track the conversion process. The results were more useful than monitoring the distillation data and the bulk properties such as API gravity and elemental analysis in following the conversion process and pinpointing the problems and potential improvements in the process.

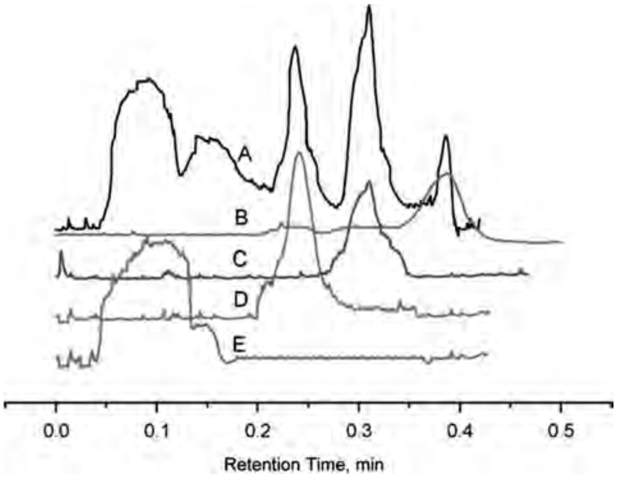


Figure 8.5—Validation TLC/FID analysis of (A) a crude oil with analyses of its fractions, (B) asphaltenes, (C) resins, (D) aromatics, and (E) saturates, separated by column chromatography [29].

Zhao et al [35] used supercritical fluid extraction and fractionation (SFEF) with pentane to cut deep into the bottoms while readily yielding enough of each fraction to allow characterization and reactivity studies on bitumen, heavy-oil, and conventional crude samples. They concluded that the determination of average structures on the basis of bulk analysis is heavily biased toward the lighter fractions and provides little information on the properties of the heavier components. A comparison of bitumen pitch with residues from benchmark crudes, heavy oils, and bitumen from non-Athabasca sources showed that the difficult processing of bitumen can be largely due to its much higher asphaltene and contaminant contents rather than differences in chemical composition between bitumen and conventional oils.

Gonçalves et al. [36] used thermogravimetry (TG) for the evaluation of heavy petroleum fractions to analyze the petroleum distillation residues from different Brazilian oils. Their method was used to predict the formation of carbonaceous residue on the basis of thermal analysis.

8.3 UPGRADING PROCESSES

8.3.1 Deasphalting Technology

8.3.1.1 PROCESS OBJECTIVE

The objective of the deasphalting process is to separate the heaviest part of an atmospheric or vacuum resid [in which the asphaltenes and metals (vanadium + nickel) are concentrated] from the lighter part (DAO) using a paraffinic solvent. No chemical reactions take place during deasphalting. The DAO is almost free of metals, and the asphalt (containing asphaltenes and resins) can be used as feedstock for blending to produce pavement asphalts according to specifications and for solvent extraction to recover blending components for lubricant production. Solvent deasphalting can be integrated with thermal and hydroprocessing for conversion of DAO in processes such as resid FCC, fixed- or ebullating-bed hydrocracking to produce lighter hydrocarbons, and to reduce sulfur [37]. Other uses of asphalt may include combustion in integrated gasification combined cycle (IGCC) power plants, coking in delayed coker units, or contribution to the fuel oil pool of the refinery. If desired, resins and asphaltenes can be separated by including additional contact stages in the deasphalting process.

8.3.1.2 PROCESS DESCRIPTION

As an example of deasphalting processes, a supercritical solvent deasphalting process is described here [38]. There are processes that do not operate under supercritical processes and commonly use propane as the deasphalting solvent. The process principles are the same in both cases. The supercritical solvent deasphalting process consists of the following main stages (Figure 8.6):

1. Introduction of resid feedstock together with the paraffinic solvent to the extraction stage.
2. Separation of the DAO and asphalt (pitch) fractions that are both rich in solvent. This separation occurs in the extractor, which is specially designed for efficient separation and minimum contamination of the DAO fraction.
3. Introduction of the DAO fraction with the solvent to the solvent separator that operates at supercritical conditions to minimize energy consumption.
4. Stripping of the asphalt and DAO with entrained solvent in a stripping column.

The solvent composition and temperature profile in the extractor are the two principal variables in the solvent extraction process.

8.3.1.3 OPERATING CONDITIONS

Typical solvents used in the process include n-paraffins, such as propane, n-C_4, n-C_5, n-C_6, and their mixtures. The solvent is selected based on the feed quality to be processed, which affects the yield of the asphaltenes and the softening point. Increasing the solvent molecular weight increases the DAO yield and decreases selectivity. If propane is used as the solvent, the selectivity to paraffinic fraction recovery will be very high. With *n*-butane or *n*-pentane, the selectivity to resins will increase, resulting in higher DAO yields, but the molecular weight and aromatic content of the DAO will also increase.

The solvent-to-residue (S/R) ratio ranges from 3:1 to 15:1 (typically 8:1). The greater the S/R ratio, the higher the yield of DAO, but the lower the quality (with lower API, and higher viscosity and metals content) along with the higher energy consumption to recover the additional solvent. Figure 8.7 shows a generic plot of DAO quality and selectivity as a function of DAO yield.

Pressure at the asphaltene separator ranges between 25 and 40 barg, depending on the solvent used. Increasing pressure will increase the DAO yield.

Temperature of the asphaltene separator varies between 50°C and 230°C. At higher operating temperature, the DAO yield decreases, but DAO quality is improved with lower metal content and lower Conradson carbon residue (CCR).

8.3.1.4 ENVIRONMENTAL IMPACT

The deasphalting process has a relatively low environmental impact. The emissions are only associated with energy consumption and solvent loss. Typical emissions are 10–15 mol % carbon dioxide (CO_2) in the flue gas flow (350–400 Nm^3/t load).

8.3.1.5 MAIN LICENSORS

MW Kellogg has licensed the ROSE process that is used in more than 36 units with an installed capacity of more than 600,000 BPD. The UOP and Foster Wheeler corporations have licensed more than fifty [40].

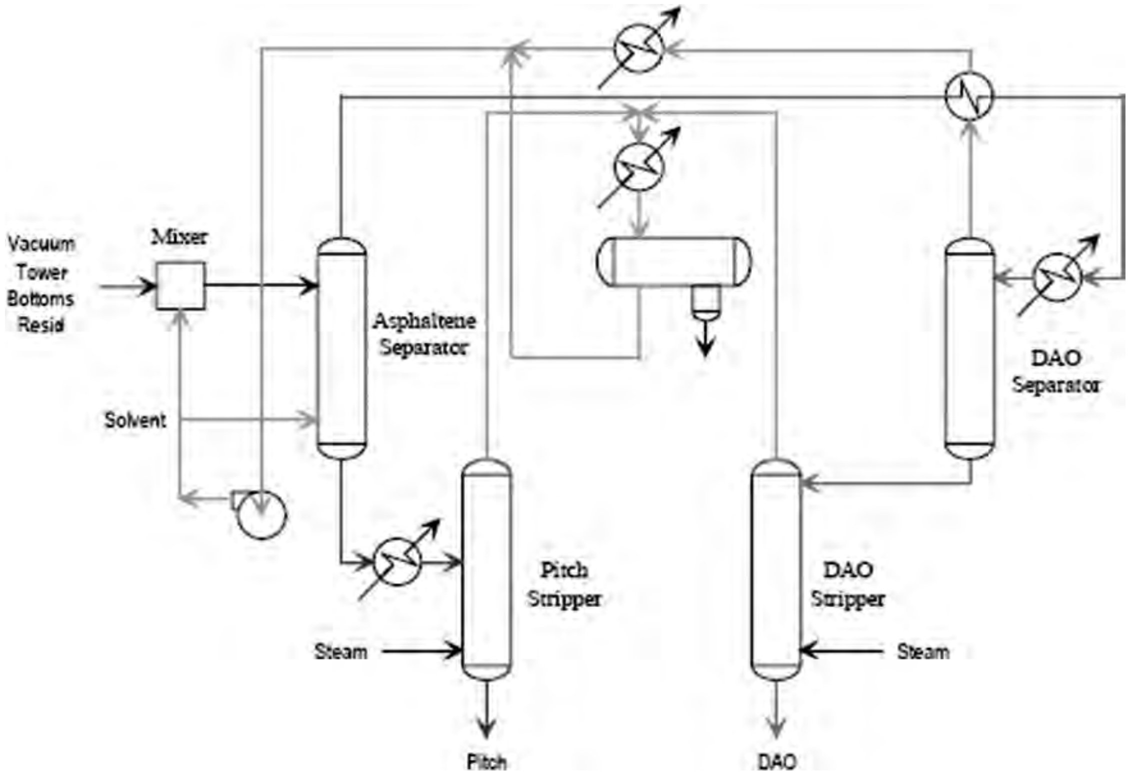


Figure 8.6—A supercritical solvent deasphalting process flow diagram [38].

8.3.1.6 OPPORTUNITIES AND THREATS

Opportunities	Threats
This process may be of interest in scenarios in which the asphaltenes can be used as fuel to generate energy in IGCC or can be mixed to produce fuel oil.	When processing residues of heavy or extra-heavy crudes, the DAO yield may be very low if the target is to maintain the levels of pollutants that are carried to the downstream conversion units (nitrogen, sulfur, metals, CCR)
If there is a well-established market for asphalt and an appropriate feedstock for the process, a good asphalt product can be produced.	The asphaltene stream used as fuel oil component concentrate contaminants and, therefore, it will be more difficult to match fuel specifications.
This process can be used as a substitute for a vacuum column because of its lower energy consumption and higher DAO yield in cases in which asphaltenes have a final use.	
Integration with hydroconversion in fixed- or ebullating-bed processes or coking processes.	

8.3.2 Thermal Conversion Technologies

8.3.2.1 VISBREAKING TECHNOLOGIES

8.3.2.1.1 Process Objective

The objective of visbreaking is to reduce the viscosity of atmospheric or vacuum residua by mild thermal cracking to produce fuel oil from the heavy ends and to increase the distillate yield in a refinery. Depending on the feedstock properties and thermal severity in the reactor, the process will typically achieve 10–25 % of conversion of the heavy ends to gas, gasoline, and distillates while producing fuel oil with the desired specifications. Carbon rejection in small quantities on the reactor surfaces during thermal cracking helps reduce the viscosity of the fuel oil product. The process decreases the demand for a cutter stock used as diluent (e.g., kerosene) that might otherwise be used to reduce the viscosity of the heavy ends to meet the fuel oil specifications. Adding a diluent may still be needed depending on the sulfur content of the product and the fuel oil specifications. Although, the proper objective of visbreaking is to reduce viscosity, some refineries may use this mild cracking process to convert fuel oil into lighter distillates.

8.3.2.1.2 Process Description

There are two types of visbreaking processes: coil or soaker visbreaking. Figure 8.8 shows a schematic diagram of the coil visbreaking process. For visbreaking, the feedstock is introduced into the coil heated in the furnace where the thermal cracking reactions take place. At the furnace outlet, the reaction products are immediately quenched using a portion of the gas oil product from the fractionator to stop the thermal cracking reactions. The quenched products are

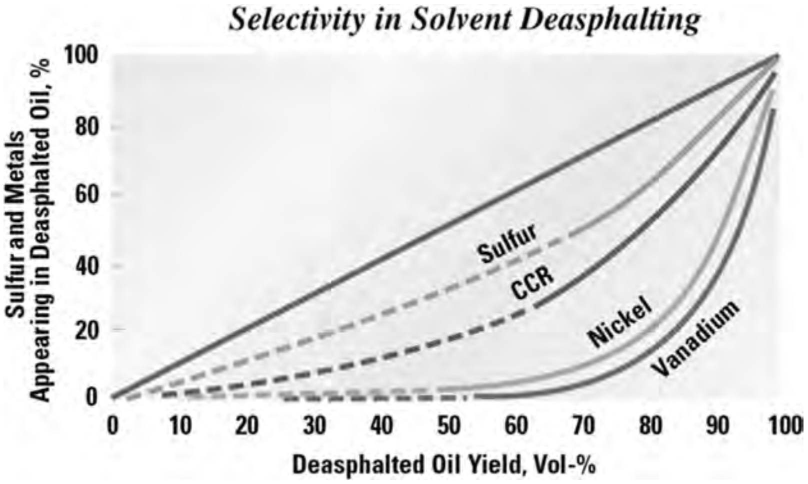


Figure 8.7—A generic plot of the concentration of DAO contaminants as a function of DAO yield [39].

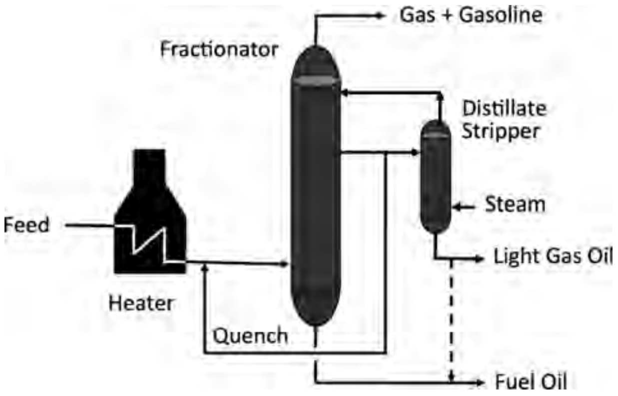


Figure 8.8—The coil visbreaking process [41].

sent to the fractionator for separation into gas, gasoline, light gas oil, and visbroken resid streams. A steam stripper can be used with the fractionator for better separation of the visbreaking products. In the soaker visbreaking process, a soak drum is placed after the furnace. Most of the thermal cracking reactions in this case take place in the soaker drum.

8.3.2.1.3 Operating Conditions

Depending on the process objectives and feedstock characteristics, reaction temperatures range from 450°C to 485°C and pressures range from 3 to 10 bar. Higher temperatures and lower residence times are used in the coil visbreaking process. Residence times can vary from 1 min (associated with high temperatures in coil visbreaking) to 10 min (for lower temperatures used in soaker visbreaking).

A relationship between the thermal severity of visbreaking (kt) and conversion (x) can be defined in terms of the reaction temperature (T) and time (t) assuming a first-order kinetic expression with a rate constant k as follows:

$$kt = -\ln(1 - x) \tag{8.1}$$

Using an Arrhenius relationship for the rate constant $k = A \exp(-E_a/RT)$ and a good estimate of the apparent activation energy (E_a), one can calculate alternative temperature and time combinations needed for a given conversion level.

Visbreaking severity is limited by the reactivity of the feedstock and the storage stability of the residual fuel in accordance with the desired conversion level and desired reduction in viscosity. Asphaltene content and concarbon of the feedstocks are important factors to consider for selecting an appropriate thermal severity for the process to prevent excessive coking in the coil or soak drum or producing unstable fuel oil.

8.3.2.1.4 Environmental Impact

Similar to deasphalting, the environmental impact of visbreaking is associated with burning fuel in the furnace to provide energy for thermal cracking, and, to a lesser extent, burning off the coke deposited in the coil or soaker drum leading to emissions of CO_2, oxides of nitrogen (NO_x), and oxides of sulfur (SO_x) in the flue gases.

8.3.2.1.5 Main Licensors

Main licensors of the visbreaking processes are ABB Lummus, Global, and UOP [40,41].

8.3.2.1.6 Opportunities and Threats

Opportunities	Threats
A low-investment and inexpensive process to treat the bottom of the barrel to produce fuel oil with some flexibility to adjust severity for increasing the yield of lighter distillate products (e.g., gasoline and light gas oil).	Producing generally low-value product that may require further processing especially when dealing with high sulfur and metal contents in crude oils.
Ability to treat a wide range of residua by selecting the appropriate process configuration, coil, or soaker visbreaking with careful consideration of the product fuel oil stability.	Loss of carbon depositing on the reactors as a byproduct of thermal cracking, limiting the processability of crudes with high asphaltene content or high CCR.

8.3.2.2 COKING TECHNOLOGIES AND PROCESS OBJECTIVE

Coking is the most severe thermal process used in the refinery to treat the very bottom-of-the-barrel vacuum residua.

Because of the high severity of thermal cracking, the residue feed is completely converted to gas, light and medium distillates, and coke with no production of residual oil. Two different coking processes are used in the refineries: delayed coking and fluid coking. The common objective of both coking processes is to maximize the yield of distillate products in a refinery by rejecting large quantities of carbon in the resid as solid coke, known as petroleum coke. Complete rejection of metals with the coke product provides an attractive alternative for upgrading the extra-heavy crude and bitumen and that is particularly useful for initial processing of tar (or oil) sands for liberating the hydrocarbons from the sand that is left behind with the coke. Finding markets for the coke product as fuel or as filler for manufacturing anodes for the electrolysis of alumina (possible only with petroleum coke from delayed coking) makes the economics of coking more attractive by creating value for the rejected carbon. Sulfur and metal contents of the petroleum coke as determined by the sulfur and metal contents of the resid feed are two important factors that affect the commercial value of petroleum coke. Of the two coking processes, delayed coking is the preferred approach in many refineries that process heavy crudes.

8.3.2.3 DELAYED COKING: PROCESS DESCRIPTION AND OPERATING CONDITIONS

The delayed coking process has a prominent place in a refinery that processes heavy crudes [42,43]. Delayed coking of vacuum distillation residue or FCC decant generates liquid products as feeds for further processing in various units to contribute to the blending pools for all of the distillate liquids, including gasoline, jet fuel, and diesel fuel. Further processing of the delayed coking products, such as hydrotreatment, is necessary particularly with the resid feeds that have high sulfur and nitrogen contents to reduce these heteroatom species according to the specifications of the final products.

Figure 8.9 shows a schematic flow diagram of the delayed coking process. The resid feed is introduced to the fractionator after being heated in the heat exchangers with the coker gas oil products. The bottoms from the fractionator, including the heavy ends of the vacuum residue feed with heavy coker gas oil recycle, are mixed with steam and sent to the tubular heater in the furnace to be heated to approximately 485°C at a pressure of 2.5 barg. Steam is added to prevent coking in the heater and the heated feed is introduced from the bottom of one of the coke drums (drum A). The coking takes place in the insulated coke drum as the drum fills up for a period of 16–18 h. While drum A is being filled up, drum B is decoked by using hydraulic cutters and the coke is removed from the bottom of the drum. As the coking in drum A is completed, drum B should be decoked, sealed, heated, and prepared for switching the feed. The coking cycle is controlled such that the vacuum residue is continuously fed to the unit (because the vacuum column works around the clock) and the fluid products are recovered continuously while coke is removed intermittently in a semicontinuous process scheme. Therefore, there are at least two coke drums in every delayed coking unit, and some units have more than two drums. All of the heat necessary for coking is provided in the heater, whereas coking takes place in the coke drum; hence, the process is called "delayed coking."

The hot product vapors and steam from the top of the drum are quenched by the incoming feed in the fractionator to prevent coking in the fractionator and to strip the lighter components of the vacuum residue feed. The fractionator separates the coking products into gases, coker naphtha, coker light gas oil, and coker heavy gas oil. A sidesteam stripper is used with the fractionator to ensure a good separation between the coker naphtha and light gas oil streams.

The delayed coking operating variables include heater outlet temperature, pressure, recycle ratio, and cycle time. These variables are selected based on feed properties such as the characterization factor, asphaltene content, and CCR to ensure that coking in tubular heaters is minimized and liquid product yield is maximized. The recycle ratio, which is typically 3–5 %, is used to control the endpoint of the coker heavy gas oil. The coke yield can vary from 20 % to 30 % depending on the feed properties and coking conditions. Gary and Handwerk [44] proposed equations to predict coke and other product yields on the basis of the CCR of the vacuum residue and gave estimates of the distribution of sulfur in the feed among the coking products, suggesting that up to 30 wt % of the sulfur in the feed ends up in the coke, 30 wt % in the gas product, and 20 wt % in the coker heavy gas oil.

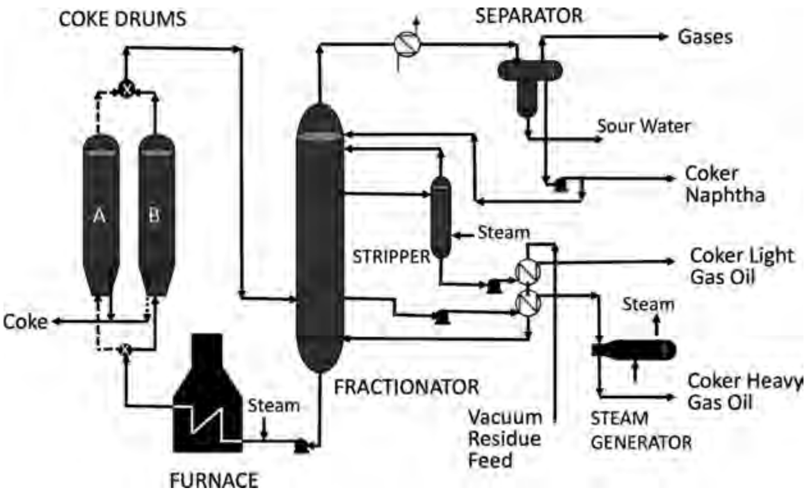


Figure 8.9—A schematic flow diagram of the delayed coking process (Modified from [44]).

8.3.2.3.1 *Structure, Properties, and Uses of Coke*

Delayed coking of vacuum residua produces two types of coke that are called “sponge coke” and “shot coke” because of their appearance. Shot coke consists of the agglomerates (10–20 cm in diameter) of discrete hard spherules that may range in diameter typically from 0.2 to 0.5 cm and resemble bee-bee shots. Vacuum residua with reactive asphaltene fractions tend to produce shot coke during delayed coking because of fast development and hardening of a liquid crystalline phase (carbonaceous mesophase) during coking [45]. Sponge coke is formed by a more slow and extended development of carbonaceous mesophase. The differences in the extent of carbonaceous mesophase development between sponge and shot coke can be identified by examining their microstructure using polarized-light microscopy. Shot coke is used mainly as fuel and in some niche applications such as the production of titanium dioxide (TiO_2). Sponge coke can also be used as fuel or for production of carbon anodes used for extraction of aluminum from alumina by electrolysis if their sulfur and metal contents are sufficiently low as identified by the specifications [43,45]. Using FCC decant oil in delayed coking under different conditions than those used for coking vacuum residua produces a more “crystalline” coke called “needle coke” that is used to manufacture graphite electrodes for use in electric-arc furnaces for recycling scrap iron and steel. The delayed coking process thus provides an interface between the petroleum refining and metal manufacturing industries.

8.3.2.3.2 *Environmental Impact of Delayed Coking*

The environmental impact of delayed coking includes air emissions from burning fuel for heating the feed and water pollution from the fractionator and decoking operations that generate wastewater that needs to be treated.

8.3.2.3.3 *Main Licensors of Delayed Coking*

Main licensors of the delayed coking process include Foster Wheeler, ABB Lummus, UOP, and ConocoPhillips.

8.3.2.3.4 *Opportunities and Threats of Delayed Coking*

Opportunities	**Threats**
Ability to process any kind of feed including extra-heavy crudes and bitumen to produce distillate products with complete rejection of metals and large portions of the heteroatoms sulfur and nitrogen.	Loss of carbon and hydrogen in the relatively low-value solid byproducts (coke and gas) and low yields of liquid products that need further processing in accordance with fuel specifications.
Shortening cycle times and increasing liquid yields and throughput with the optimization of operating conditions and process innovations.	Material problems with processing more corrosive and sour feedstocks increasing the cost of processing in this relatively inexpensive upgrading option.
Finding markets for the byproduct cokes improves the economics of delayed coking.	Increasing heteroatom and metal contents, particularly with the heavy crudes, limits the use of byproduct cokes, which may need to be landfilled at additional cost.

8.3.2.4 FLUID COKING AND FLEXICOKING PROCESS DESCRIPTION, OPERATING CONDITIONS, AND PRODUCTS

Fluid coking and flexicoking are fluid-bed processes developed from the basic principles of FCC with close integration of endothermic (cracking, coking, or gasification) and exothermic (coke burning) reactions. In fluid coking and flexicoking processes, part of the coke product is burned to provide the heat necessary for coking reactions to convert vacuum residua into gases, distillate liquids, and coke. Flexicoking, as a variation of fluid coking, provides the options of partial or complete gasification of the coke product to produce a fuel gas with some or no coke in the product slate. Different from the bulk liquid-phase coking in delayed coking, coking takes place on the surface of circulating coke particles of coke heated by burning the surface layers of accumulated coke in a separate burner. Figure 8.10 shows a schematic flow diagram of the fluid coking process [46]. The preheated vacuum residue is sprayed onto the hot coke particles heated in the burner by partial combustion of coke produced in the previous cycle. Using fluid beds in the reactor and burner provides efficient heat transfer and fast coking on a collectively large surface area of the small coke particles circulating between the reactor and burner. The products of coking are sent to a fractionator (similar to that used in delayed coking after recovery of fine coke particles). Steam is also added at the bottom of the reactor (not shown in the figure) in a scrubber to strip heavy liquids sticking to the surface of coke particles before they are sent to the burner. This steam also provides fluidization of coke particles in the reactor. The reactor and the burner operate at temperatures of 510–570°C and 595–675°C, respectively.

Higher temperatures and short residence times in the reactor lead to higher liquid and lower coke yields compared with those of delayed coking. Coke is deposited layer by layer on the fluidized coke particles in the reactor. Air is injected into the burner to burn 15–30 % of the coke produced in the reactor, part of the particles are returned to the reactor, and the remainder are drawn out as the fluid coke product. The flue gas from the burner is sent to a carbon monoxide (CO) boiler to raise additional heat for the refinery [41,43]. Hammond [47] reported data on the product yields from fluid coking and uses of fluid coke that include combustion for power generation and fuel for the cement industry.

Figure 8.11 shows a schematic diagram of flexicoking. A fluid bed is added for partial combustion and gasification of coke produced in the reactor with air and steam to produce a synthesis gas. The hot coke particles from the gasifier are sent to the heater to heat the cold coke particles removed from the reactor that are circulated back to the reactor to provide the heat necessary for coking. After removing the fine particles from the gas particles by cyclones, the gas is cooled in a direct-contact cooler to condense the sour water and recover the flexigas. Maples et al. [48] reported correlations between the CCR of the vacuum residue and the product yields and gas composition.

The environmental impact of fluid and flexicoking include air emissions in the flue gases from the CO boiler in fluid coking and the production of sour water in flexicoking. The licensors of fluid coking and flexicoking include ExxonMobil, ConocoPhillips, and Haliburton KBR [37].

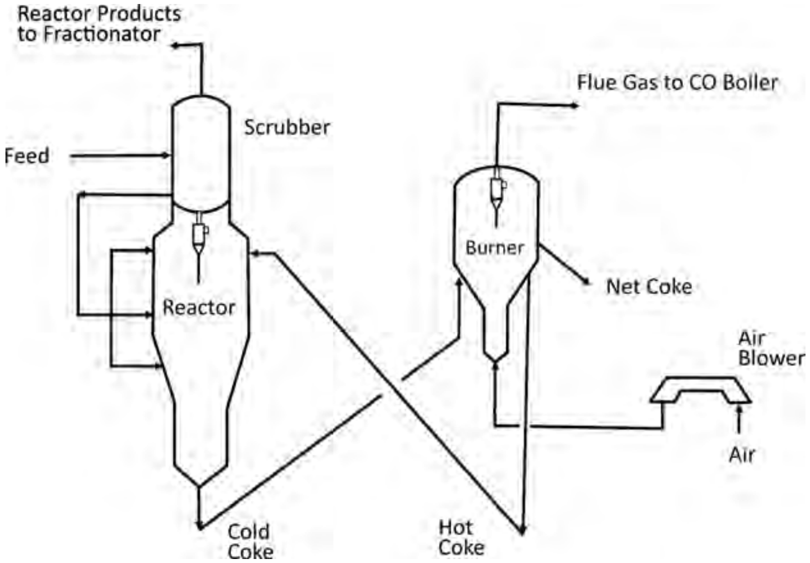


Figure 8.10—A schematic flow diagram of the fluid coking process [46].

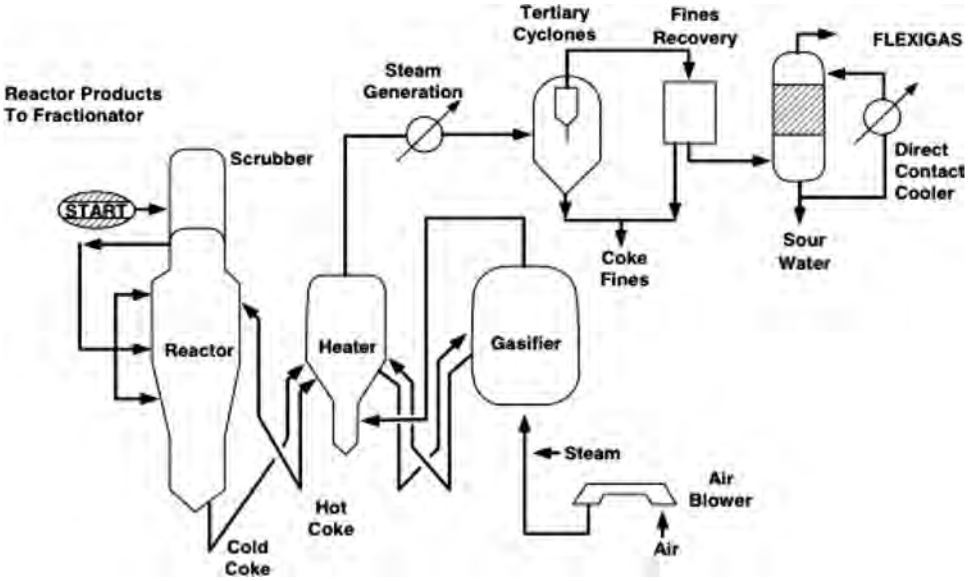


Figure 8.11—A schematic diagram of the flexicoking process [46].

8.3.2.4.1 Opportunities and Threats for Fluid Coking and Flexicoking Processes

Opportunities	Threats
Using the low-value coke byproduct as an energy source without needing any other fuel could provide a significant opportunity with high-energy prices.	Although the liquid yields are higher than those obtained by delayed coking, the quality of the liquid products is inferior compared with delayed products.
Easy integration with power generation because of small coke particle size (fluid coking) or gas production (flexicoking).	Increasing the metal and sulfur contents in the residua, and thus in fluid or flexicoke, would make flue gas treatment more costly.

8.4 CATALYTIC HYDROTREATING AND HYDROGEN ADDITION TECHNOLOGIES

8.4.1 Catalytic Fixed-Bed Processes

8.4.1.1 OBJECTIVE

The objective of catalytic hydrotreating [including hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallation (HDM), and aromatics hydrogenation] and catalytic hydrocracking of residua (atmospheric, vacuum residue, and residues from other conversion processes) and crude oils is to produce higher-quality residua and small amounts of lighter products (naphtha, diesel, VGO) with lower contaminants in the treated residue such as sulfur, nitrogen, and metals (vanadium + nickel). In many cases, the residue hydrotreating units are pretreatment processes to other downstream conversion units such are resid-FCC, delayed coking, and ebullating-bed hydroconversion processes, among others [37].

TABLE 8.2—Typical Characteristics of Venezuelan and Canadian crudes and their vacuum residua

		Cold Lake		Lloydminator		Athabasea		Hamaca	
Production properties		Whole Crude	Rosld	Whole Crude	Rosld	Whole Crude	Rosld	Whole Crude	Rosld
TRP cut point	°F	C5+	1049+	C5+	1049+	C5+	1049+	C5+	1049+
TRP cut point	°C	C5+	585+	C5+	585+	C5+	585	C5+	585+
Yield	vol %	100	43.1	100	41.5	100	44	100	
Yield	wt %	100	46.5	100	44.5	100	47.1	100	59.5
Gravity	API	11	0.5	15	5.1	7.9	-1.2	7.9	-0.07
Specific gravity		0.993	1.072	0.958	1.038	1.015	1.096	1.016	1
Sulfur	wt %	4.6	6.5	3.6	5.5	4.9	6.7	4.1	4.8
Nitrogen	wt %	0.37	0.69	0.23	0.37	0.4	0.7	0.8	
CCR	wt %	12.9	27.3	10	22.1	13.4	27.7	14.5	24.2
Vanadium	ppmw	182	390	120	270	222	471	466	783
Nickel	ppmw	65	140	50	113	87	184	96	161

8.4.1.2 TYPICAL FEEDSTOCKS

Table 8.2 shows the typical characteristics of heavy-crude oil and vacuum residua from Canadian and Venezuelan heavy crudes. Generally, as shown in the table, the heavy crudes have a high sulfur content that is distributed among the different fractions. Typical sulfur compounds are mercaptans, thiophene, benzotiophenes, and dibenzothiophene, particularly its alkyl-substituted analogs, which require severe catalytic hydrotreating because of their low reactivity. Another important parameter that affects the hydrotreating of heavy residua is the metal (such as vanadium and nickel) content. These metals tend to deposit on catalysts during catalytic hydrotreating and reduce the activity of the catalysts. It can be expected that when the amount of heavy crude increases in the refinery crude base, the hydrogen demand for hydrotreating processes will increase and the expected life of the catalyst will decrease because of the deactivation of catalyst by the deposition of metals on the active sites of catalysts. Therefore, the operating costs to process such heavy crudes will increase. Sometimes, depending on the type of feedstock, revamps of hydrotreating units will be required to maintain an economical operation with a larger on-stream factor between the catalyst replacements.

Table 8.3 shows a comparison of the vacuum residua of light crudes and heavy crudes. The vacuum bottoms of Arabian light and heavy crudes have a high sulfur but low metal content when compared with a typical residue of a heavy crude like Maya that also has a high sulfur, but also a higher metal, CCR (concarbon), and asphaltene contents. Asphaltenes and CCR are also important feed parameters for hydrotreating because they increase the tendency to deposit coke on the catalyst bed (especially at the top), reducing the activity of the catalyst and increasing the reactor pressure drop.

8.4.1.3 MAIN CHARACTERISTICS OF FIXED-BED PROCESSES

There are different configurations and reactors used in the fixed-bed hydrotreating processes. Depending on the quality of the feedstock and the required yields and quality of the products, the configuration of the unit, the operating conditions, and the nature of the catalysts need to be adequately designed.

The deposition on the catalyst of the impurities of the feed such as vanadium, nickel, and iron or carbon residue reduces the catalytic activity and plugs the reactor bed. When that happens, the catalyst must be replaced. This phenomenon has led to innovative reactor designs that permit continuous replacement of the poisoned catalyst with the new catalyst.

Figure 8.12 shows the main criteria to follow for selecting the type of technology for HDS and/or hydrocracking of residues. Typically, the parameters to take into account are the metal content and the level of conversion required.

The content of asphaltenes and their thermal stability during the preheating stage of the process is another factor that needs to be taken into account. They may show a tendency to produce a small fraction of unstable asphaltenes that may be deposited on top of the reactor, which forms coke and causes poisoning and early plugging of the catalytic bed.

Another important factor for fixed-bed reactors is the amount of ash in the feed (mainly FeS) causing pressure drop due to bed plugging. This is especially important when processing acidic crudes because they might corrode the metal units upstream of the hydrotreating unit and such corrosion products are concentrated in the bottoms of the crude (vacuum or atmospheric residue) that are fed to the hydrotreating fixed-bed reactor. Typically, commercial operation of this type of unit allows a maximum content of metals of approximately 200–250 ppm (vanadium + nickel).

The current worldwide residue fixed-bed hydroprocessing capacity is approximately 2.4 million bbl/day in 60 installations.

At present, the commercial processes for hydrotreating and hydrocracking the residua are based on conventional fixed-bed reactors and fixed-bed reactors with moving-bed guard reactors.

8.4.1.4 CONVENTIONAL FIXED-BED REACTORS

This type of unit needs to be shut down periodically to replace the demetallation catalyst (HDM) of the guard

TABLE 8.3—Typical Characteristics of light crudes vacuum residua compared with the Maya heavy crude vacuum residua

		Arabian Light	Arabian Heavy	Ural Odessa	Maya
Vacuum Resid Properties	**Unit**	**538+ °C**	**538+ °C**	**538+ °C**	**538+ °C**
Yield	v %	16.71	25.09	21.33	32.82
Yield	wt %	20.14	30.86	25.12	38.31
Density at 15°C	g/ml	1.0323	1.0448	1.0180	1.0730
Specific gravity at 15,6/15,6 °C	g/ml	1.0330	1.0455	1.0187	1.0738
API	°API	5.48	3.93	7.40	0.28
Sulfur	wt %	4.160	5.350	2.610	5.230
Kinematic Viscosity					
Viscosity @ 135°C	cSt		5859	1059	9143
Viscosity @ 150°C	cSt		597.1	178.0	3727
Viscosity Brookfield					
Viscosity Brookfield @ 135°C	cP		5.825	1059	9,100
Viscosity Brookfield @ 150°C	cP		581	178.0	3,673
TAN	mg KOH/g	0.10	0.20	0.85	1.15
Nitrogen	ppm	409		3693	5287
Nickel	ppm	25.8	47.0	76.0	111.0
Vanadium	ppm	91.6	171.0	226.0	564.0
Sodium	ppm	1.3	<5	1.0	28.0
Concarbon	wt %	21.13	23.32	16.69	29.52
Asphaltenes	wt %	11.20	11.65	6.36	26.30

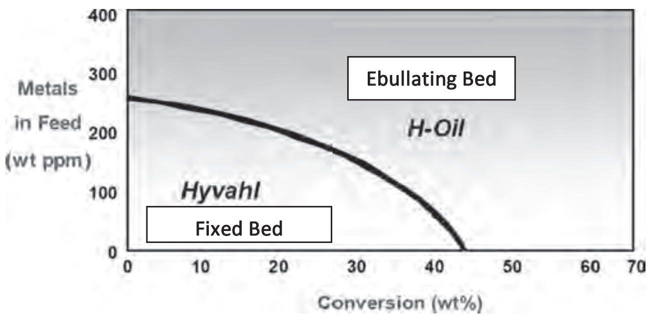


Figure 8.12—Range of metals and residue conversion for fixed-bed reactors processing [49].

reactor or the HDM catalyst of the main reactor if a guard reactor is not installed.

The main process licensors are Chevron, UOP/Unocal, Exxon, Shell, and IFP.

Hydrogenation units that use fixed-bed reactors use between one and six reactors in series and can operate in two modes—HDS and HDS + hydroconversion (HDC)—by increasing the reaction temperature, increasing the residence time, and using a different type of catalyst. When the catalyst is deactivated by coke and metal deposition and the operational limitations (such as high-pressure drop and maximum reactor temperature) are reached, the units are shut down to replace the catalyst.

Figure 8.13 shows a typical process layout of a residue hydrotreating fixed-bed unit. It consists of one guard reactor with a HDM catalyst and one or more HDS reactors. The main limitation of this type of process (Table 8.4) when processing feeds with high metal content is the deactivation of the catalyst bed and the potential differential pressure increase in the guard reactor, which indicates the plugging of the catalytic bed by metals, solid carryover with the feed, and coke deposition. All of these phenomena reduce the duration of the operating cycle.

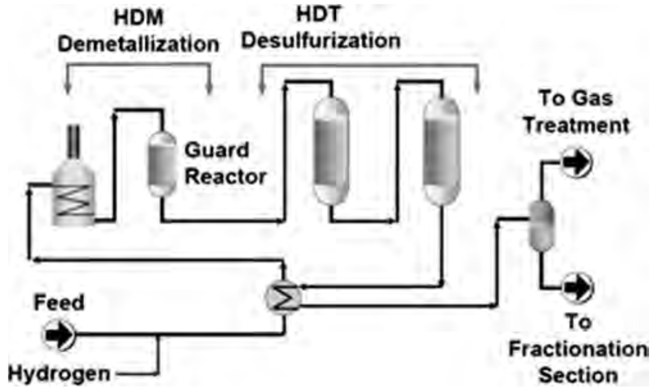


Figure 8.13—Typical fixed-bed residue hydrotreating configuration using guard reactor [50].

TABLE 8.4—Factors Affecting the Conventional Fixed-Bed Hydrotreating Reactors and the Duration of the Operating Cycle

Factors	Impact
Solids deposition carried with the feed and increase in pressure drop	Unit processing capacity decreases because of unit shutdown
Coke deposition due to asphaltene decomposition	Catalyst deactivation, bed plugging, reduced cycle length
Metal deposition	Deactivation of HDM and HDS catalyst

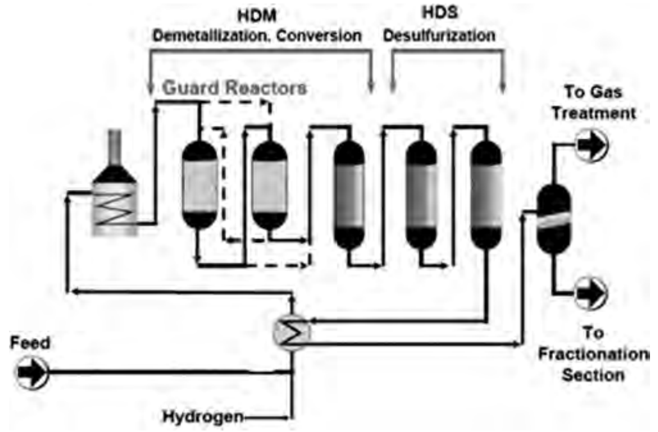


Figure 8.14—Typical fixed-bed residue hydrotreating configuration using a permutable guard reactor [51].

To avoid the shutdown of the unit because of high pressure drop or deactivation of the HDM catalyst of the guard reactor, low-cost bypass distributors may be placed at the top of the reactors to bypass the catalytic bed when high pressure drop is reached, thereby allowing longer operating cycles. This solution tends to stretch a little further the cycle of operation and therefore the processing capacity of the unit without shutdown.

Other alternatives include using a permutable guard reactor system such as in the Axens Hyvahl swing reactor process, shown in Figure 8.14, which allows for the replacement of the deactivated or plugged guard reactor in the operation without shutting down the unit. Normally, the guard reactors operate in series. When the HDM catalyst in the first guard reactor becomes deactivated or experiences a high pressure drop, the reactor is taken out of operation. The unit continues in normal operation using the second guard reactor. After the catalyst in the plugged reactor is replaced, the reactor is put back into operation, but in the second position. This configuration allows for longer operating cycles while processing feed with high metal and asphaltene contents. Typical feeds for this type of process are atmospheric or vacuum residua of light/heavy Arabian crudes.

8.4.2 Fixed-Bed Hydrotreating Reactors with Moving-Bed Guard HDM Reactors

Another alternative to hydroprocess residues with fixed-bed reactors is to use guard reactors with moving beds. In this case, the catalyst is circulated by gravity through the interior of the reactor, with periodic addition of fresh catalyst at the top of the reactor and a purge of the used catalyst at the bottom. The main advantage of this technology and the permutable fixed-bed technology is that they enable processing of feeds with high metal content while maintaining longer operating cycles.

The main commercial processes include OCR from Chevron, which uses an upflow (feed and H_2) catalytic guard bed in a minimum fluidization state of the catalyst. The catalyst is added and removed on a regular basis in a batch operation to maintain the catalytic activity. The OCR reactor precedes the conventional down-flow fixed-bed reactors. This technology can also be applied without catalyst replacement to avoid the bed plugging in existing fixed-bed units, allowing for hydrotreating of heavier feeds [52].

Another commercial process is HYCON from Shell, which uses a bunker flow guard reactor. In this case the catalyst flows down for removing the spent catalyst at the bottom of the reactor and replaces it with fresh catalyst at the top of the reactor while maintaining the normal operation of the unit. Here the feed and the H_2 flow down as in a conventional fixed-bed reactor configuration. The catalyst is also added periodically to maintain its catalytic activity (Figure 8.15). The catalyst is replaced at a rate to ensure a total plant running time of at least 1 year [53,54].

8.4.2.1 CATALYSTS USED IN FIXED-BED REACTORS

The catalysts using fixed-bed reactors for hydrotreating residua consist typically of Mo, nickel, Co, and W oxides, among others, that are dispersed on an alumina, silica, or silica/alumina base. Zeolites could also be used depending on the target in conversion and the quality of the feed used. The catalysts are active sulfided forms. Therefore the metal oxides from the fresh catalyst need to be sulfided before the catalyst is put in contact with the residue. Typically, dimethyl disulfide (DMDS) is used to sulfide the catalyst at specific conditions indicated by the catalyst manufacturer.

To process feeds with high metal and asphaltene contents, catalysts with large pore diameter and pore volume are required to store the maximum amount of metals and coke from the residue and maintain, as long as possible, the HDM activity of the catalyst in the guard reactor.

Because most of the metals are removed from the residue in the HDM stage, the HDS catalyst should have a smaller pore diameter and a large surface area (200–300 m^2/g) to maximize the HDS activity. Typically, molybdenum sulfide

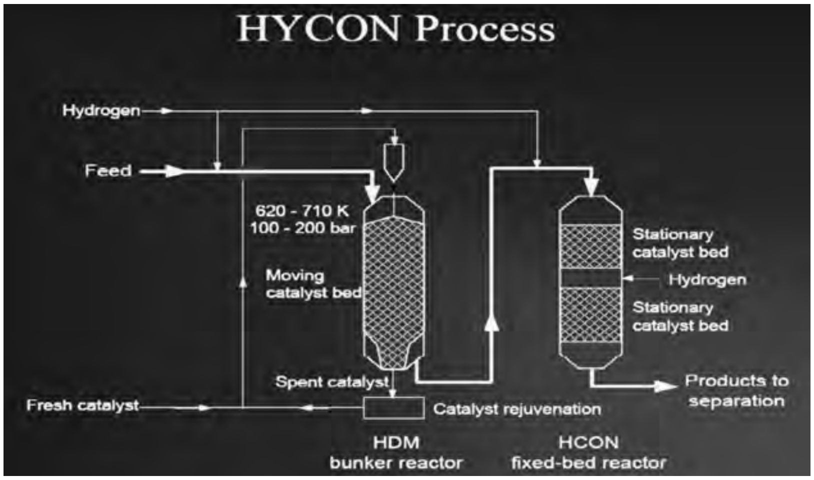


Figure 8.15—Shell HYCON bunker flow HDM guard reactor [53,54].

(MoS_2) promoted with cobalt sulfide (CoS) usually supported on alumina is widely used in HDS processes. The nickel sulfide (NiS)/MoS_2 catalyst is used when HDN and aromatic saturation is also desired. Tungsten sulfide (WS) is used to promote the aromatic saturation activity. Table 8.5 shows a qualitative comparison of the activity of the different HDS catalysts used in fixed-bed reactors.

TABLE 8.5—Relative Activity of Different Hydroprocessing Catalysts

Catalyst Composition	HDS	HDN	Aromatic Saturation
MoS_2/CoS	Excellent	Good	Fair
MoS_2/NiS	Very good	Very good	Good
NiS/WS	Good	Good	Excellent

8.4.2.2 OPERATING CONDITIONS FOR FIXED-BED REACTORS

Table 8.6 shows typical ranges of the operating conditions of conventional fixed-bed, permutable fixed-bed, and moving-bed processes. As main characteristics, high operating pressures and low space velocities can be noted. Operating conditions are defined mainly by the type of feedstock that a refinery needs to process and the level of HDS and conversion required.

TABLE 8.6—Typical Operating Conditions for Fixed-Bed and Moving-Bed Reactors for Residue Hydrotreating Processes

	Conventional Fixed Bed	Permutable Fixed Bed	Moving Bed
Pressure (Bar)	70–100	70–150	100–200
Temperature (°C)	360–420	360–420	360–420
LHSV (h^{-1})	0.1–0.5	0.1–0.5	0.1–0.5
Nickel + Va in feed (ppm)	<100	<200–300	<200–300
Conversion, wt %	Very low	Low	Low
Residue stability	Good	Good	Good

8.4.2.3 ENVIRONMENTAL IMPACT

Table 8.7 shows a summary of the environmental impacts of the residue hydrotreating processes.

TABLE 8.7—Environmental Impact of Residue Hydrotreating Processes

Atmosphere emissions	CO_2 emissions coming from preheating furnace and from the hydrogen production unit. H_2S produced is recovered as elemental sulfur product C_1–C_4 is consumed as fuel gas in the refinery.
Liquid effluents	Not significant.
Solid residues	Spent catalyst with the metals removed from the residue (vanadium, nickel) that is normally processed for metal recovery. HDT of residues generate more spent catalysts than other HDT units existing in the refineries.

8.4.2.4 OPPORTUNITIES AND THREATS

Opportunities	Threats
Commercial technologies widely used to reduce sulfur of atmospheric and vacuum residues to be fed to other conversion processes such as resid FCC or to prepare components to produce low-sulfur fuel oil.	Limited commercial application to heavy crudes with high metal and high asphaltene contents, typically limited to lower than 200 ppm.
Integration with deasphalting process in which the DAO with low asphaltenes and metal is processed in resid hydrotreating/hydrocracking reactors. Feeding the asphaltenes to coking units or gasification units may be an interesting alternative to improve liquid yields in refineries while increasing heavy-oil processing.	Limited conversion capacity compared with ebullating bed or delayed coking processes. Susceptible to premature cycles because of sudden pressure drop increases.

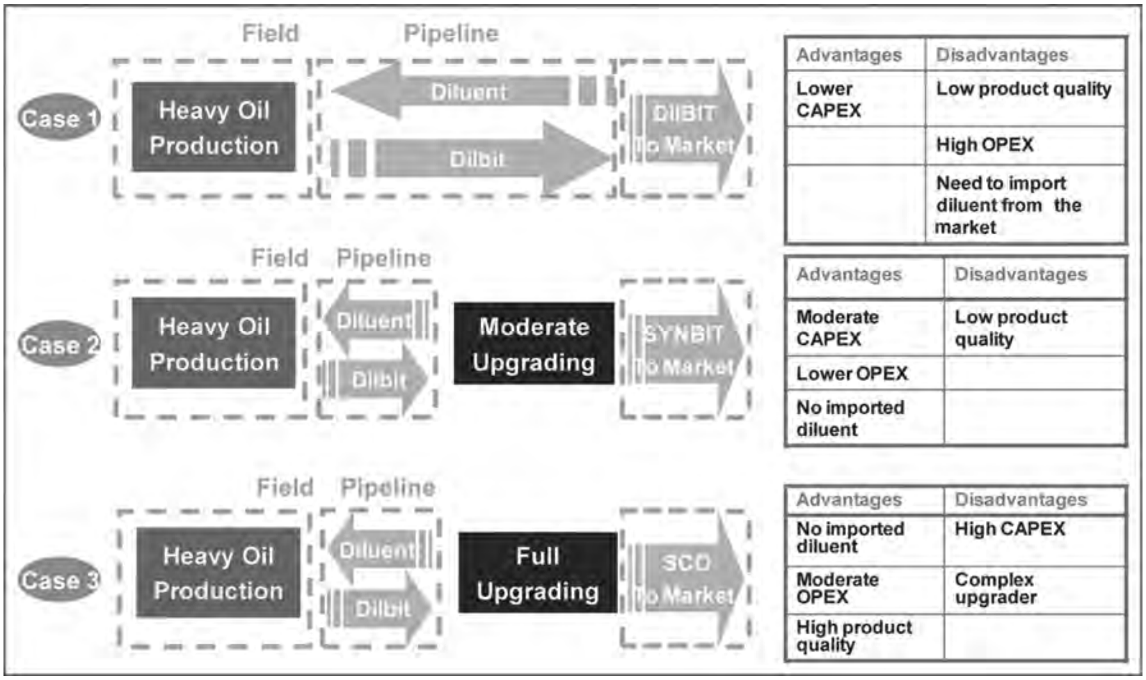
Opportunities	Threats
Development of new hydrotreating with higher metal retention capacity catalysts to improve the economics of this technology. Deeper knowledge of the chemistry of asphaltenes and metal deposition on the catalyst will be required. New developments in HDM catalyst support to improve metal retention capacity and minimize coke deposition in guard reactors. Nanotechnologies may contribute in such new developments.	High CAPEX compared with other conversion technologies because of high residence time and operating pressure.
Bunker fuel is a growing market and will be regulated to lower sulfur and metal specifications.	New slurry hydroconversion technologies, now in demonstration stage or large pilot units, integrating a slurry reactor of the residue with a fixed bed of the distillates in the same unit. This could be a new refining process to produce higher-distillate yields with products almost free of sulfur and nitrogen while processing residues with high metals and asphaltenes.

8.5 INTEGRATED PROCESSES: COMMERCIAL PROCESS SCHEMES FOR HEAVY-OIL UPGRADING

Considering the typical characteristics of the heavy crudes, several strategies are used to transport them to the market (Figure 8.16). Because of its high viscosity, heavy crude needs to be diluted or upgraded so that it can be transported in oil pipelines. Typical viscosity specifications for transportation in oil pipelines are on the order of 300 cSt at 30ºC. To reach such a viscosity, the heavy crude needs to be diluted between 20 % and 50 % depending on the type of diluent used. Diluents used could range from naphtha to diesel or other light-crude oils or condensates. This operation typically needs a low capital expenditure, but the diluent consumption may be an issue if it is not possible to maintain the diluent in a closed cycle. On the other hand, heavy crudes could be partially upgraded to produce a synbit (heavy crude or bitumen diluted with synthetic distillates) or totally upgraded to produce a light SCO. In either case, an imported diluent is not needed. In the case of partial upgrading, the quality of the synbit should be compatible for transportation in an oil pipeline; that is, with an API gravity between 16°API and 25°API. In the case of SCO production, transportation in a pipeline is a less significant issue than the quality of SCO required in the market or the integration with the refinery where it is going to be processed. The API gravity of SCO typically ranges between 25°API and 32°API. Integrated commercial upgrading schemes of heavy crude are in operation mainly in Canada and Venezuela.

Figure 8.17 shows the process scheme used by SUNCOR located in Canada. SUNCOR, with a base capacity of 267 Mbbl/day, has an upgrading scheme that includes delayed coking followed by independent hydrotreating of the naphtha, diesel, and VGO distillates to produce low-sulfur SCO. The present SUNCOR configuration has the flexibility to produce various sweet and sour products and diluted bitumen.

The Syncrude upgrader is also in operation in Canada (Figure 8.18) with a capacity of 350 Mbbl/day and includes in its process scheme light-crude fining and fluid coking processes. The light-crude fining unconverted vacuum



Advantages	Disadvantages
Lower CAPEX	Low product quality
	High OPEX
	Need to import diluent from the market

Advantages	Disadvantages
Moderate CAPEX	Low product quality
Lower OPEX	
No imported diluent	

Advantages	Disadvantages
No imported diluent	High CAPEX
Moderate OPEX	Complex upgrader
High product quality	

Figure 8.16—Typical options to transport and upgrade heavy crudes.

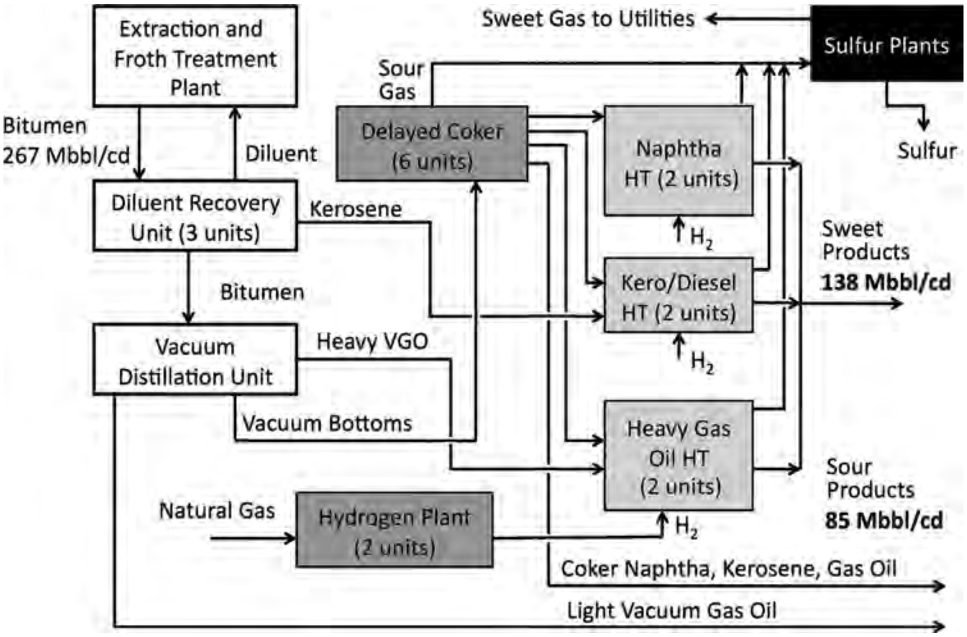


Figure 8.17—SUNCOR process flow diagram [55].

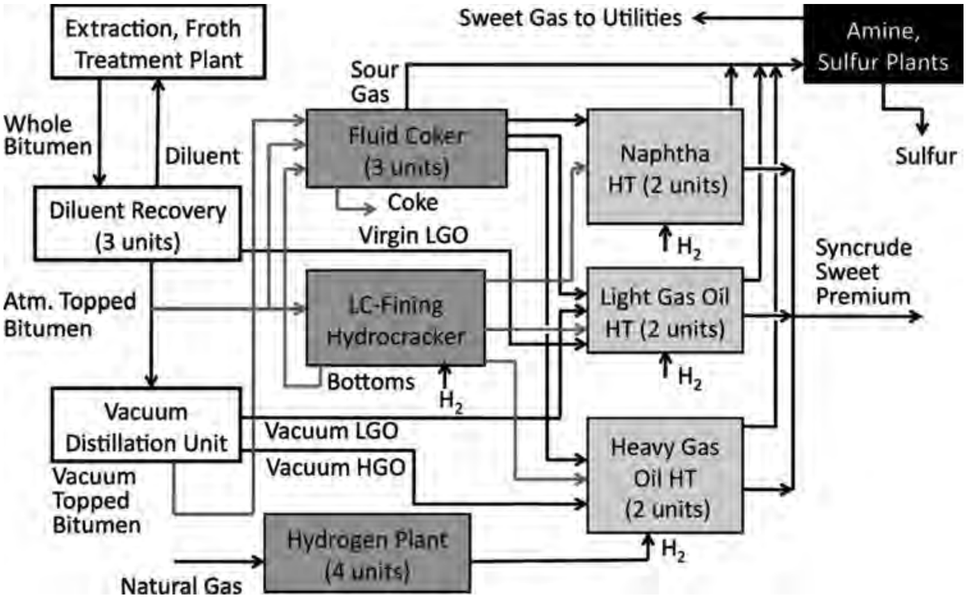


Figure 8.18—Syncrude process flow diagram [56].

bottoms are processed in the fluid coker, producing more distillates and coke. The products from the conversion units are hydrotreated in conventional fixed-bed hydrotreating units to produce a high-quality SCO called "SSB" (Syncrude synthetic blend) of 31°API and approximately 0.1 % sulfur without the vacuum bottoms. The Scotford Upgrader, which is a part of the joint venture project between Shell Canada, Chevron Canada, and Marathon Oil Sands L.P., is operated by Shell Canada and has a capacity of 155 Mbbl/day. Light-crude fining hydrocracking ebullating bed is the primary upgrading technology used in this approach.

The partial removal of the asphaltenes and very fine sand in the production facility improved its operation stability at higher conversion levels. The lower concarbon and metals in the feed also reduce the catalyst consumption. The upgrader also includes an integrated hydrotreating reactor to reduce the sulfur and nitrogen content in the distillates produced. The HUSKY BiProvincial upgrader in Canada with a capacity of 65 Mbbl/day uses a H-OIL process as a primary upgrading unit. The unconverted residue from the H-OIL unit is sent to the delayed coker unit. In this case, the amount of produced coke is reduced significantly, increasing the liquid yield of the upgrader. The H-OIL and delayed coking products are hydrotreated together, producing 59 Mbbl/day of high-quality SCO.

Figure 8.19 shows the OPTI process scheme of the Long Lake project in Canada located in an area of cold production in Athabasca that requires the use of steam

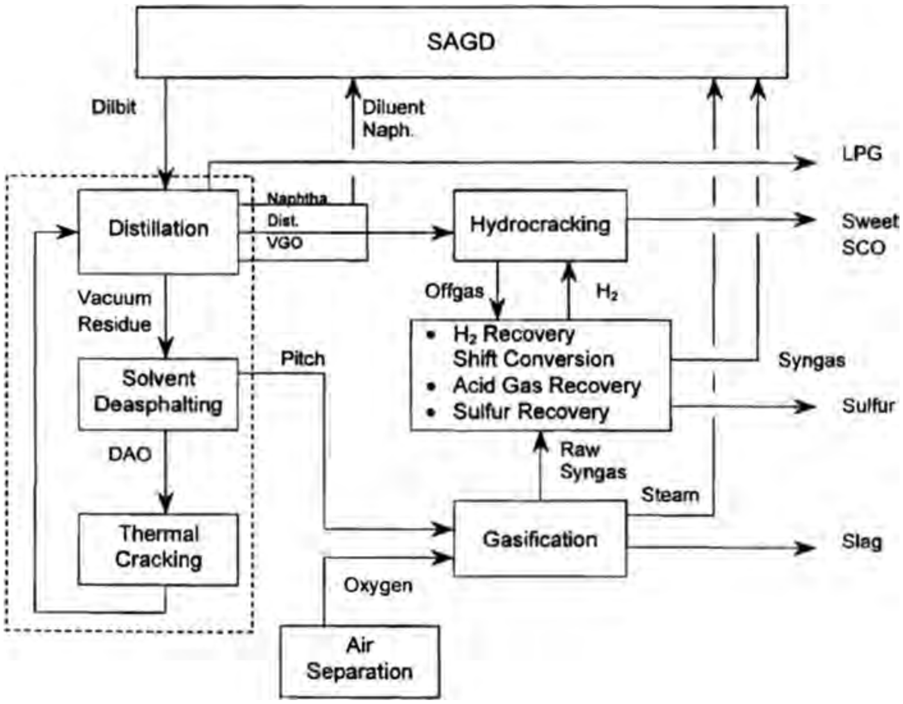


Figure 8.19—Long Lake project upgrader configuration with OPTI technology [55].

TABLE 8.8—Upgraders in the Orinoco Oil Belt in Venezuela. Capacity, SCO and Coke Yield (Source Reference [57])

Upgrader	Upgrading Process	Heavy Oil Production, Mbbl/d	Synthetic Crude Oil Production, Mbbl/d	Synthetic Crude Oil, °API	Coke Production Mt/d
Petrozuata	Delayed Coking	120	104	14–22	3,000
SINCOR	Delayed Coking, and Hydrocracking	180	156	27–32	5,000
Cerro Negro	Delayed Coking	120	108	14–22	2,000
Hamaca	Delayed Coking, and Hydrocracking	200	180	27–32	5,000

for the heavy crude production with steam-assisted gravity drainage (SAGD) technology. The capacity of the first stage will be 70 Mbbl/day and it is going to be expanded up to 140 Mbbl/day of heavy crude in the future. The OPTI process is a new technology. This project is at this moment in the first stage of construction. The process scheme integrates solvent deasphalting with thermal cracking and VGO hydrocracking. The vacuum resid from the crude is sent to a solvent deasphalting unit where the DAO is separated from the asphaltenes. The DAO is sent to the thermal cracking unit. The product from the thermal cracker unit is recycled back to distillation where unconverted residue is fed again to the process together with the virgin residue. All of the distillates are sent to a hydrocracker to produce 59 Mbbl/day of synthetic crude of approximately 40° API gravity and almost no sulfur. The asphaltenes coming from the solvent deasphalting are sent to a gasification unit where the hydrogen required by the upgrader is produced as well as the energy to generate the steam required by the SAGD technology in the production field. The energy required by the production field represents approximately 21 % of the total heavy oil produced.

In the case of heavy Venezuelans crudes in the Orinoco Oil Belt, the only considered technology is delayed coking. As shown in Table 8.8, two classes of synthetic crude are produced. One is of low quality (14–22°API) in the associations of PETROZUATA and Cerro Negro, where only the coker naphtha is stabilized by very mild hydrotreating (saturation of diolefines via hydrogenation) to avoid fouling and solids precipitation by the diolefin polymerization. The coker distillates are mixed with virgin heavy crude to produce a Synbit of the required quality. The other synthetic crude is produced in the associations of SINCOR and Hamaca that are of high quality (27–32 °API). In this case, the virgin and coker atmospheric gas oils (AGO) are hydrotreated together and the virgin + coker vacuum gas oils (VGO) are sent to a mild hydrocracking unit to increase the distillate yields and quality of the SCO. Considering the four upgraders together represents a total heavy-oil production of 620 Mbbl/day with a syncrude production of 550 Mbbl/day and 15,000 t/day of coke.

REFERENCES

[1] Ramírez, J., Rana, M.S., and Ancheyta, J., "Characteristics of Heavy Oil Hydroprocessing Catalysts," in *Hydroprocessing of Heavy Oil and Residua*, J. Ancheyta and J.G. Speight, Eds., Taylor & Francis, New York, 2007.

[2] Rana, M.S., Ancheyta, J., Maity, S.K., and Marroquin, G., "Comparison between Refinery Processes for Heavy Oil Upgrading: A Future Fuel Demand," *Int. J. Oil Gas Coal Technol.*, Vol. 1, 2008, pp. 250–282.

[3] *International Energy Outlook 2009*, DOE/EIA-0484(2009), Energy Information Administration, Office of Integrated Analysis and Forecasting, U.S. Department of Energy, Washington, DC, 2009.

[4] Meyer, R.F., and Attanasi, E.D., *Heavy Oil and Natural Bitumen Strategic Petroleum Resources*, Fact Sheet 70-03, Online Version 1.0, U.S. Geological Survey, Washington, DC, 2003.

[5] Altgelt, K.H., and Boduszynsky, M.M., *Composition and Analysis of Heavy Petroleum Fractions*, Marcel Dekker, New York, 1993.

[6] Strausz, O.P., and Lown, E.M., *The Chemistry of Alberta Oil Sands Bitumens and Heavy Oils*, Alberta Energy Research Institute, Calgary, Alberta, Canada, 2003.

[7] Mullins, O., Sheu, E.Y., Hammami, A., and Marshall, A.G., Eds., *Asphaltenes, Heavy Oils and Petroleomics*, Springer, New York, 2007.

[8] Wiehe, I.A., *Process Chemistry of Petroleum Macromolecules*, CRC Press, Boca Raton, FL, 2008.

[9] Ancheyta, J., Trejo, F., and Rana, M.S., *Asphaltenes: Chemical Transformation during Hydroprocessing of Heavy Oil*, CRC Press, Boca Raton, FL, 2010.

[10] Barman, B.N., Cebolla, V.L., and Membrado L., "Chromatographic Techniques for Petroleum and Related Products," *Crit. Rev. Anal. Chem.*, Vol. 30, 2000, pp. 75–120.

[11] Sharma, B.K., Lal, S., Sarowha, S, and Bhagat, S.D., "Chromatographic Characterization of High-Boiling Petroleum Fractions," *J. Sep. Sci.*, Vol. 26, 2003, pp. 1657–1664.

[12] Kaminski, M., Kartanowicz, R., Gilgenast, E., and Namiesnik, J., "High-Performance Liquid Chromatography in Group-Type Separation and Technical or Process Analytics of Petroleum Products," *Crit. Rev. Anal. Chem.*, Vol. 35, 2005, pp. 193–216.

[13] ASTM Standard D2007: Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Adsorption Chromatographic Method, *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 1986.

[14] Kharrat, A.M., Zacharia, J., Cherian, V.J., and Anyatonwu, A., "Issues with Comparing SARA Methodologies," *Energy & Fuels*, Vol. 21, 2007, pp. 3618–3621.

[15] Rahimi, P.M., and Gentzis, T., "The Chemistry of Bitumen and Heavy Oil Processing," in *Practical Advances in Petroleum Processing*, Vol. 2, C.S. Hsu and P.R. Robinson, Eds., Springer, New York, 2006.

[16] Leontaritis, K.J., and Mansoori, G.A. "Fast Crude-Oil Heavy Component Characterization Using Combination of AST, HPLC, and GPC Methods," *Int. J. Petrol. Sci. Technol.*, Vol. 2, 1989, pp. 1–12.

[17] Woods, J., Kung, J., Kingston, D., Kotlyar, L., Sparks, B., and McCracken, T., "Canadian Crudes: A Comparative Study of SARA Fractions from a Modified HPLC Separation Technique," *Oil Gas Sci. Technol.*, Vol. 63, 2008, pp. 151–163.

[18] Islas-Flores, C.A., Buenrostro-Gonzalez, E., and Lira-Galeana, C., "Comparisons between Open Column Chromatography and HPLC SARA Fractionations in Petroleum," *Energy & Fuels*, Vol. 19, 2005, pp. 2080–2088.

[19] Hannisdal, A. Hemmingsen, P.V., and Sjoblom, J., "Group-Type Analysis of Heavy Crude Oils Using Vibrational Spectroscopy in Combination with Multivariate Analysis," *Ind. Eng. Chem. Res.*, Vol. 44, 2005, pp. 1349–1357.

[20] Sastry, M.I.S, Mukherjee, S., Kapur, G.S., Sarpal, A.S., Jain, S.K., and Srivastava, S.P., "Modified Method for Hydrocarbon Type Analysis of Blended Base Stocks by Infrared Spectroscopy," *Fuel*, Vol. 74, 1995, pp. 1343–1346.

[21] Wise, A., Chesler, S.N., Hertz, H.S., Hilpert, L.R., and May, W.E., "Chemically-Bonded Aminosilane Stationary Phase for the High-Performance Liquid Chromatographic Separation of Polynuclear Aromatic Compounds," *Anal. Chem.*, Vol. 49, 1977, pp. 2306–2310.

[22] Grizzle, P.L., and Sablotny, D.M., "Automated Liquid Chromatographic Compound Class Group-Type Separation of Crude Oils and Bitumens Using Chemically Bonded Silica-NH2," *Anal. Chem.*, Vol. 58, 1986, 2389–2396.

[23] Wang, Z., Fingas, M.K., and Li, K., "Fractionation of a Light Crude Oil and Identification and Quantitation of Aliphatic, Aromatic, and Biomarker Compounds by GC-FID and GC-MS, Part I," *J. Chromatogr. Sci.*, Vol. 32, 1994, pp. 361–366.

[24] Saravanabhavan, G., Helferty, A., Hodson, P.V., and Brown, R.S., "A Multi-Dimensional High Performance Liquid Chromatographic Method for Fingerprinting Polycyclic Aromatic Hydrocarbons and Their Alkyl-Homologs in the Heavy Gas Oil Fraction of Alaskan North Slope Crude," *J. Chromatogr. A.*, Vol. 1156, 2007, pp. 124–133.

[25] Pasadakis, N., Gaganis, V., and Varotsis, N., "Accurate Determination of Aromatic Groups in Heavy Petroleum Fractions Using HPLC-UV-DAD," *Fuel*, Vol. 80, 2001, pp. 147–153.

[26] Wang, G., and Eser, S., "Molecular Composition of the High-Boiling Components of Needle Coke Feedstocks and Mesophase Development," *Energy & Fuels*, Vol. 21, 2007, pp. 3563–3572.

[27] Hinkle, A., Shin, E.-J., Liberatore, M.W., Herring, A.M., and Batzle, M., "Correlating the Chemical and Physical Properties of a Set of Heavy Oils from Around the World," *Fuel*, Vol. 87, 2008, pp. 3065–3070.

[28] Jewell, D.M., Weber, J.H., Bunger, J.W., Plancher, H., and Latham, D.R., "Ion-Exchange Coordination and Adsorption Chromatography Separation of Heavy-End Petroleum Distillates," *Anal. Chem.*, Vol. 44, 1972, pp. 1391–1395.

[29] Wang, S., Guo, G., Yan, Z., Lu, G., Wang, Q., and Li, F., "The Development of a Method for the Qualitative and Quantitative Determination of Petroleum Hydrocarbon Components Using Thin-Layer Chromatography with Flame Ionization Detection," *J. Chromatogr. A*, Vol. 1217, 2010, pp. 368–374.

[30] Rudzinski, W.E., and Aminabhavi, T. M., "A Review on Extraction and Identification of Crude Oil and Related Products Using Supercritical Fluid Technology," *Energy & Fuels*, Vol. 14, 2000, pp. 464–475.

[31] Dutriez, T., Courtiade, T.M., Thiébaut, D., Dulot, H., and Hennion, M.-C., "Improved Hydrocarbons Analysis of Heavy Petroleum Fractions by High Temperature Comprehensive Two-Dimensional Gas Chromatography," *Fuel*, Vol. 89, 2010, pp. 2338–2345.

[32] Sheu, E.Y., "Petroleum Asphaltenes Properties, Characterization, and Issues," *Energy & Fuels*, Vol. 16, 2002, pp. 74–82.

[33] Mullins, O.C., "The Modified Yen Model," *Energy & Fuels*, Vol. 24, 2010, pp. 2179–2207.

[34] Sánchez, V., Murgia, E., and Lubkowitz, J.A., "Size Exclusion Chromatographic Approach for the Evaluation of Processes for Upgrading Heavy Petroleum," *Fuel*, Vol. 63, 1984, pp. 612–615.

[35] Zhao, S., Sparks, B.D., Kotlyar, L.S., and Chung, K.H., "Correlation of Processability and Reactivity Data for Residua from Bitumen, Heavy Oils and Conventional Crudes: Characterization of Fractions from Super-Critical Pentane Separation as a Guide to Process Selection," *Catalysis Today*, Vol. 125, 2007, pp. 122–136.

[36] Gonçalves, M.L.A., Angélica, D., Mota, P., Cerqueira, W.V., André, D., Saraiva, L.M., Coelho, M.I.F., Ana Maria, A., Teixeira, R.F., and Teixeira, M.A.G., "Knowledge of Petroleum Heavy Residue Potential as Feedstock in Refining Process Using Thermogravimetry," *Fuel Process. Technol.*, Vol. 91, 2010, pp. 983–987.

[37] Rana, M.S., Samano, V., Ancheya, J, and Diaz, J.A.I., "A Review of Recent Advances on Process Technologies for Upgrading of Heavy Oils and Residua," *Fuel*, Vol. 86, 2007, pp. 1216–1231.

[38] Bosworth, D., "Improving Bottom of the Barrel Profitability," *Third Bottom of the Barrel Technology Conference*, October 20-21, 2004, Antwerp, Belgium.

[39] "UOP/FWUSA Solvent Deasphalting Process," http://www.uop.com/processing-solutions/refining/residue-upgrading/#solvent-deasphalting, (accessed October 4, 2012).

[40] *2008 Refining Process Handbook*, http://www.hydrocarbonprocessing.com (accessed July 8, 2009).

[41] "FWUSA/UOP Visbreaking Process," http://www.uop.com (accessed July 8, 2009).

[42] Threlkel, R., Dillon, C., Singh, U.G., and Ziebarth, M., "Increase Flexibility to Upgrade Residuum Using Recent Advances in RDS/VRDS-RFCC Process and Catalyst Technology," *J. Japan Pet. Inst.*, Vol. 53, 2010, pp. 65–74.

[43] Fahim, M.A., Al-Sahhaf, T.A., and Elkilani, A.S., *Fundamentals of Petroleum Refining*, Elsevier, Amsterdam, 2010.

[44] Gary, J.H., Handwerk, G.E., and Kaiser, M. J., *Petroleum Refining: Technology and Economics*, 5th ed., CRC Press, New York, 2007.

[45] Eser, S., and Andresen, J., "Properties of Fuels, Petroleum Pitch, Petroleum Coke, and Carbon Materials," in *Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing*, G.E. Totten, R.J. Shah, and S.R. Westbrook, Eds., ASTM International, West Conshohocken, PA, 2003, pp. 757–786.

[46] Kamienski, P., Gorshteyn, A., Phillips, G., and Woerner, A., "ExxonMobil, Delivering Value for Resid and Heavy Feed," *First Russia & CIS Bottom of the Barrel Technology Conference*, April 19, 2005, Moscow, Russia.

[47] Hammond, D.G., "Review of Fluid Coking and Flexicoking Technologies," *Pet. Tech. Quart.*, Vol. 8, 2003, pp. 27–33.

[48] Maples, R.E., *Petroleum Refinery Process Economics*, PennWell Books, Tulsa, OK, 1993.

[49] Plain, C., Duddy, J., Kressmann, S., Le Coz, O., and Tasker, K., *Options for Resid Conversion*, Axens North America, Inc., Princeton, NJ, http://www.axens.net/upload/presentations/fichier/options_for_resid_conversion.pdf (accessed July 8, 2009).

[50] Plain, C., *Improve Economics of Existing AR/VRDS Units with the PRS Permutable Reactor System*, http://www.axens.net/upload/presentations/fichier/bbtc_04.pdf (accessed July 8, 2009).

[51] Plumail, J.-C., *Two Routes to Residue Upgrading via Hydroconversion*, http://www.axens.net/upload/presentations/fichier/tworoutestoresidueupgradingviahydroconversionjcp.pdf (accessed July 8, 2009).

[52] "OCR Moving Bed Technology for the Future," http://www.chevron.com/products/sitelets/refiningtechnology/residuum_hydro_5b.aspx (accessed July 8, 2009).

[53] de Wilde, H.P.J., Kroon, P., Mozaffarian, M., and Sterker, T., *Quick Scan of the Economic Consequences of Prohibiting Residual Fuels in Shipping,* ECN-E-07-051, http://www.ecn.nl/docs/library/report/2007/e07051.pdf (accessed July 8, 2009).

[54] "Residue Hydroconversion Shell, Refining Processes 2000," *Hydrocarbon Process.*, 2000, p. 139.

[55] Biasca, F.E., Dickenson, R.L., Chang, E., Johnson, H.E., Bailey, R.T., and Simbeck, D.R., *Upgrading Heavy Crude Oils and Residues to Transportation Fuels; Technology, Economics and Outlook Phase 7*, SFA Pacific, Inc., Mountain View, CA, 2003.

[56] Yui, S., and Chung, K.H., "Syncrude Upgrader Revamp Improves Product Quality," *Oil Gas J.*, Volume 105, 2007, pp. 52–59.

[57] Scheffer, B., Van Koten, M.A, Robschlager, K.W., and De Boks, F.C., "The Shell Residue Hydroconversion Process: Development and Achievements," *Catal Today*, Vol. 43, 1998, pp. 217–224.

9

Advances in Petroleum Refining Processes

Isao Mochida[1], Ray Fletcher[2], Shigeto Hatanaka[3], Hiroshi Toshima[4], Jun Inomata[5], Makato Inomata[6], Shinichi Inoue[7], Kazuo Matsuda[7], Shigeki Nagamatsu[6], and Shinichi Shimizu[7]

9.1 INTRODUCTION

This chapter describes some recent advances in selected processes used in petroleum refineries. The advancements include process innovations and modeling for increasing the flexibility of refining processes to treat the feedstocks and intermediate products for handling increasingly heavy and high-heteroatom-content feeds to produce fuels according to increasingly strict environmental regulations on the fuel products and refinery operations. Some recent publications have reviewed the advancements in the field and provide good references to the processes that are not covered here because of space limitation [1–4]. The developments and advancements in catalyst design and use in refining processes are discussed in Chapter 10 following a similar outline used in this chapter.

9.2 ADVANCES IN FLUID CATALYTIC CRACKING (FCC) AND HYDROTREATMENT OF CRACKER NAPHTHA

9.2.1 The Birth and Evolution of FCC and Innovation in Unit Design

The FCC unit possesses perhaps the most unique history of all the chemical processes in existence today. By 1910, there were an estimated 500,000 cars on the roads of North America [5]. This resulted in the first gasoline shortages in history. This demand served as a driving force for innovation [6]. Many new refining processes evolved from this need including multiple thermal processes such as the Dobbs unit (the origin of UOP), the Houdry unit (the forefather of the FCC), and eventually the fluidized catalytic cracker. Additionally, with the advent of aviation warfare in World War II, there was a critical shortage of aviation jet fuel. This jet fuel was produced primarily via sulfuric alkylation units which produced a demand for butylenes.

The steady development of refining processes to supply the gasoline shortages of the early 1900s in conjunction with the war effort culminated in the startup of the first FCC unit (Powdered Catalyst Louisiana No. 1, PCL1, 1942) in Baton Rouge, LA. By 1945, approximately 30 % of the liquefied petroleum gas (LPG) and olefins being produced as feedstock for alkylation units had their source in the FCC. Following World War II, the striking advantages of the FCC unit resulted in a wave of new unit construction. Innovation during this period was unparalleled. By 1950, over 500 patents had been issued related to FCC technology alone.

One key element in the development of FCC was an exceptional collaboration between multiple companies for the development of this new process. In 1938, the Standard Oil of New Jersey (now Exxon Mobil) formed a consortium of eight companies including M.W. Kellogg Co., Royal Dutch Shell, the Standard Oil Co. of Indiana, Anglo-Iranian Oil Co. (today's BP), Universal Oil Products Co. (today's UOP), the Texas Corp. (which would become Texaco), and IG Farben (which was eventually dropped in 1940). This group of eight companies became known as the Catalytic Research Associates (CRA). In addition, American wartime legislation required sharing of FCC patents for the duration of the war plus 7 years. The CRA group plus government action catapulted the swift development of the fluidized catalytic cracker.

Several key discoveries were made by the CRA associates, which were critical in overcoming the many engineering obstacles in design of the first few FCC units. These include: the concept of the standpipe [7] (for transferring solids from regions of lower pressure into regions of higher pressure), the dense bubbling bed [7,8] (which far exceeded the Stokes' law settling velocity of particles), and liquid feed injection (alleviating fears of "mud" formation in the injection zone).

The FCC unit rapidly matured into the process that we recognize today as the FCC unit. The first operating unit, PCLA No. 1, was designed as an "up flow" unit possessing no bubbling beds. Even prior to PCLA No. 1 start up, the next two units were being designed as "bed crackers" possessing bubbling beds in both the reactor and regenerator vessels.

A significant milestone in the development of the FCC process was the result of incorporation of zeolites into the alumina-based synthetic catalysts used at the time (Plank and Rosinski, Mobil Oil, 1962). The inclusion of zeolite into the amorphous catalysts produced a step change increase in activity. The improved catalytic activity resulted in increased delta coke on spent catalyst requiring improved regenerator metallurgy to withstand the increased combustion temperatures. Additionally, riser technology (plug flow tubular reactors) was incorporated into existing units to

---

[1] Kyushu University, Kasuga, Fukuoka, Japan
[2] INTERCAT, Inc., Vleuten, The Netherlands
[3] JX Nippon Oil & Energy Corp., Yokohama, Kanagawa, Japan
[4] Albemarle, Amsterdam, The Netherlands
[5] Fuji Oil Company, Ltd., Sodegaura, Chiba, Japan
[6] JGC Corp., Yokohama, Kanagawa, Japan
[7] Chiyoda Corp., Kawasaki, Kanagawa, Japan

take advantage of the improved intrinsic activity and yield selectivities. The risers also served to minimize over-cracking and maximize gasoline production.

An additional FCC milestone was the inclusion of residue feedstocks into the FCC feed slate. This was made possible by unit design advances developed by Total Petroleum USA, Kellogg, and UOP.

The third major milestone in the development of the process came as a result of rocketing propylene prices in the mid-1990s, transforming the FCC into a platform for producing maximum propylene yield. This led to the development of the DCC (deep catalytic cracking) process (Sinopec and Shaw Stone & Webster), RxCat process (UOP), and the Superflex (Kellogg) unit.

9.2.2 Low Sulfur Gasoline Production from FCC Products

9.2.2.1 INTRODUCTION

Catalytically cracked gasoline (CCG) produced from FCC of vacuum gas oil (VGO) or atmospheric residue supplies one of the major components of motor gasoline produced in a refinery. CCG containing high levels of sulfur requires hydrodesulfurization (HDS) to reduce the sulfur levels for compliance with environmental regulations. It is important, however, to note that CCG contains 20–40 vol % olefins and using the current naphtha HDS process would reduce the octane number (e.g., Research Octane Number [RON]) due to the hydrogenation (HG) of olefins in the HDS process [9]. Therefore, a selective CCG HDS process providing higher HDS activity and lower olefin HG must have been developed. In 2009, more than 100 CCG HDS units were operating in the world, and the commercial units are mostly selective CCG HDS except several demonstration units. This section focuses on the properties of CCG and the desulfurization processes. The catalysts used in CCG HDS are described in Chapter 28.

9.2.2.2 ANALYSIS AND HDS OF CCG

Main sulfur compounds in CCG are alkylthiophenes and alkylbenzothiophenes. They are produced by the cracking of heavier thiophenic compounds or newly produced by chemical reactions during FCC. Olefins are also produced by the cracking reactions. Because beta-scission is a major reaction pathway in catalytic cracking, theoretically, the same amount of paraffins and olefins should be produced. A CCG is distilled to each 10 °C fraction and the amounts of sulfur and olefin are measured (Figure 9.1) [10]. As seen in Figure 9.1, the light fraction (that boils below 90 °C) contains much olefin, but little sulfur. Therefore, only the heavy fraction (HCCG), where most of the sulfur is concentrated, is usually treated in the HDS unit. The properties of HCCG produced from low sulfur atmospheric residue are summarized in Table 9.1 [11]. The CCG contains olefins, saturates, and aromatics. Internal and branched olefins are dominant in the olefins of CCG, but some n-olefins are also present. Concerning the RON drop, n-olefin HG causes more concern than the HG of branched olefins.

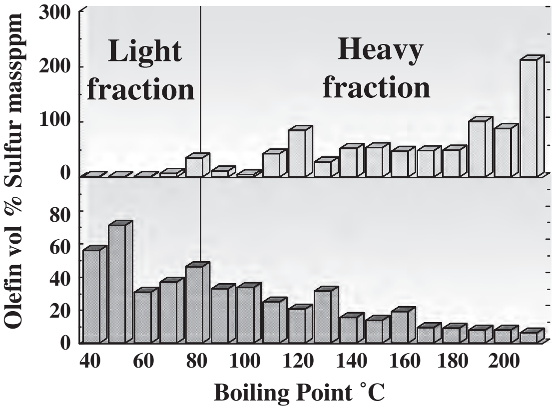


Figure 9.1—Sulfur and olefin distribution in CCG [10].

The GC-AED analysis of this HCCG is shown in Figure 9.2 [11]. Alkylthiophenes, alkylbenzothiophenes, alkylthiocyclopentanes, and disulfides are identified on the chromatogram. Table 9.2 shows the composition of these sulfur compounds [11]. The total amount of alkylthiophenes is about half of alkylbenzothiophenes. These results agree with a report analyzing the CCG containing 1000 massppm sulfur [12].

CCG is hydrodesulfurized on a Co-Mo/g-Al_2O_3 catalyst under the following conditions: 200–290 °C, 1.6 MPa, liquid hourly space velocity (LHSV) 3.5–10/h, and H_2/feed ratio 338 NL/L. The composition of the sulfur compounds in the HDS products of CCG are shown in Table 9.2. After HDS, the total sulfur content decreased from 229 ppm to 81 ppm at 220 °C, whereas 17 ppm of thiols were produced in the reaction. The thiols produced in CCG HDS are not intermediates from the HDS reactions of sulfur compounds. Thiols are produced by the reactions between H_2S and olefins

TABLE 9.1—Properties of CCG [11] (Reprinted with Permission)

Composition vol %		
Saturates		41.9
Aromatics		27.7
Olefins		30.4
Olefins by structure		
1-Olefins	H2C=CR2	2.3
	H2C=CHR	5.0
Internal olefins	HRC=CR2	9.8
	HRC=CHR	13.3
Isoolefin ratio in C=7%		78.9
Total sulfur massppm		229
Density 15 °C g/cm^3		0.778
Research octane number		87.0
Distillation Temperature °C		
IBP		48
10 %		88
30 %		110
50 %		136
70 %		165
90 %		201
EP		231

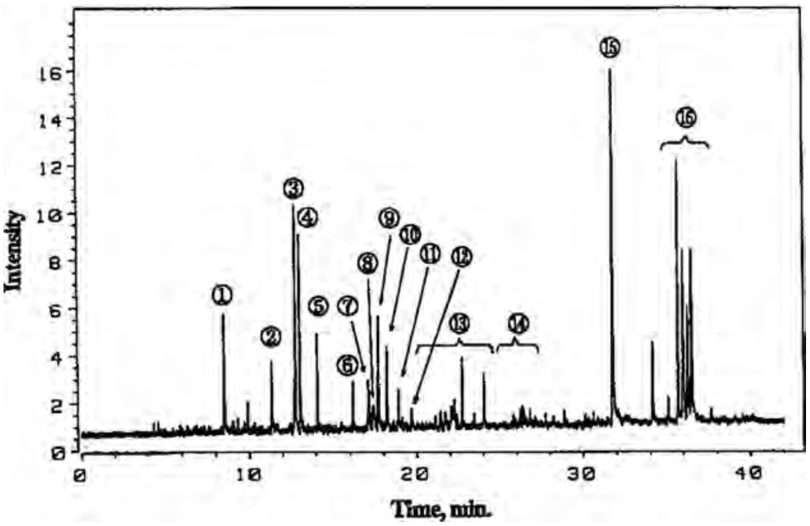


Figure 9.2—Sulfur compounds in HCCG identified by GC-AED (see Table 9.2 for the peak identification numbers) [11]. Reprinted with permission.

TABLE 9.2—Sulfur Compounds in CCG before and after HDS at Different Conditions [11] (Reprinted with Permission)

			Reaction temperature, °C			
			210		220	
GC-AED No.	Sulfur compound	Feedstock sulfur, ppm	Sulfur, ppm	Conversion, %	Sulfur, ppm	Conversion, %
1	Thiophene	7	4	43	3	57
5	Thiacyclopentane	5	2	60	1	80
3	2-methylthiophene	11	7	36	6	46
4	3-methylthiophene	10	5	50	3	70
6	2-methylthiacyclopentane	3	3	0	2	33
7	3-methylthiacyclopentane + 2-ethylthiophene	5	5	0	4	20
10	2,3-dimethylthiophene	5	3	40	2	60
9	2,4-dimethylthiophene	7	5	29	4	43
8	2,5-dimethylthiophene + 3-ethylthiophene	4	2	50	2	50
11	3,4-dimethylthiophene	3	1	67	1	67
13	C3-thiophenes	15	15	0	12	20
14	C4-thiophenes	7	6	14	5	29
15	Benzothiophene	63	2	97	0	100
16	Methylbenzothiophenes	63	28	56	12	81
2	Dimethyldisulfuide	4	1	75	0	100
12	Diethyldisulfuide	1	1	0	0	100
	Unknown	16	15	6	7	56
	Thiols	0	22		17	
	Total sulfur	229	127		81	
		HDS%		45		65
		Conversion%		54		72

Reaction conditions: Pressure, 1.6 MPa, LHSV 3.5/h, H2/feed ratio, 338 NL/L contained in CCG. It is noted that alkylbenzothiophenes are more reactive than alkylthiophenes, and the reaction rate constant of benzothiophene is 6 times larger than that of thiophene. With the increasing number of alkyl substitution groups, the HDS reactivity decreases. The 2-methylthiophene is less reactive than 3-methythiophene because of the steric hindrance of a methyl group substituted at the 2-position of thiophene.

The intrinsic reactivity of sulfur compounds contained in CCG was examined by HDS of individual sulfur compounds dissolved in toluene [11]. The obtained conversions at several temperatures are shown in Figure 9.3, indicating that the reactivity decreases in the order benzothiophene > thiophene > 3-methylthiophene > 2-methythiophene > 2-ethylthiophene > 2,5-methythiophene within the temperature range examined. It is noted that the order of the reactivity is the same as that of sulfur compounds in CCG HDS. However, the rate of reaction of sulfur compounds in toluene is much faster than that in CCG. It is considered that olefins in CCG depress the HDS reactivity by competitive adsorption on HDS active sites of the catalyst.

During the HDS reaction, olefins in CCG are hydrogenated and RON is decreased (Figure 9.4). Because the decrease in RON is a serious problem in deep HDS, a selective HDS process is desired to preserve the olefins during the reaction [13].

9.2.2.3 PROCESS DESIGN OF CCG HDS USING A THEORETICAL MODEL

Special reaction conditions should be carefully selected for CCG HDS, because of thiol formation. CCG HDS was tested and a simulation model was studied [14]. The reaction conditions were selected as follows: Temperature = 200–300 °C, pressure = 1.0–5.0 MPa, hydrogen/feed = 100–500 m^3/m^3, and LHSV = 2–6 h^{-1}.

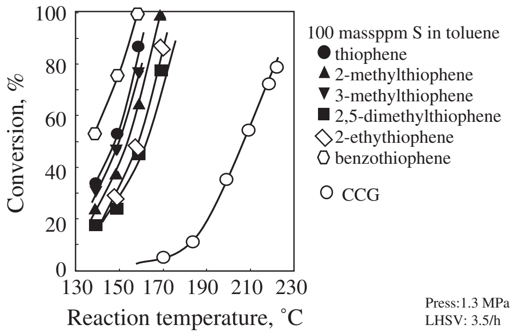


Figure 9.3—HDS conversion of individual sulfur compounds and CCG [11]. Reprinted with permission.

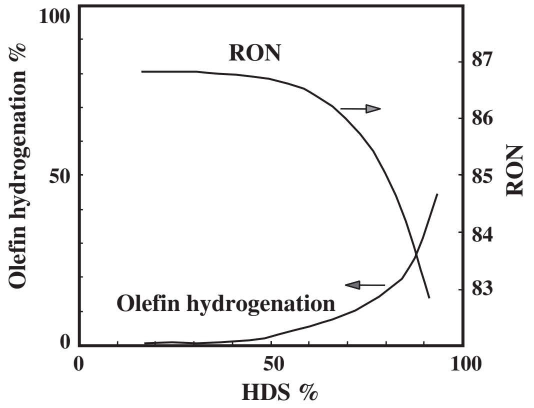


Figure 9.4—Olefin HG and reduction of RON by HDS [10].

9.2.2.3.1 *Modeling Thiol Formation*

A thiol formation model is shown in Figure 9.5

The equilibrium constant for the reversible reaction in the model is given by Eqs 9.1 and 9.2, as follows:

$$Kp = [\text{Thiol}]/([\text{Olefin}][H_2S]\theta) \tag{9.1}$$

$$Kp = \exp((-\Delta H + T\Delta S)/RT) \tag{9.2}$$

where Kp is the equilibrium constant, [ ] represents each compound's partial pressure, and θ is the H_2S coverage of the catalyst surface, calculated from Eq 9.3

$$\theta = K[H_2S]/(1 + K[H_2S]) \tag{9.3}$$

where K is the equilibrium constant of H_2S adsorption. In Eq 9.2, ΔH and ΔS denote the enthalpy and entropy of thiol formation, respectively. These are calculated employing the NASA thermochemical polynomials [15] shown in Eqs 9.4 and 9.5:

$$\Delta H/RT = a_1 + a_2T/2 + a_3T^2/3 + a_4T^3/4 + a_5T^4/5 + a_6/T \tag{9.4}$$

$$\Delta S/R = a_1\ln T + a_2T + a_3T^2/2 + a_4T^3/3 + a_5T^4/4 + a_7 \tag{9.5}$$

Each constant a_1 through a_7 was calculated using THERGAS [16,17], which is a program for calculating the thermochemical properties of organic compounds in gas and liquid phase. In this case, the 2-methyl-1-hexylthiol was designated a model thiol compound. This thiol is a typical thiol contained in heavy CCG. For the CCG HDS, thiophene HDS and olefin HG ratios are calculated from Eqs 9.6 and 9.7, respectively.

$$-d[\text{Olefin}]/dt = [\text{Olefin}]^{n1}[H_2]^{m1}A_1\exp(-E_1/RT)\,(1/(1 + \alpha_1[H_2S]) \tag{9.6}$$

$$-d[\text{Thiophene}]/dt = [\text{Thiophene}]^{n2}[H_2]^{m2}A_2\exp(-E_2/RT)(1/(1 + \alpha_2[H_2S]) \tag{9.7}$$

In Eqs 9.6 and 9.7, A denotes the apparent frequency factor and E the apparent activation energy. The sulfur and olefin content in hydrotreated CCG can be estimated by including these equations in the simulation model.

9.2.2.3.2 *Verification of the Simulator Model*

Figure 9.6 shows the effect of temperature on the estimated and experimental results for thiol production. The theoretical calculations showed a good correspondence with

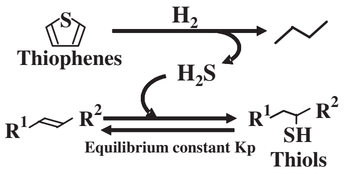


Figure 9.5—A thiol formation model.

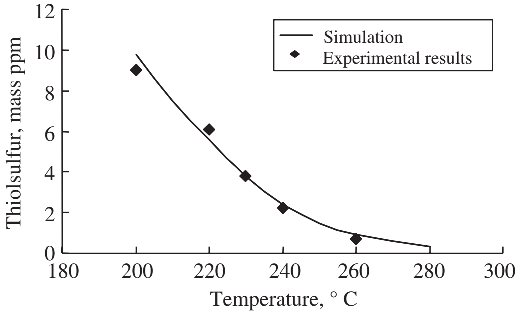


Figure 9.6—The effect of temperature on CCG HDS [19]. Reprinted with permission.

the experimental results. It is clear that the higher the temperature, the lower the thiol formation. In general, the equilibrium constant *Kp* depends on the temperature; *Kp* decreases with the increasing reaction temperature.

The effect of pressure is shown in Figure 9.7. For most HDS reactions, the higher the reaction pressure, the lower the sulfur content. In contrast, Figure 9.7 shows that the sulfur content of hydrotreated CCG increases as the reaction pressure increases. This increase is attributed to the increasing thiol production as the pressure increases, indicating that a lower pressure is favorable for reducing the sulfur content in hydrotreated CCG. In this case, the calculated results agree very well with experimental results. Most of the total sulfur in hydrotreated CCG derives from the generated thiol. It is, thus, essential to set up a simulation model that includes thiol formation.

Most of *ΔT* comes from olefin HG in CCG HDS. The olefin HG ratio is calculated by Eq 9.6. Figure 9.8 shows the effect of the hydrogen/feed on olefin HG. The theoretical calculations showed a good correspondence with the experimental results. Figure 9.9 shows the reactor temperature profile for the reaction. In this case, the estimated results obtained by the simulator agree with the experimental results as measured in an adiabatic reactor [18].

9.2.2.4 SELECTIVE HYDRODESULFURIZATION PROCESSES FOR CCG

The selective CCG HDS process is the most widely used process and over 100 units are being operated, under design, or under planning. A selective CCG HDS catalyst is employed in the main reactor to achieve deep HDS with low olefin HG.

The ROK-Finer [19] process has been developed by Nippon Oil Corporation with three units operating since 2004 and producing low-sulfur gasoline with sulfur level is less than 10 ppm. Figure 9.10 shows a photograph of ROK-Finer in Sendai, Japan. This process consists of a single reactor system (Figure 9.11) and is used for low to middle sulfur level CCG HDS.

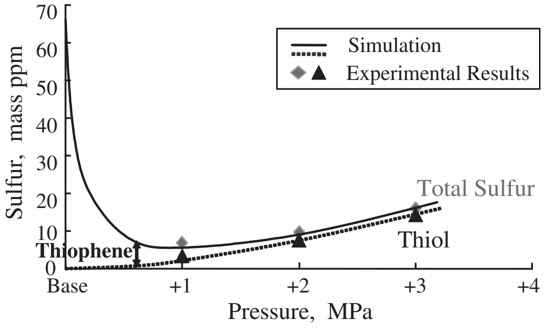


Figure 9.7—The effect of pressure on CCG HDS [19]. Reprinted with permission.

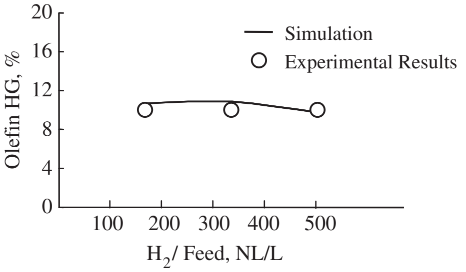


Figure 9.8—The effect of H_2/feed in CCG HDS.

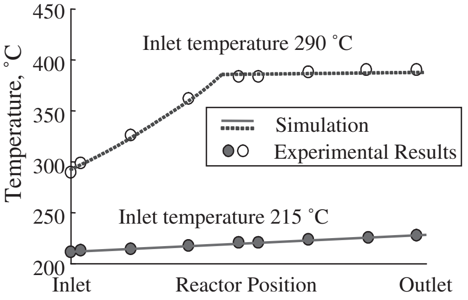


Figure 9.9—The temperature profile in the reactor.

A selective CCG HDS catalyst is used in this process, where the whole CCG (WCCG) is separated into low-boiling (LCCG) and high-boiling fractions (HCCG). The HCCG is hydrotreated in a fixed-bed reactor (Rx) and the effluent is sent to an amine unit for recovering H_2S. The low-sulfur LCCG fraction is not hydrotreated to preserve the olefins. The sweetening unit removes thiols produced in the HDS reactor.

The SCANfining process [20] developed by ExxonMobil and Akzo Nobel has two reactors, one for selective HG of diolefin and the main reactor for selective HDS. Diolefins

Figure 9.10—ROK-Finer in Sendai refinery, Japan.

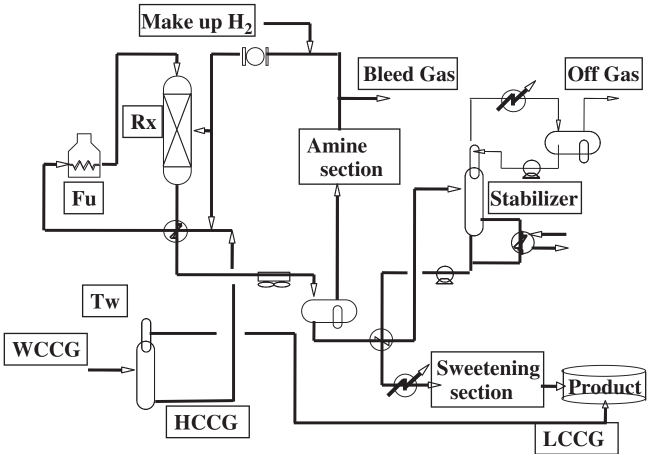


Figure 9.11—ROK-Finer process flow.

cause fouling problems in the heat exchanger and the HDS reactor. Therefore, they are hydrogenated in the selective hydrogenation reactor.

The Prime-G+ (Axenes-IFP) process [21] has three reactor units, for selective hydrogenation of diolefin, for the main selective HDS, and a finisher. The finisher is a unique reactor system in which thiol is decomposed into H_2S and an olefin at high temperatures (over 300 °C). Prime-G+ can even be applied to high-sulfur-level CCG.

In the light CCG, thiols, sulfides, and other sulfur compounds are included. In the case of high-sulfur-level CCG, some treatment of LCCG is necessary. The CDHydro process [22] developed by CDTech and the OATS process [23] developed by BP convert these sulfur compounds into large molecules by reaction with olefin or diolefin and transfer them to HCCG by distillation. As CCG HDS products contain thiols, a sweetening process is often added for posttreatment.

The other processes including OCT-Gain™ [24] developed by ExxonMobil and ISAL™ [25] developed by INTEVEP and UOP are HDS processes with octane value recovery section. CCG undergoes deep HDS in the first HDS section where olefins are hydrogenated completely. In the next section, octane value is recovered by the isomerization and alkylation of the paraffins.

The S-Zorb™ [26] developed by Phillips Petroleum Co. is an adsorption process in which a metal base solid sorbent is used. The sorbent extracts sulfur compounds in a fluid-bed reactor and some sorbent is constantly regenerated in the regenerator.

Other HDS processes are also proposed and well reviewed in previous reports [27].

9.3 DEEP HDS OF DIESEL FUELS

9.3.1 Challenges in Deep Desulfurization of Diesel Fuels

The production of environmentally conscious low-sulfur diesel fuels has been of high priority in the petroleum refineries in the world. This is because environmental regulations have been introduced in many countries around the world to reduce the sulfur content of diesel fuels to very low levels. Limiting the sulfur levels of diesel and other transportation fuels to very low levels are certainly beneficial from an environmental point of view, but it poses major operational and economic challenges in the petroleum refining industry. The tightening of sulfur specifications of diesel fuel requires deep desulfurization of diesel feed streams.

The problem of deep desulfurization has become more serious due to the increasingly more stringent limits of sulfur content in finished fuel products, while the sulfur contents of crude oils have been increasing. The shift from normal to deep desulfurization introduces complicated technical issues. Many factors such as the catalysts, process parameters, and the nature of sulfur compounds present in the feed can have a significant influence on the degree of desulfurization of diesel feeds. Among these, the feedstock quality plays an important role on deep desulfurization because the types of sulfur, nitrogen, and aromatic compounds and their concentrations are different in different feedstocks.

Diesel fuel feedstocks mainly consist of middle distillates in the boiling range of 220–360 °C. Straight-run gas oil obtained from atmospheric distillation of crude oil and their blends with the cracked middle distillates such as light cycle oil and coker gas oil are extensively used in diesel fuel production. These feedstocks usually contain different amounts of sulfur, nitrogen, and aromatic compounds. Distributions of sulfur compound types in different blending streams are also different. The contents of the least-reactive sulfur compounds in the feeds depend to a large extent on the end boiling point of the feedstock. This section overviews deep desulfurization of diesel fuels in terms of catalysis and chemistry as well as processes.

9.3.2 Designing Approaches to Deep Desulfurization of Diesel Fuels

Approaches to ultradeep desulfurization include: (1) improving catalytic activity by new catalyst formulation for HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT); (2) increasing operating severity; (3) revamping existing unit including internals; (4) designing new reactor system; and (5) developing new processes. One or more approaches may be employed by a refinery to meet the challenges of producing ultraclean fuels at affordable cost.

Figure 9.12 shows the relative volume of catalyst bed required for achieving various levels of diesel sulfur using conventional HDS of gas oil over a commercial hydrotreating catalyst [28].

The modeling is based on HDS using a commercial catalyst for the production of 500 wtppm sulfur diesel. In this simulation, Middle East straight-run gas oil containing 1.0 wt % sulfur was selected as a feedstock. Hydrogen partial pressure, reaction temperature, H_2/oil ratio, and other conditions were the same as those for the commercial desulfurization (500 wtppm sulfur level).

According to this simulation, the amount of catalysts must be increased by a factor of 2.5 to achieve deep desulfurization (50 wtppm sulfur level) and by a factor of 4.5 for ultradeep desulfurization (10 wtppm, for example). The second-generation catalyst has been reported to obtain about 1.3 times higher activity than those of the first-generation catalysts. Ultradeep desulfurization would require over three times more amount of the second-generation catalyst compared to the production of 500 wtppm sulfur diesel by the same catalyst. To accommodate this amount, it is necessary to add two or three reactors. If the reaction temperature is increased by about 20 °C, the amount of catalysts needed would be twice as much as the amount used in the

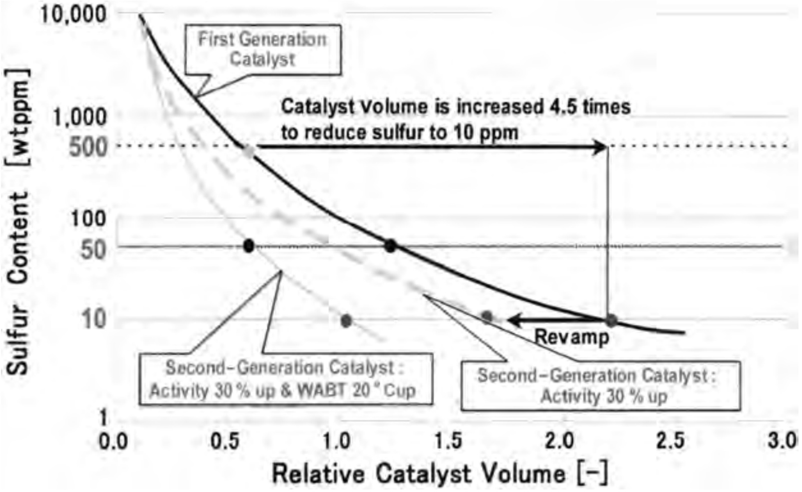


Figure 9.12—Simulation of sulfur content in diesel desulfurization [28]. Reprinted with permission.

production of 500 wtppm sulfur diesel, requiring one more reactor. An increase in reaction temperature would cause deterioration of the color of the product, and shorten the catalyst life, because of the deposition of coke on catalyst surfaces. The catalyst life is an important factor for the prolonged continuous operation and cost efficiency.

9.3.3 Improving the Catalytic Activity

Design approaches for improving catalytic activity for ultradeep desulfurization focus on the more effective removal of 4,6-DMDBT by modifying catalyst formulations through (1) enhancing the hydrogenation of aromatic ring in 4,6-DMDBT by increasing hydrogenating ability of the catalyst; (2) incorporating acidic feature in the catalyst to induce isomerization of methyl groups away from the 4- and 6- positions; and (3) reducing inhibiting effects of some substances (such as H_2S). Tailoring the reaction conditions must be optimized for specific catalytic functions [29]. New catalyst formulation and commercial catalyst development are discussed in Chapter 10.

9.3.4 Increasing the Severity of Operation

Operating parameters, such as reaction temperature, play a significant role on the degree of desulfurization and affect the properties of the HDS products, such as sulfur content, color, aromatics content, density, cetane index, and pour point. Such changes in the properties are briefly described below [30].

1. Sulfur content
   To achieve deep desulfurization of sulfur level from 500 wtppm to 50 wtppm and from 500 wtppm to 10 wtppm, temperatures should be increased by 16–18 °C and 28–31 °C, respectively.
2. Color
   In case of deep desulfurization (sulfur level: 500 wtppm), Saybolt color of product ranges about +20 in any contact time (LHSV). However, it is expected to get worse by higher severity such as higher reaction temperature under high LHSV conditions.
3. Chemical hydrogen consumption
   For decreasing the sulfur levels from 500 wtppm to 50 wtppm and from 500 wtppm to 10 wtppm, the chemical hydrogen consumption increases by about 10 Nm^3/kL and 20 Nm^3/kL, respectively.
4. Density
   For decreasing sulfur levels from 500 wtppm to 50 wtppm and from 500 wtppm to 10 wtppm, respectively, by increasing the reaction temperature, the density of the product decreases by 0.003 g/cm^3 and 0.005 g/cm^3, respectively.
5. Cetane index
   For decreasing the sulfur level from 500 wtppm to 50 wtppm and from 500 wtppm to 10 wtppm due to increase in reaction temperature, the centane index of product increases by 1 and 2, respectively.
6. Pour point
   The pour point of the product is not improved by deep desulfurization up to a sulfur level of 10 wtppm.
7. Total aromatics content
   In case of deep desulfurization to reduce the sulfur level from 500 wtppm to 50 wtppm by increasing the reaction temperature with any LHSV, total aromatics content of product decreases by 2–3 vol %. In case of reducing the sulfur level from 500 wtppm to 10 wtppm by increasing the reaction temperature with LHSV of lower than 1 h^{-1}, total aromatics content of product decreases by 7 vol %. In contrast, in case of reducing the sulfur level from 500 wtppm to less than 50 wtppm by increasing the reaction temperature with LHSV of higher than 2 h^{-1}, the total aromatic content tends to increase. Therefore, high pressure and low LHSV are required to decrease the total aromatics content.
8. Polyaromatic aromatic hydrocarbons (PAH) content
   Regardless of degree of desulfurization, ranging from 500 wtppm to 10 wtppm, PAH content remains almost the same. To decrease PAH content, high pressure is required.
9. Distillation properties
   Regardless of degree of desulfurization, ranging from 500 wtppm to 10 wtppm, temperature of 90 vol % distillation remains almost the same. Deep desulfurization is not expected to improve the distillation properties.

9.3.5 Revamping an Existing HDS Unit

Ultradeep desulfurization would inevitably require modification or renewal of existing equipment, unless significant improvement is achieved in the performance of catalysts.

To minimize the cost of modification, it is important not only to improve the equipment but also to take steps on the process side, such as the maximization of the operation efficiency of existing equipment and the optimization of operating conditions. Tailoring process conditions aim at achieving deeper desulfurization with a given catalyst in an existing reactor without changing the processing scheme, with minimum capital investment. The parameters include some relatively minor changes in processing scheme or some capital investment (such as expansion in catalyst volume or density, H_2S scrubber from recycle gas, and improved vapor-liquid distributor). Any new capital investment (space velocity, temperature, pressure) must be avoided.

The conditions for ultradeep desulfurization are expected to increase H_2 consumption and the H_2/oil ratio, reflecting the influence on the catalyst life. The increase in the H_2/oil ratio as well as installation of more reactors would result in an increase in the pressure loss in the hydrogen gas recycle system. Therefore, such alteration would require modification and/or renewal of existing equipment. Usually, the make-up hydrogen compressor and the recycle hydrogen compressor may be upgraded by the replacement of motors and other partial modification. These compressors must be replaced, if the new conditions lead to a significant increase in hydrogen gas flow or pressure drop.

If the operating pressure in the existing units, such as the heating furnace and heat exchanger, would exceed the design limit, these units must also be replaced. Such replacement would inflict a considerable increase in the cost of modification.

9.3.6 Designing a New Reactor System

1. Counter-current flow system

   The reactor design and configuration involve both one- and two-stage desulfurization. The H_2S and NH_3 produced by hydrotreatment strongly suppress the activity of the catalyst for converting the refractory sulfur compounds, which should occur in the major downstream part of a co-current trickle-bed reactor during deep desulfurization [29]. The normal co-current trickle-bed single reactor is, therefore, not the optimal configuration for deep desulfurization. A new reactor design involves two or three catalyst beds that have both co-current and counter-current flows. The beds can be accommodated in a single or two to three reactors as shown in Figure 9.13. This new design was proposed by ABB Lummus and Criterion, as represented by their SynSat process [31,32]. The hydrogen is mixed together with the distillates at the entrance of the traditional reactor and flows through the reactor together with the oil in the reactor. The disadvantages of this kind of flow include having the highest H_2 concentration at reactor inlet and the lowest H_2 concentration at the outlet. The H_2S concentration has the reverse trend, creating unfavorable conditions for the deep HDS in the last part of the reactor. The solution to this problem is to design a counter-current reactor as proposed by SynSat, where fresh H_2 is introduced at one end of the reactor and the liquid distillate at the other end. Here, the hydrogen concentration is highest (and the hydrogen sulfide concentration is lowest) where the most difficult-to-desulfurize sulfur compounds, such as 4,6-DMDBT are removed.
2. Under-cutting of feedstock

   While many species of sulfur compounds are contained in diesel oil, the difficult-to-desulfurize compounds are mostly contained in the heavy end (high boiling point range) as shown in Figure 9.14 [33]. Alkyldibenzothiophenes, such as 4,6-DMDBT, are extremely difficult to desulfurize, and these compounds are mostly found in the fractions above 340 °C boiling point.

Straight-run gas oil is first fractionated into the fraction containing mostly easy-to-desulfurize components (light gas oil) and that containing mostly difficult-to-desulfurize components (heavy gas oil), and each fraction is then

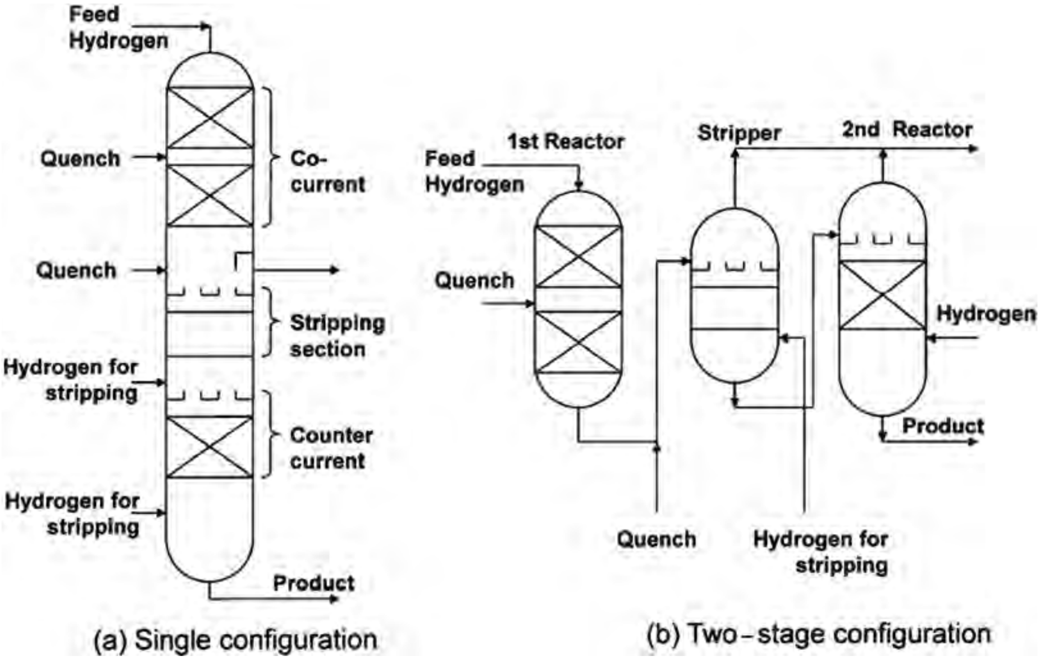


Figure 9.13—A schematic diagram of the SynSat process [31,32]. Reprinted with permission.

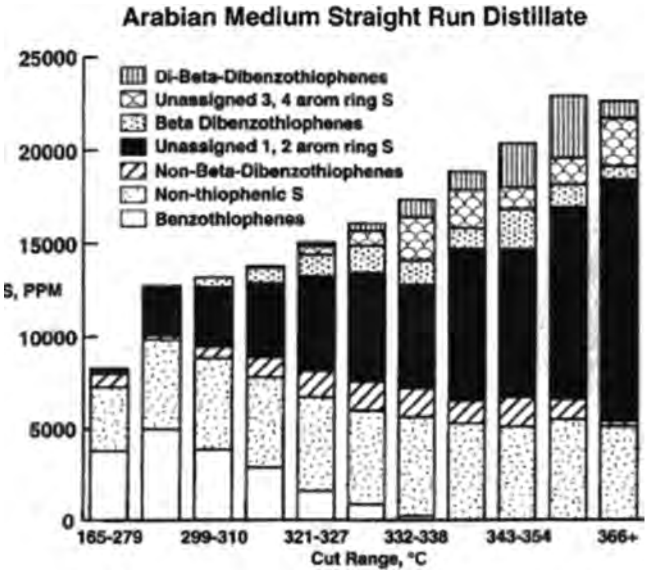


Figure 9.14—Types of sulfur compounds as a function of boiling range [33]. Reprinted with permission.

desulfurized under appropriate conditions. Depending on the type of crude oil, fractionation of straight-run gas oil at 320–340 °C results in the production of heavy gas oil in a proportion of 10–20 vol % to the amount of straight-run gas oil, and this heavy gas oil contains concentrated levels of difficult-to-desulfurize sulfur compounds. The heavy gas oil is desulfurized effectively to remove 4,6-DMDBT, if the reaction is conducted using higher H_2/oil ratio, higher hydrogen partial pressure, and longer reaction time as compared with the desulfurization of straight-run gas oil. On the other hand, the light gas oil can be desulfurized under the conditions that are the same as or milder than the conditions for the desulfurization of the typical straight-run gas oil.

Figure 9.15 shows the conceptual diagram of the HDS system to desulfurize two streams of feedstocks. After the fractionated light gas oil and heavy gas oil are fed into separate reactors, the total H_2/oil ratio is set at 200–300 Nm^3/kL.

Desulfurization is conducted with H_2/oil of 150–200 Nm^3/kL for light gas oil and 250–500 Nm^3/kL for heavy gas oil. Thereafter, both are treated in the same separation unit. Milder treatment conditions may be selected for heavy gas oil by using the following method: The light gas oil, which is not prone to colorization, is subjected to ultra deep desulfurization at high temperature over 360 °C down to 5 wtppm or less, and the heavy gas oil is treated under milder conditions down to about 30 wtppm [34]. In cases where the existing equipment of the HDS unit is to be modified, the existing reactor may be used for the desulfurization of light gas oil, while the relatively small quantity of heavy gas oil may be treated in a newly installed reactor. The increase in pressure drop and the increase in compressor load can be mitigated in this way, providing an opportunity for selecting a more economic path for equipment modification.

The integration with VGO HDS unit or a hydrocracking unit may expand the operation range of the diesel oil desulfurization unit, enabling efficient production of ultra low sulfur diesel. The above system was evaluated more quantitatively in the case of producing ultra low sulfur diesel by using an existing HDS unit [35].

9.3.7 *Developing New Processes*

1. Adsorption process

In advance of commercial scale unit results from its Borger refinery application of Phillips' S-Zorb process, diesel sulfur removal technology has been demonstrated in a small-scale test unit to produce diesel feed with less than 10 wtppm sulfur [36]. Diesel feeds ranged from 500 to 3,300 wtppm sulfur containing a mixture of hydrotreated and straight-run gas oil and LCO. Mixing was determined to evaluate the process requirements if off-road diesels were specified at the same sulfur levels as on-road diesel, and if an existing diesel HDS were shut down when S-Zorb™ was installed. Figure 9.16 shows a schematic flow diagram of the S-Zorb™ process.

In each situation, net H_2 consumption is reduced, in comparison with conventional HDS, because hydrogen is not used for desulfurization. In addition, the unit operates in a temperature region 38 to 66 °C above conventional HDS (371 to 454 °C), and at lower pressures

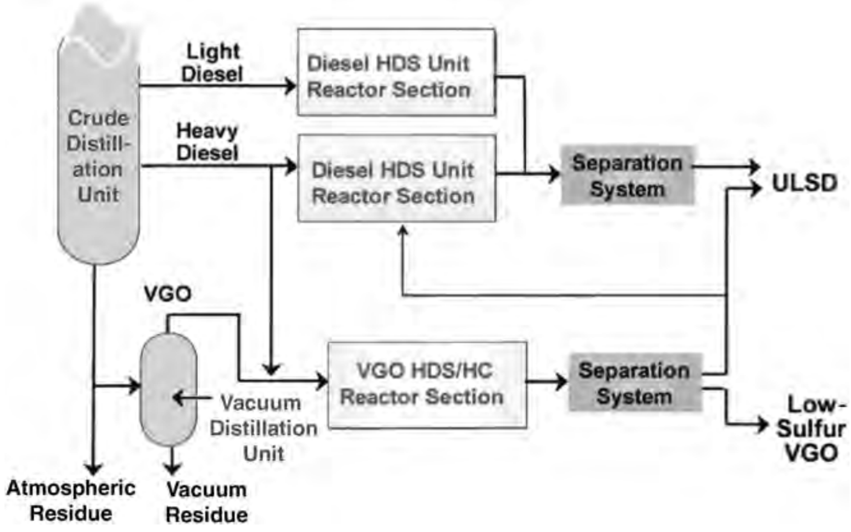


Figure 9.15—A conceptual flow scheme for HDS of undercut feedstock [34]. Reprinted with permission.

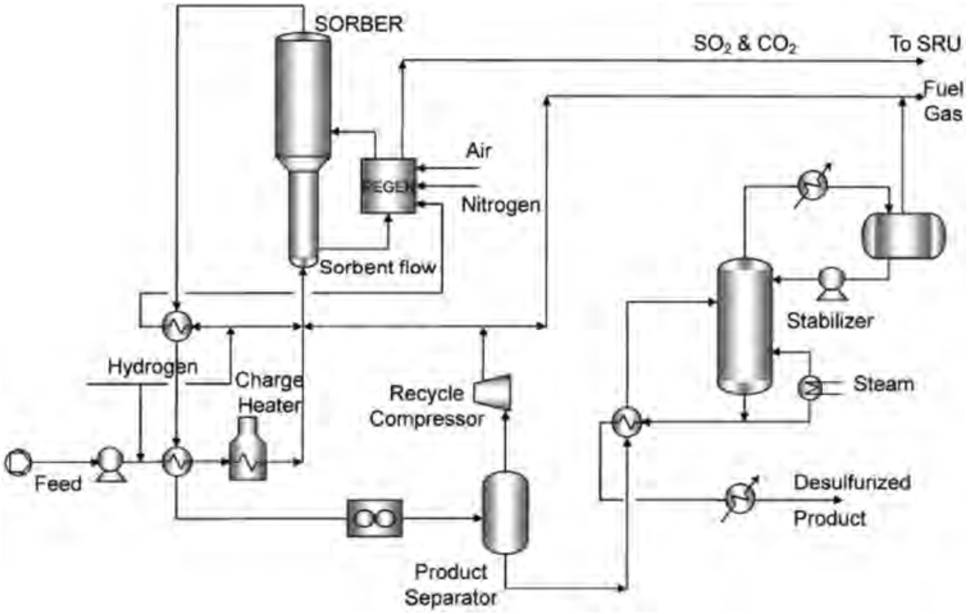


Figure 9.16—A schematic flow diagram of the S-Zorb™ process [36]. Reprinted with permission.

(up to 3.5 Mpa), and with minimum hydrogen partial pressure. Under these conditions, 2- and 3-ring aromatics are in equilibrium with their partially saturated counterparts, rather than being saturated, as they would be in conventional packed bed HDS. Net hydrogen consumption without untreated LCO in the feed blend can be essentially zero.

Sulfur is removed by the partially sulfided adsorbent with no requirement for hydrogen consumption other than the minimum amount required to replace the sulfur in the bonds with carbon molecules. This is a ring-opening reaction as sulfur is removed from the thiophene molecules, and cetane improvement results.

Hydrogen is necessary to stabilize the catalyst system and to partially saturate the nonequilibrium aromatics in untreated LCO. Sulfur is removed from the diesel by the adsorbent, not H_2. Of course any cetane upgrading that may be achieved by aromatics saturation is also eliminated.

2. Oxidative process
Unipure, working with ChevronTexaco and Mustang Engineering, has developed an effective process for oxidation of sulfur compounds in diesel fuels [37]. Using hydrogen peroxide and a liquid phase catalyst, sulfur-containing hydrocarbons are converted to sulfones that are adsorbed in an alumina bed, then recovered in methanol. Reaction proceeds with a mechanism as shown in Figure 9.17.

Other than treating the sulfones, which could be done at another location, no hydrogen or hydroprocessing is required for this process. Thus, the process could be located at a pipeline terminal and used to process interface materials that do not meet ultra-low sulfur diesel specifications.

Another approach is to process current 500 wtppm sulfur diesel to produce ultra-low sulfur diesel (ULSD). The oxidation process is selective toward reactions with the highly substituted dibenzothiophene, and thus complements the existing fixed bed HDS processes.

Stanislaus et al. [38] have reviewed the recent advances in the ULSD production. An overview of recent approaches to deep desulfurization for ultraclean fuels was provided by Song [39]. Whitehurst et al. [40] discussed the challenges for HDS of polyaromatic sulfur compound, and Babich and Moulijn [41] reviewed the science and technology of novel processes for deep desulfurization of refinery streams.

Figure 9.17—A reaction mechanism for oxidative desulfurization.

9.4 ADVANCES IN VGO HYDROPROCESSING

There are principally three major fixed-bed processes in VGO hydroprocessing: FCC-pretreating (FCC-PT), mild hydrocracking (MHC), and hydrocracking (HC). This section focuses on the latest advances in hydroprocessing of VGO.

FCC-PT is a trickle-bed hydrotreating process to reduce VGO sulfur initially from 1.0–3.0 wt % in the feed to typically 0.1–0.3 wt % range in the product; consequently, a HDS conversion of approximately 90 % is expected. The primary objective of FCC-PT is to produce a high-quality VGO feedstock having a higher hydrogen content and lower sulfur content for the subsequent FCC unit while finally reducing the sulfur oxide emission from the refinery. The process normally applies an operating temperature of 330–400°C, LHSV of 0.3–2.0 h^{-1}, hydrogen partial pressure of 35–100 bar, inlet hydrogen rate of 150–500 nl/litre and hydrogen consumption of 40–120 nl/litre The MHC process option is typically applied to a low to medium conversion (<50 %) HC process, operating at a relatively moderate pressure as an FCC-PT at 35–100 bar, and often using a start-of-run temperature of 380°C or higher. The main objective of MHC process is to gain more naphtha and distillate of lower sulfur content from the VGO hydrotreater while producing a high-quality FCC feedstock.

The latest VGO hydrotreating technologies developed by the licensors are summarized in Table 9.3. One of the notable process developments is UOP's APCU (advanced partial conversion unicracking) technology. The process produces a high-quality FCC feedstock, in an MHC type of operation, while simultaneously producing a higher cetane ULSD through hydrotreating the enhanced hot separator

TABLE 9.3—VGO Hydrotreating and MHC Processes from Various Licensors

Process	Licensor	Pressure	Catalyst	Characteristics
Go-fining [42]	ExxonMobil	Wide range	Unspecified	VGO hydrotreating with a variety of feeds of virgin, thermally cracked, cat cycle, and deasphalted oils for sulfur and nitrogen removal, conversion to clean products (MHC), and better-quality FCC feedstock. Advanced Go-fining/FCC modeling, design flexibility around feed fouling through proprietary internal by-pass design and by-passable guard reactor.
Unionfining/APCU [43,44]	UOP	< 100 bar	Specific pretreating and unicracking catalysts	APCU at a moderate conversion of 20–50 % for ULSD and FCC feedstock. High-sulfur feeds of VGO and HCGO are treated with high activity pretreat catalyst and distillate-selective Unicracking catalyst. The distillate product is separated via an EHS, subsequently hydrotreated in an APCU finishing reactor for high-cetane ULSD.
ISOCRACKING [45–47]	CLG	Wide range	Unspecified	ISOCRACKING or optimized partial conversion. ISOCRACKING by SSOT, single-stage recycle (SSREC), or TSR. SSOT used to produce high-quality FCC feedstock or high viscosity index (VI) basestock, and SSREC and TSR for clean naphtha and distillate fuels. SSOT can be revamped to partial or full recycle TSR using reverse-stage ISOCRACKING with an additional smaller reactor.
CFHT/HyC-10 [48,49]	Axens/IFP	Wide range	NiMo-Alumina of HR548 and HR568 NiW-ASA of HDK776	Once-through VGO hydrotreating (CFHT) or partial hydrocracking MHC process (HyC-10) to produce low-sulfur FCC feedstock while producing ULSD in the downstream polishing reactor section. Applicable specific EquiFlow distributor and quenching device.
IsoTherming [50,51]	DuPont	Wide range	Applicable conventional hydrotreating or MHC catalysts	Diesel/VGO hydrotreating or MHC using liquid phase reactor in which hydrogen is dissolved in liquid, and no gas passes through catalyst-bed. Hydrogen is supplied by recycling liquid product, and the adiabatic temperature rise is much less (isothermal) than trickle-bed. Cost is expected to be lower due to lack of recycle compressor and high-pressure vessels.
Syn Technology [52–54]	ABB Lummus, Criterion and SGS	Typically 35–70 bar	Specialized SynCat from Criterion	Hydroprocessing middle distillates including coker and visbreaker gasoils, and heavier feeds in the co-current and/or counter-current reactors with an interstage HP stripper to remove H_2S, NH_3, and light-ends from the liquid. Syn technology includes SynHDS for deep HDS, SynShift for cetane improvement and density reduction, SynSat for aromatic saturation, and SynFlow for cold flow improvement.

(EHS) product in the APCU finishing reactor in the same high-pressure loop. Chevron's ISOCRACKING™ process technology provides a CFHT (cat-feed hydrotreating) and MHC process approach through a single-stage once-through (SSOT) configuration. They claim that an SSOT unit can be revamped to a partial or full recycle mode in two-stage recycle (TSR) configuration by applying a Reverse Stage ISOCRACKING™ system with an additional small reactor. Axens/IFP developed the MHC process of HyC-10, wherein the product distillate from the downstream distillation column is fed to a polishing hydrotreater with fresh hydrogen for ULSD production. DuPont has developed IsoTherming process in which the hydrogen is dissolved in a liquid and no gas passes through the catalytic bed. Consequently, the adiabatic temperature rise observed is much less (more like isothermal).

The latest noticeable progress in the VGO hydrotreating involves the following three technology elements:

1. Catalytic technology in guard-bed and main-bed
2. Reactor internals of distributor tray and quenching devices
3. New reactor concepts to maximize utilization of catalytic activity

The guard-bed catalyst technology in the reactor top layer is very important to protect the main-bed catalyst against fouling and catalyst poisons for optimizing the expected activity and cycle length. The guard-bed needs to collect the particulates to remove potential hot spot and pressure buildup, and also to protect the main-bed catalyst from the various poisonous contaminants, e.g., Ni, V, Si, As, Na, Ca, and Fe. The catalytic grading and contaminant control technologies have been extensively improved in the last decade so as to fully utilize the improved performance of the main-bed catalytic technology. The catalytic size and shape grading used in a given catalyst loading has been particularly addressed and improved to effectively trap particulates in addition to catalytic activity grading technology for multiple contaminants trapping. Advances in main-bed catalytic technology are also remarkable. The catalytic activities have been improved 5- to 10-fold in the last decades compared to the classic technologies used in the 1960s, as illustrated in Figure 9.18. Thus, the advances of catalytic technologies in the guard-bed and main-bed are significant, and they are described in detail in Chapter 10.

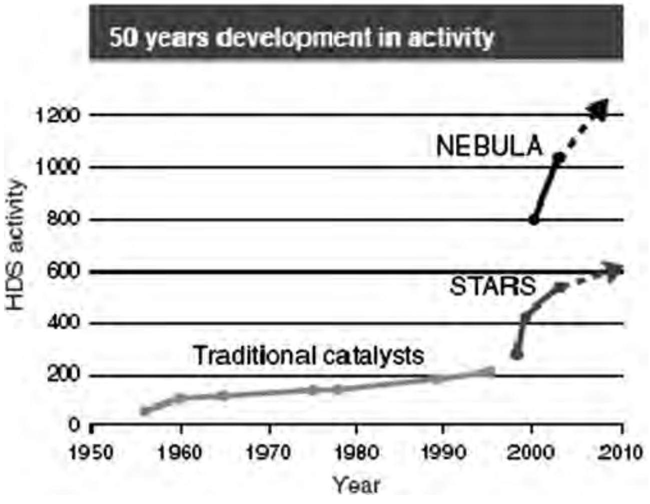


Figure 9.18—History of hydroprocessing catalytic activity [55].

In line with the catalytic activity enhancement described above, the importance of reactor internals has gradually been recognized to fully utilize the credit provided by increased catalytic performance. The licensors have paid considerable attention to developing better reactor internals especially since the 1990s. One of the commercially available unique inventions is Albemarle's PLEX distributor device technology [55]. The PLEX technology includes D-PLEX (liquid distribution device), M-PLEX (liquid/liquid or gas/liquid mixer), and Q-PLEX (gas/liquid quench and mixing device), where the innovation involves:

- Enhanced liquid distribution uniformity by minimizing liquid entrainment present in the gas phase through distribution-unit redesign
- Superior distribution at a wider range of liquid flows, which enables operation at liquid flow rates as low as 20 % of the design rate
- Improved fouling resistance with additional capacity for scale collection

The quench mixer, comprising sub-mixers in series with equilibration after each sub-mixing, achieves highly efficient mixing of the fluids and gases. As a result, the height of Q-PLEX distributor device becomes significantly compacted in relation to other commercial devices, as summarized in Figure 9.19. Thus, PLEX technology improves the liquid/liquid and liquid/gas mixing in a more compact device, which enables a smaller reactor or higher catalyst charge for higher performance.

The distribution trays in use commercially are typically either perforated, chimney-type, or bubble-cap trays. In the last decades, the licensors have developed several state-of-the-art distribution devices. The fundamentals in the device improvement include uniform volumetric and thermal distribution of liquid and gas in the radial direction, inter- and intramixing, quench performance, and fouling resistance. Various companies have been involved in the hardware modification and unique distribution devices have been developed. UOP invented a specific two-phase distribution device using variable vapor-flow and liquid-flow rates through given upflow channels to create a better mixing performance [56]. They also patented a specific reactor mixer/distributor of three circular trays and mixing chamber for better quench liquid mixing [57]. ExxonMobil's improved Spider Vortex distributor technology relies on baffles contained within the mixing chamber [58]. Chevron developed their own distributor and mixing devices involving turbulent and circulating flow regimes [59]. The key technology characteristics of these latest developments are summarized in Table 9.4.

Last, but not least, new reactor concepts are worthy of discussion. Since the 1990s when low sulfur regulation was enforced on a global scale, many researchers then started to look more deeply into the HDS, HDN (hydrodenitrogenation), and HDA (hydrodealkylation) reactions on the molecular basis, to achieve an in-depth understanding of the reaction chemistry so as to enhance novel catalytic and process ideas. Mochida has conducted intensive research on the inhibition effects of H_2S and NH_3 on HDS and HDN reactions. His group has revealed that inhibition effects for desulfurization of sterically hindered alkyl-substituted sulfur compounds were much more pronounced than for nonsterically hindered and nonalkyl-substituted compounds. Moreover, the HG (HYD) active site was much

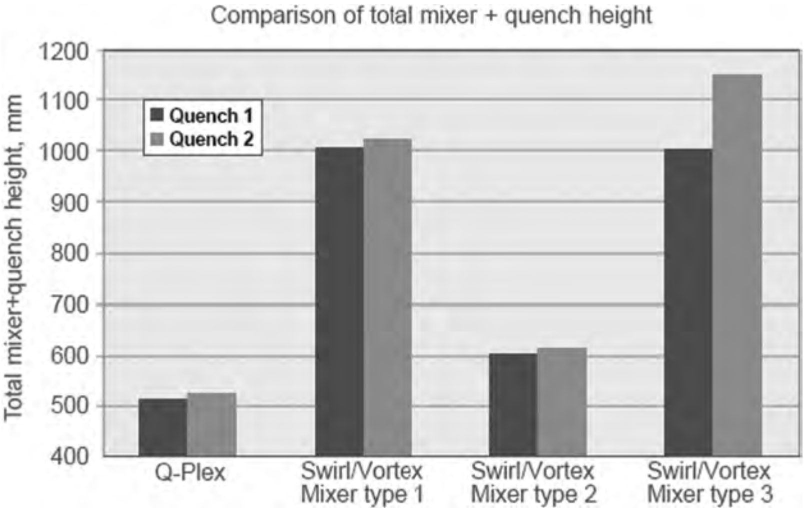


Figure 9.19—Device height to achieve same degree of mixing [55].

TABLE 9.4—Latest Developments of Concurrent Downflow Distribution Devices

Company	Invention/Product	Characteristics
Albemarle [55]	PLEX distributor device	PLEX technology of enhanced liquid-distribution uniformity by distribution unit redesign, superior distribution at wider liquid flow range to allow a liquid rate as low as 20 % of design rate, and improved fouling resistance. Q-PLEX applies a specific swirl mixer for enhanced performance and lower device height.
UOP [56]	Two-phase distribution apparatus and process	A plurality of distributor assemblies have fluid flow-paths with different resistance to liquid flow by having vapor inlets of at least two different sizes located on different assembly.
UOP [57]	Hydroprocessing reactor / mixer/distributor	A quench fluid and downward-flowing liquid mixed by an apparatus comprising three circular trays and mixing chamber. Quench fluid and liquid are admixed in a mixing chamber, a first distributor tray, and then second tray of a plurality of mixing caps.
ExxonMobil [58]	Distributing system for downflow reactors	A distributor tray in multiple-bed downflow reactor comprising a collection tray, mixing chamber, a first rough distributor tray, and a second final distributor tray of a plurality of open-topped tubes with a side aperture.
Chevron [59]	Distributor assembly for multi-bed downflow catalytic reactors	The distributor assembly comprising a centrally located mixing chamber, and an annular collecting and mixing trough surrounding the mixing chamber. The mixing chamber mixes the liquid raining down from the catalyst bed with a quench liquid and gas by circulating through the trough of turbulent and circulating flow pattern, which later goes to the distributor tray.
M. Muller [60]	Mixing device for two-phase concurrent vessels	The fluids flow through horizontal mixing box having at least one mixing orifice for the heat and mass transfer. Each mixing orifice is followed by structure that divides the process stream into lower velocity streams, whereby turbulent flow conditions are generated for heat and mass transfer.
Fluor [61]	Reactor distribution and quench zone mixing apparatus	A quench zone mixing apparatus of low vertical height and improved mixing efficiency, with a swirl chamber, a rough distribution network, and a distribution apparatus. In swirl chamber, reactant and quench fluids are mixed by swirl action, and the mixture goes to rough distributor tray, and final tray of a number of bubble caps for symmetrical fluid distribution.
Shell [62]	Multi-bed downflow reactor	Multi-bed downflow reactor comprising a) at least one device for injecting liquid or gas for temperature control, b) liquid collecting tray, c) compartment to receive gas, d) mixing zone of gas and liquid, and e) distributor tray.
Haldor Topsoe [63,64]	Two-phase downflow liquid distribution device (vapor lift dist. tray)	Two-phase downflow distribution tray named “Vapor Lift Distribution Tray.” The tray has perforated evenly spaced holes across the surface with an inverted U-shaped device of “Vapor Lift Tube.” The Vapor Lift Tube has similar advantage to bubble-cap device of better gas-liquid mixing and has more dripping points due to a smaller footprint for the improved performance.

more hindered than the Direct DeSulfurization site (DDS) [65–67]. Mochida then developed better catalysts showing much less inhibition via optimization of the catalytic Brönsted acid function and metal active sites for the first sour and the second sweet conditions in the two-stage hydrotreating process [67,68]. Yang [69] and Nakamura [70] reported that a CoMo-alumina catalyst was inhibited more by NH_3, whereas NiMo-alumina is affected more by H_2S. Egorova and Prins explained the adsorption of amine compounds perpendicular to the catalyst surface hinders π adsorption of DBT and 4,6-DMDBT and thus the HYD pathway was more inhibited, whereas the occupation of sulfur vacancies by H_2S inhibits the DDS pathway [71]. All literature cited addressed that the inhibition effect of H_2S and NH_3 is significant, and their removal should dramatically increase the HDS and HDN reaction rates.

One of the noticeable process technologies to minimize inhibition effects is Syn Technology licensed by ABB Lummus, Criterion and SGS, as summarized in Table 9.3. The process was developed for middle distillates, including coker and visbreaker gasoils, and even heavier feeds in co-current and/or counter-current reactors with an interstage HP stripper. The feed is hydrotreated in the first co-current reactor. H_2S, NH_3, and light-ends are stripped out from the liquid in the subsequent interstage HP Stripper, and the effluent is fed to the second reactor, which can be either of co-current or counter-current flow with fresh hydrogen. This system looks to minimize the H_2S/NH_3 inhibition in the second reactor. This is particularly the case in the bottom of the counter-current reactor, which is an ideal environment for the remaining refractory sulfur and nitrogen compounds to be removed. The licensor claimed different types of technologies, i.e., SynHDS for deep HDS, SynShift for cetane improvement and density reduction, SynSat for aromatic saturation, and SynFlow for cold flow improvement, by applying specific catalytic technologies.

The multiple-stage hydrotreating process with an interstage stripper or reverse treat gas-flow technology has been developed by several licensors. UOP has developed process innovations with back-staged series flow reactors and EHS technologies [43]. UOP's HyCycle™ Back-Staged reactor configuration, wherein fresh hydrogen is routed first to the hydrocracking reactor and then to a hydrotreating reactor, uses a low per-pass conversion to minimize the undesired cracking reaction, and produce more high-cetane distillate with less hydrogen consumption. This process allows a 25 % lower pressure and a higher space velocity without sacrificing catalyst life and distillate quality. Chevron's Single Stage Reverse Staging (SSRS) ISOCRACKING hydroprocesses a recycled unconverted-bottom with fresh hydrogen in the second reactor to produce high-quality diesel products and achieve higher conversion with difficult feeds or reduced reactor volume [72]. Chevron also patented a hydroprocessing method having at least two stages, wherein the second stage reactor includes flash separation zones in between the beds to strip out the treatgas and then introduce the effluent back with fresh hydrogen into the next bed [73].

Sie and De Vries invented a hydrotreating reactor in which fresh hydrogen is introduced from the top of the reactor, and the fresh feed inlet and product outlet are positioned at the middle of the reactor [74]. The process allows fresh feed desulfurization with high H_2S and NH_3 treat-gas first at the lower half of the reactor, and then the liquid is separated from the gases and is fed to the top of the reactor with fresh hydrogen. Finally, the product is taken out of the middle of the reactor just above the feed inlet. This invention allows for reactions in the upper bed with fresh hydrogen to remove refractory sulfur effectively. Mochida proposed a new, unique reactor concept with both co-current and counter-current flows in a reactor, as illustrated in Figure 9.20 [68]. The feed is introduced to an intermediate position of the reactor, and the hydrogen is introduced at the bottom of the reactor in an upflow mode. The lighter feed of easily removable sulfur compounds is drawn upward with the upcoming treatgas in the upflow co-current mode, and the heavier portion, containing the refractory sulfur, then flows downward in a counter-current mode with the upflow hydrogen. Mochida also proposed suitable catalysts for each of the co-current and counter-current beds to offset inhibition of HDS reactions.

Consequently, various new reactor concepts have been developed by several groups in order to minimize the H_2S/NH_3 inhibition effect and maximize the reactor performance to produce high-quality products with reduced capital investment. It is believed that such new reactor process technology, in association with an in-depth understanding of molecular chemistry, should greatly contribute to overall process performance improvement and the advances of catalytic reactor technologies.

9.5 ADVANCES IN SOLID ALKYLATION PROCESS FOR MOTOR FUEL ALKYLATE

Alkylate, the gasoline boiling range product of the reaction of isobutane with light olefins (C_3–C_5), is an ideal gasoline blend stock due to its high octane, low vapor pressure, absence of toxic aromatics or reactive olefins, low sulfur, and paraffinic nature. Worldwide gasoline specifications continue to force reductions in olefins, Reid vapor pressure, aromatics, sulfur, and benzene. Many refiners would like to introduce alkylation units, which are well-established hydrofluoric (HF) and sulfuric (H_2SO_4) liquid acid catalyzed alkylation processes, in order to meet severe gasoline specifications. However, because both of these processes use corrosive and potentially hazardous HF and H_2SO_4 liquid acid, many researchers have tried to develop solid acid catalysts as safer and more environmentally benign technologies.

Some innovative processes coupled with solid acid catalysts to produce a paraffinic alkylate equivalent to the product from liquid acid catalysts at a cost comparable to traditional liquid acid alkylation technologies have been developed and have resulted in commercial realization. The Alkylene™ Process, the Alkyclean™ Process, the Fixed-Bed Alkylation (FBA™), and ExSact™ Process apply unique reactor systems as shown in Table 9.5.

The Alkylene™ process applies the transport riser reactor coupled with a reactivation vessel as in an FCC process as shown in Figure 9.21 [75]. The transport riser reactor is used to reduce the degradation of alkylate product through side reactions by short contact time and the catalyst deactivation per pass by minimizing the deposition of heavy hydrocarbons on the catalyst.

Olefin feed is mixed with isobutane and is injected into the bottom of the riser where it contacts with freshly reactivated catalyst recycled from the regeneration vessel. The reactants and catalyst flow up the riser where the

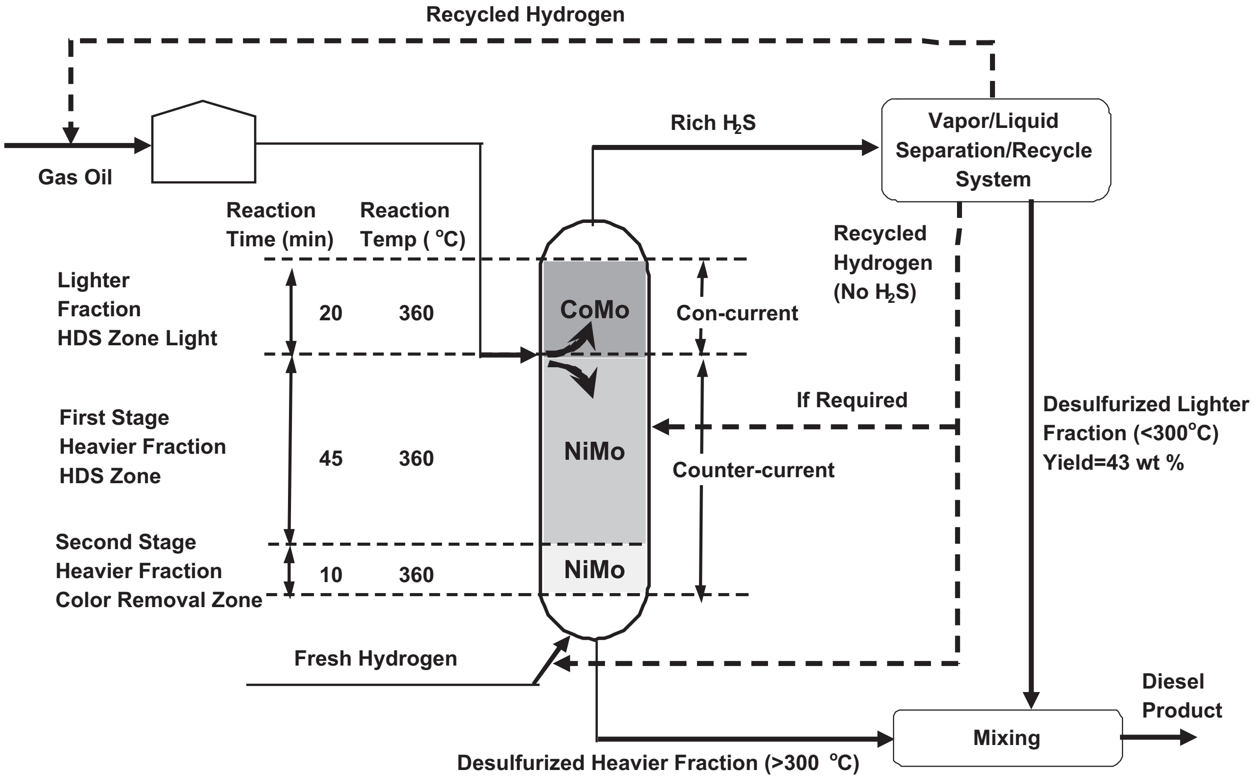


Figure 9.20—New reactor design for deep HDS by Mochida [68]. Reproduced with permission.

TABLE 9.5—Solid Acid Catalyst Alkylation Processes

Process	Licensor	Reactor Type
Alkylene™	UOP	FCC Type
Alkyclean™	ABB Lummus Global	Swing Reactor
	Akzo Nobel Catalysts	
FBA™	Topsoe	Fixed Bed
ExSact™	Exelus	Swing Reactor

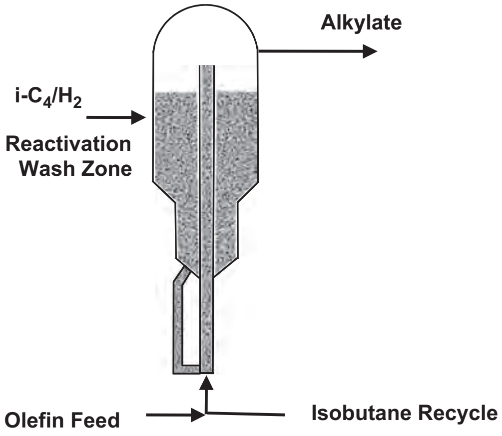


Figure 9.21—Reactor of the Alkylene™ process (modified after [75]).

alkylation reaction proceeds. Reactor effluent, which is separated from the catalyst by gravity at the outlet of the riser, flows out of the top of the reactor to the fractionation section, and the catalyst falls by gravity into the regeneration vessel, where it is reactivated by contacting with H_2 adsorbed in isobutene, so the heavy hydrocarbons are hydrogenated and desorbed from the catalyst. With the riser, the feed isobutane to olefin (I/O) ratio could be kept close to that used in traditional liquid acid alkylation.

A fixed-bed reactor of the FBA™ process is shown in Figure 9.22 [76]. Olefin feed is mixed with both isobutane and part of the reactor effluent and is introduced into the top of the reactor. Recycling part of reactor effluent to the reactor inlet has the two advantages of a reduction of the temperature increase in the adiabatic reactor by decreasing the olefin concentration and the adjustment of the reactor inlet temperature by cooling of the reactor effluent. The typical external isobutane/olefin ratio is 10. The olefins are converted into alkylate by a liquid superacid catalyst adsorbed on a solid support in the fixed-bed reactor system. The FBA™ process applies a unique fixed-bed reactor system with a liquid superacid catalyst adsorbed on a solid support and confined within a mobile, well-defined catalyst zone. The reactor effluent is split into two streams, and the net reactor effluent is sent to the effluent treatment section where traces of dissolved acid and moisture contained in the reactor effluent are completely removed. The acid-free net reactor effluent is sent to the fractionation section and the removed acid is sent to the acid recovery unit. The acid-soluble oil formed is selectively removed from the reactor system to maintain the catalyst activity and sent

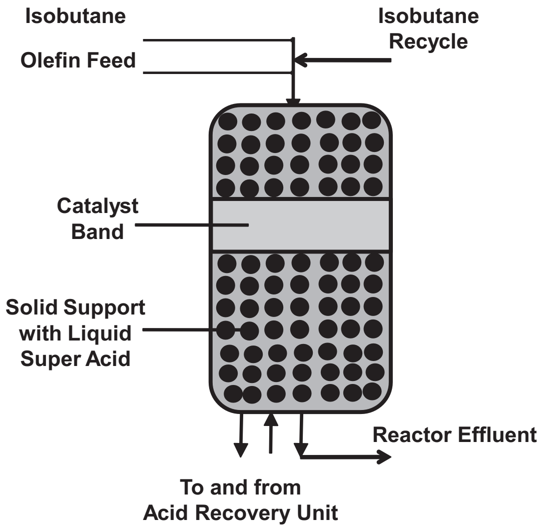


Figure 9.22—Reactor of the FBA™ process (modified after [76]).

to the acid recovery unit. The recovered acid is returned to the reactor section.

The alkylate quality and yield from Alkylene™ is shown in Table 9.6 in comparison with those of traditional sulfuric acid processes. The product qualities of the solid alkylation processes are equal to or slightly better than those of a sulfuric acid process. The capital cost of FBA™ is as much as 15 % lower compared with the sulfuric acid process without on-site spent acid regeneration.

A process flow diagram of the AlkyClean™ process is shown in Figure 9.23 [77]. The process consists of four main sections: feedstock pretreatment, the reactor system, catalyst regeneration, and product distillation The reactor system operates in the liquid phase at a temperature range of 50–90 °C. The extensive refrigeration requirements associated with liquid acid processes are eliminated. The external isobutane/olefin ratio is in the range of 8/1 to 10/1, comparable to the H_2SO_4 process.

A system of multiple reactors enables continuous alkylate production by cyclic operation between periods of alkylation and rejuvenation. The rejuvenation step removes accumulated heavier molecular weight species that lead to catalyst-pore plugging and deactivation. The zeolite catalyst is reactivated by contacting with H_2 adsorbed in liquid-phase isobutane. The two reactors under cyclic operation allow for continuous production of alkylate, and the third reactor operates as an additional swing reactor where the slowly deactivated catalyst during the cycle operation is regenerated in vapor phase with H_2 at a moderate temperature (250 °C).

TABLE 9.6—Comparison of the Alkylate Product Octane and the Economics of the Alkylene Process and the FBA Process with Traditional Liquid Acid Process

		Case 1	Case 2	Case 3[a]	Case 4[b]
		Alkylene	FBA	H_2SO_4	H_2SO_4
C_5 + Alkylate Capacity	BPSD	8,000	6,000	6,000	6,000
C_5 + Alkylate	RONG	95.0	96.1	96.0	96.0
MONG		92.9	93.2	93.1	93.1
(R + M)/2		94.0	94.6	94.5	94.5
Investment	MM US$	2.39[c]	34.00	50.00	40.00
Utilities	US $/bbl	1.74	1.70	1.80	3.10

[a] With on-site regeneration
[b] Without on-site regeneration
[c] US $/bbl

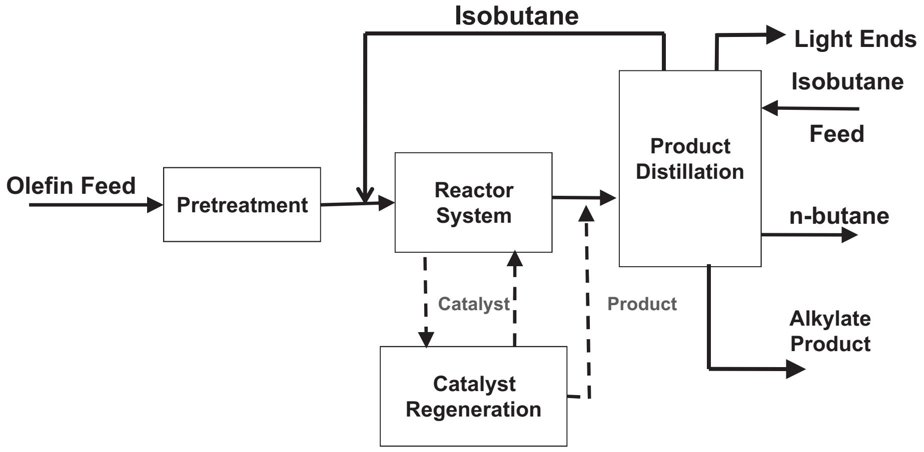


Figure 9.23—Process flow diagram of the AlkyClean™ System (modified after [77]).

When the catalyst and operating conditions are optimized, the RON numbers of the alkylate are as high as 97 to 98. When the temperature is lowered from 65 °C to 55 °C, the RON of the alkylate increases from 97 to 98.1.

Table 9.7 compares the economics of the AlkyClean™ process with the H_2SO_4 acid process.

The investment cost for the AlkyClean™ process is 11.8 % lower than for the H_2SO_4 unit.

A process scheme of the ExSact™ process consists of feed treatment, two multistage fixed-bed reactors with multi olefin feed and a separation section. One reactor is used for reaction, while the other is on catalyst regeneration. Alkylation cycle lengths are between 12 and 24 h, typically 12 h, followed by a 2-h regeneration cycle. Catalyst is regenerated with hydrogen/hydrocarbon mixture at 250 °C. The reactor system operates at a temperature range of 60–90 °C and a pressure of 20 barg. The external isobutane/olefin ratio is in the range of 10/1 to 15/1. Compared with other solid acid catalysts and conventional liquid catalysts processes, the investment cost of the ExSact™ process is considerably lower by greatly simplifying operation and reducing the amount of equipment required. For example, the ExSact™ process requires only two reactors because of the long on-stream cycle time. The noble metal content of the catalyst is largely reduced because of the ability to perform a complete regeneration at 250 °C.

TABLE 9.7—Comparison of the Economics of the FBA Process with the Traditional Liquid Acid Process [78]

		Case 1 Alky Clean	Case 2 H_2SO_4
C_5 + Alkylate Capacity	BPSD	10,000	10,000
C_5 + Alkylate	RONC	96.0	96.0
Investment	MM US $	32.2	36.5

9.6 RESIDUA THERMAL CRACKING—EUREKA PROCESS

The Eureka process is a commercially proven residue thermal cracking process to convert heavy residue to valuable light oil at a high residue conversion similar to that of coking technologies, and to produce petroleum pitch [79,80]. The pitch produced can be handled in its liquid state, which enables the refiners to keep the plant yard clean as well as to charge a liquid pitch to the direct gasification scheme [81]. Sodegaura Refinery of Fuji Oil Company, Ltd. (FOC) commenced the operation of the first commercial plant of the Eureka in 1976 and has been successfully operating it over 30 years.

9.6.1 Process Description

A simplified flow diagram of the Eureka process is presented in Figure 9.24. A wide range of heavy residues including Canadian bitumen and Venezuelan heavy oil can be processed as feedstocks in the process [82].

For processing, the feedstock is preheated to 340 °C and sent to the bottom of the fractionator, where it is combined with recycle oil. The combined feedstock is sent

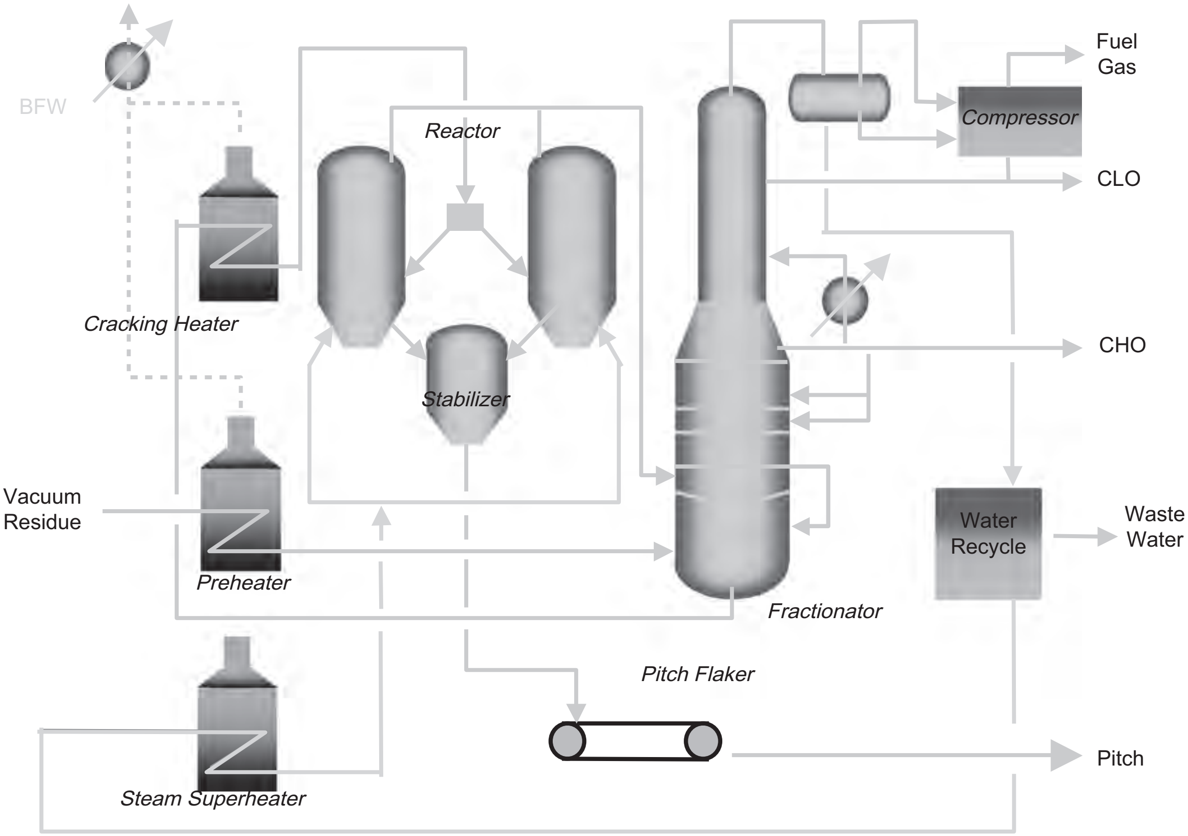


Figure 9.24—A flow diagram for the Eureka process [82]. Reprinted with permission.

to the cracking heater and heated up to 470–490 °C. The heated and partially cracked feed is then supplied to one of the two reactors, which are switched batch-wise in a specified schedule. The cycle time on a given reactor is 3–4 h because of the short reaction time.

In the reactor, both cracking and polycondensation reactions take place in the presence of the injected superheated steam (SHS). The ratio of the SHS to the vapour in the reactor is in the range of 0.2–0.45. The SHS injected into the reactor is not only for supplying a part of the heat of reaction required, but to strip the cracked oil immediately out of the reactor as a light product.

The reaction in the reactor proceeds at 30–80 kPa(g), 400–430 °C, which are lower than those of the other thermal cracking processes. These mild reaction conditions at the SHS injection give lower cracked gas yield as well. The pitch reached to the specified softening point is blown down to the stabilizer and then continuously withdrawn to the pitch flaker. In case of the liquid pitch gasification, the pitch is transferred directly to the gasifier from the bottom of the stabilizer bypassing the pitch flaker.

From the reactor overhead, cracked gas and cracked oil vapour along with the steam are transferred to the fractionator, where cracked gas, cracked light oil (CLO), and cracked heavy oil (CHO) are obtained. As the produced gas yield including LPG fraction is less than the fuel required in the Eureka unit, LPG recovery section is not necessary, which is usually installed in coking processes to recover the LPG from the large amount of cracked gas. The cracked gas is internally utilized as a fuel for the Eureka unit, after sweetening the compressed gas. The CLO and CHO are usually hydrotreated to stabilize olefinic molecules, after rundown from the Eureka unit.

9.6.2 Advantages of the Eureka Process

The Eureka process has design advantages including low pressure, short reaction time, and steam injection, as described in the previous section. The advanced design allows the following advantages as key process performances.

High cracked oil, low gas, and low-pitch yields: High conversions of residua are achieved by the Eureka process under mild reaction conditions. This also means to reduce the pitch yield, which is at a similar level to that of the coking technologies. The Eureka could attain the lowest gas yield and the highest liquid product yield among the residue thermal cracking technologies.

Good product quality with less overcracking and polycondensation reactions: The Eureka reaction design depresses a formation of polycondensed molecules in the distillates; thus the cracked distillates are easily hydrotreated. It can moderate the reaction severity in the downstream hydrotreating and lead to high-quality distillate products.

Two years of continuous operation provided by extending decoking cycle of reactor: Steam injection under the low pressure in the reactor makes the cracked oil immediately vaporized from cracked residue. Thus, the cracked residue stays homogenous liquid, highly aromatic without light oil, and stable with low propensity for coking reaction. As a result, 2 years continuous operation is achieved without decoking the reactors.

Properties and use of liquid pitch: The homogenous and stable liquid pitch is withdrawn from the reactor section and stably transferred to pitch flakers by pipelines. When integrating the Eureka process with a gasification process, the hot liquid pitch, as it is, is transferred and directly charged to the gasification process, and can be diluted with distillates to adjust a viscosity specified for the gasification burners.

The pitch from the Eureka process that can be transferred as liquid at the rundown has stable properties, high ratio of hydrogen to carbon compared with a petroleum coke, high heating value, high volatile matter content, a high Hardgrove Grindability Index, a high softening point, and better compatibility to coal. Characteristics of the Eureka pitch are presented in Table 9.8.

The Eureka pitch can be utilized for the following applications.

1. **Binder pitch:** The Eureka pitch can be used as a binder for a metallurgical coke. The binder enables the steel industry to utilize noncoking coal as an alternative of expensive hard coking coal, thus to expand and optimize its selection of coal blends. The pitch produced in the FOC's Eureka unit is mainly utilized as a binder.
2. **Boiler fuel:** Another practical utilization of the pitch was developed for a boiler fuel. Existing boilers can be applied in solid pitch burning with minor modifications, due to the high heating value, high volatile matter, and high Hardgrove index (fragile) of the Eureka pitch. FOC's captive boiler burns the solid pitch for their utility supply.
3. **Gasifier feed:** For gasification, the liquid pitch can be charged directly to the gasifier [82]. A facility for liquid-charge gasification costs less than that for solid-charge gasification. Further, high H/C ratio of the Eureka pitch leads to more efficient gasification than that of petroleum coke.

9.6.3 Applications of the Eureka Process

The Eureka process can be widely applied in the residue conversion installed in a refinery and now expanded to

TABLE 9.8—Typical Pitch Properties

Properties	Unit	Pitch
Density	g/cm^3	1.20
Softening point[a]	°C	225
Volatile matter	% (mass)	40
Heating value	kcal/kg	8,800–9,200
Hardgrove index	–	150–170
Solvent insolubles		
n-Heptane Ins.	% (mass)	76
Benzene Ins.	ditto	50
Quinoline Ins.	ditto	15
H/C (atomic ratio)		0.80

[a] Ring and ball method.

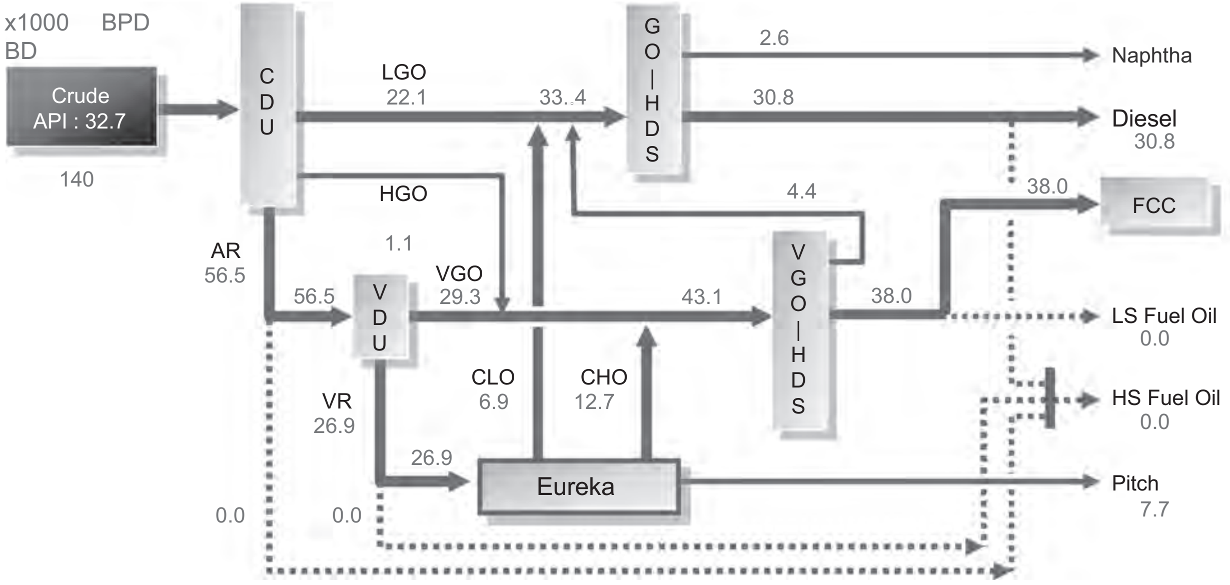


Figure 9.25—A residue upgrading scheme with Eureka.

TABLE 9.9—Impacts of Residue Upgrading in Refinery: Yield Comparison, with and without Eureka Scheme, % (vol.) on Crude

	Scheme with Eureka	Scheme without Eureka	Increments
LPG	2.7	2.7	0
Naphtha	22.2	20.3	+1.9
Jet fuel	19.3	19.3	0
Diesel	22.0	4.2	+17.8
FCC feed (LSFO)	27.2	20.9	+6.3
HSFO	0.0	31.4	-31.4
Pitch	5.5	–	+5.5

upgrade the unconventional heavy oil to produce synthetic crude. Some examples are given below.

The Eureka unit is operating in the Sodegaura Refinery to convert the heavy residue to the distillate products and to produce the pitch which is mostly shipped to the steel industry for use as the binder, and the remainder is used as a boiler fuel in the refinery. Figure 9.25 presents a simplified block flow diagram of the Sodegaura Refinery, and Table 9.9 summarizes the impact of installation of Eureka on the refinery product slate toward zero high sulfur fuel oil (HSFO) production.

An example of upgrader for Canadian Athabasca Bitumen is presented in Figure 9.26. In a heavy oil upgrader, one of the objectives is to maximize the liquid product yield. Table 9.10 represents test results in the Eureka pilot plant indicating that the pitch yield is significantly reduced by the SHS injection.

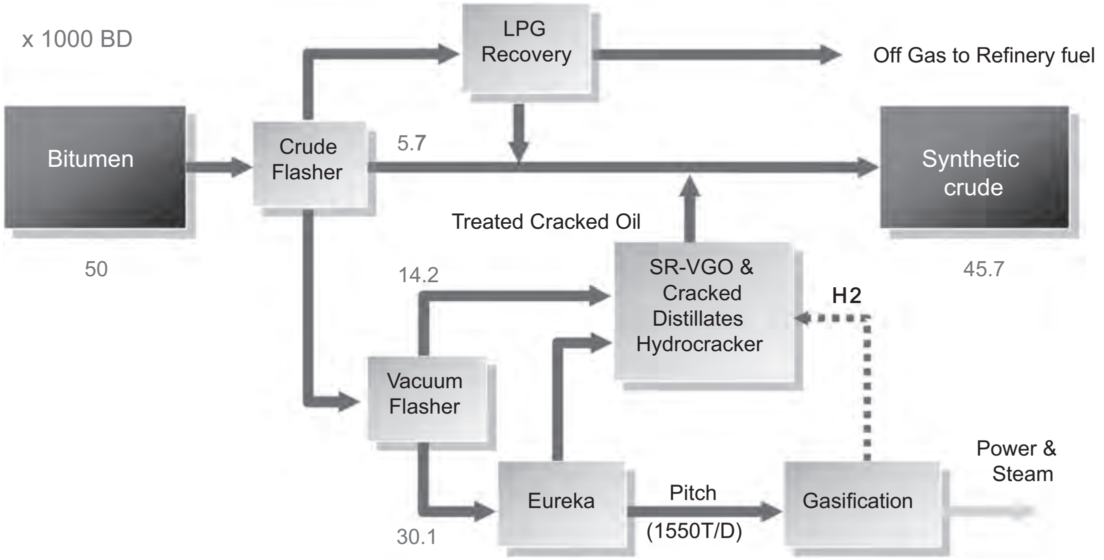


Figure 9.26—A bitumen upgrader with Eureka.

TABLE 9.10—Product Yield of Eureka for Athabasca Bitumen VR

		Low SHS case	High SHS case
Cracked Gas	(C4 minus)	5.0	4.6
Naphtha	(C5-190°C)	7.3	7.5
Middle Distillate	(190–360°C)	20.8	20.1
VGO	(360°C plus)	29.4	35.8
Pitch		37.5	32.0

SHS=superheated steam.

9.7 INTEGRATED PROCESSES: THE DEVELOPMENT OF ENERGY SHARING IN INDUSTRIAL AREAS OF JAPAN WITH PINCH TECHNOLOGY

In recent years, there has been a common understanding in Japan that there is little room for further energy reduction in major industrial fields such as oil refining and petrochemicals. However, our recent studies have determined that despite the very high efficiency of the individual sites in a complex, the potential exists for large energy savings by area-wide energy sharing. Area-wide sharing would make the best use of energy across a large industrial area by utilizing surplus heat from one or more sites to provide energy for the others. As a result of the study, a successful energy sharing project was developed between two sites in one of the major industrial areas in Japan.

In the 1980s, Linnhoff et al. [83] introduced the concept of "target before design" using pinch technology for the design of individual processes. Pinch technology for Heat Exchanger Network (HEN) design was developed by Linnhoff and Hindmarsh [84]. Later, a HEN retrofit framework was established based on the "process pinch" [85,86] and "network pinch" [87] concepts. Over time, pinch technology has been applied to increasingly large and complex sites, facilitated by the development of a variety of tools and techniques to enhance the methodology and simplify analysis.

Pinch technology had been applied to a single site to analyze the process system and the energy system, whereas area-wide pinch technology enables an entire industrial area to be analyzed. The latter consists of two existing analysis techniques: "Site Source Sink Profile (SSSP) analysis technique" [88,89], and "R-curve analysis technique" [90–92].

Supported by the New Energy and Industrial Technology Development Organization (NEDO), an affiliated organization of Japan's Ministry of Economy, Trade and Industry, a 3-year research project was started in fiscal 2000, which was the first study to apply area-wide pinch technology analysis to a large industrial area in Japan.

9.7.1 Area-Wide Pinch Technology

The SSSP analysis technique uses the data obtained from heat exchangers, such as steam heaters, reboilers, steam generators, and condensers, etc., on the interface between the energy system and the process system in a single site and analyzes the energy-saving potential by optimal effective utilization with the best heat recovery.

The R-curve analysis technique uses the data of an energy system, such as boilers, gas turbines, steam turbines, steam headers, and steam users in a single site. By using this technique, the energy-saving potential can be analyzed by introducing the optimal gas turbine combined system.

Figure 9.27 shows the procedure for applying area-wide pinch technology to an industrial area composed of multiple sites. Initially, the operation data for the SSSP analysis and the R-curve analysis are collected from all the sites in the industrial area, which are then analyzed with respect to each single site by the SSSP analysis and the R-curve analysis. The results of the analyses determine which site has the highest performance and which site has the lowest performance from the point of view of energy saving. The data are then combined and condensed into one virtual site and then again analyzed by the SSSP and the R-curve analyses, which eventually evaluate the total energy saving potential in an industrial area composed of multiple sites.

During the studies of the major industrial areas in Japan with area-wide pinch technology, it became clear that theoretically a large energy saving potential exists. The results are shown in Table 9.11.

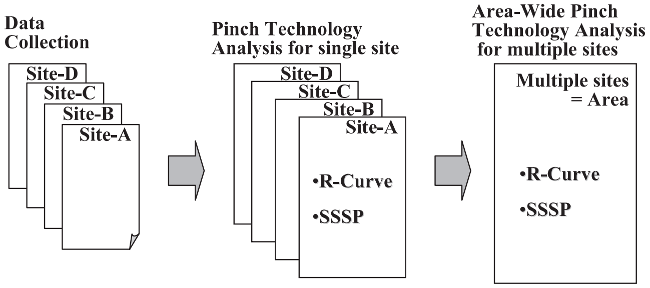


Figure 9.27—Analysis from single site to multiple sites.

TABLE 9.11—Energy-Saving Potential in the Industrial Areas[a]

	Industrial area	Chiba (kL/year)	Mizushima (kL/year)	Mizushima/Chiba (kL/year)
1	No. of sites	23	35	1.5
2	Integrated fuel consumption (Fuel + power)	2,880,000	3,785,000	1.3
3	Energy-saving potential by R-Curve analysis	510,000	1,002,000	2.0
4	Energy-saving potential by SSSP analysis	130,000	211,000	1.6
	Total	640,000	1,213,000	
	Domestic crude consumption	1 day	2 days	

[a] Annual crude oil conversion is shown as kilolitres per year.

Table 9.11 shows Chiba industrial area and Mizushima industrial area. Chiba has 23 sites and its integrated fuel consumption, which is the sum of the fuel consumption and the electrical power consumption in the energy system, is 2,880,000 kL/year (annual crude oil equivalent). The R-curve analysis determined that Chiba has potentially 510,000 kL/year of energy saving, while the SSSP analysis shows it to have a potential 130,000 kL/year of energy saving. Chiba, therefore, has the potential to save a total of 640,000 kL/year of energy, which is equivalent to almost 1 day of crude oil consumption of Japan. Table 9.11 also shows the result for Mizushima. Mizushima's energy-saving potential is equivalent to almost 2 days of crude oil consumption of Japan.

In comparison, Mizushima industrial area has 1.5 times more sites than Chiba industrial area, but its integrated fuel consumption is only 1.3 times larger than Chiba. In contrast, the energy-saving potential of Mizushima is almost twice that of Chiba. The conclusion is that the equipment in the energy system in Mizushima industrial area performs less efficiently than that in Chiba. The conclusion is supported by the fact that Mizushima industrial area was established well before that of Chiba.

Data were collected from 1,222 heat exchangers from all the sites in Chiba industrial area, and many proposals for an energy sharing project were developed. After much discussion with the various sites, we could produce 8 feasible project proposals using 31 sets of heat exchangers. The energy saving from the 8 projects resulted in 90,000 kL/year.

Of the eight projects selected, the leading project proposal was finally selected, with the cooperation of the corresponding sites, based on its economical efficiency. The amount of energy saving was a little more than 10,000 kL/year for two sites, namely those of FOC and Sumitomo Chemical Company (SCC). FOC is a mid-size refinery with a considerable track record in undertaking improvements to make more efficient use of energy. SCC is a leading petrochemical site that is adjacent to FOC.

The SSSP analysis identified which heat region of energy could be shared. Figure 9.28 shows the results of SSSP only for FOC. The left half of the chart in Figure 9.28 led to the conclusion that FOC had a large energy saving potential in the region below 120 °C. Although the heat below 120 °C could be recovered and collected, it could not be utilized adequately in FOC because the heat demand was located only at a temperature higher than 120 °C, as shown in the right half of the chart in Figure 9.28.

Once FOC and SCC were combined in the SSSP, it would produce a new possibility for energy sharing as shown in Figure 9.29. There were two energy-sharing cases: one case was the sharing of very low pressure steam and the other case was hot water sharing. Eventually FOC and SCC selected the hot water case and implemented the energy-sharing project between two sites.

FOC, SCC, and Chiyoda together developed a 3-year business plan for the energy-sharing project and, with NEDO's support, it was implemented in the second half in fiscal 2003 and completed in the summer of fiscal 2005.

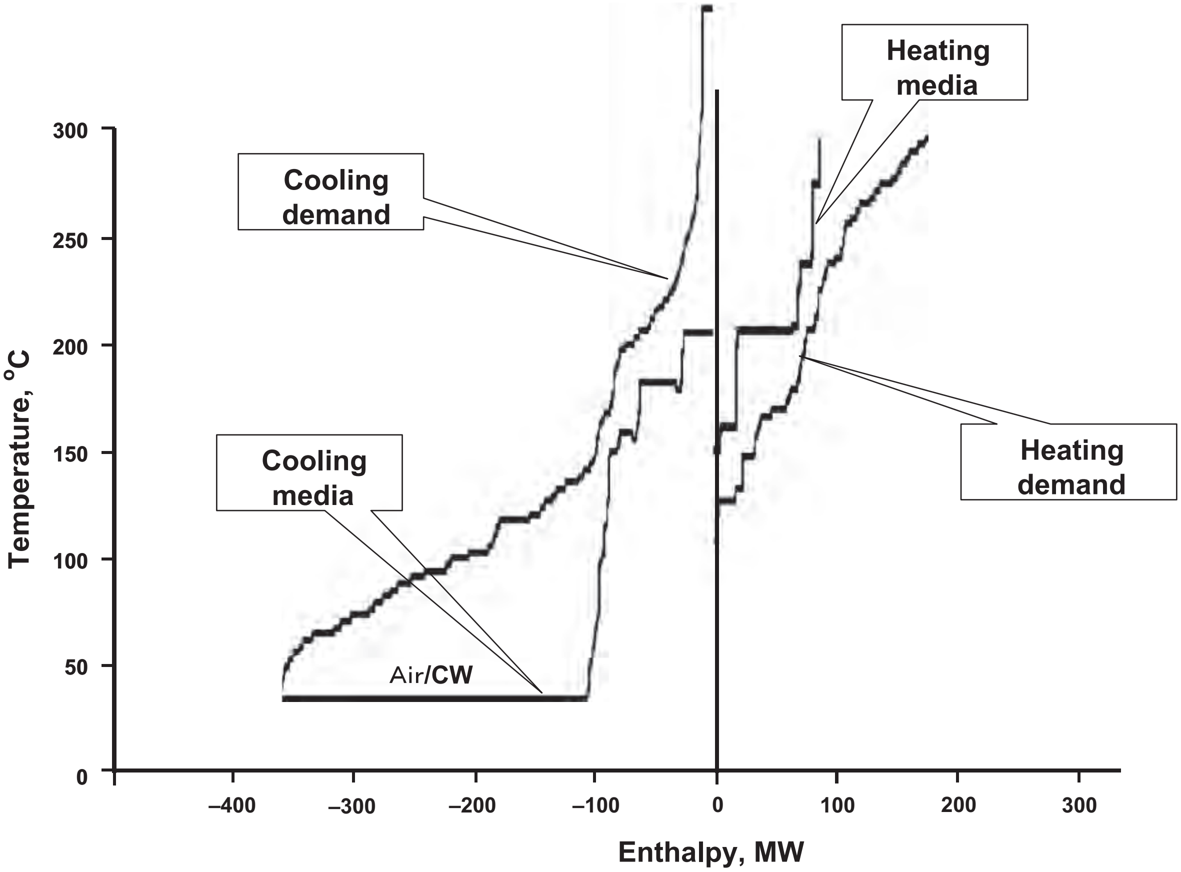


Figure 9.28—SSSP analysis for FOC.

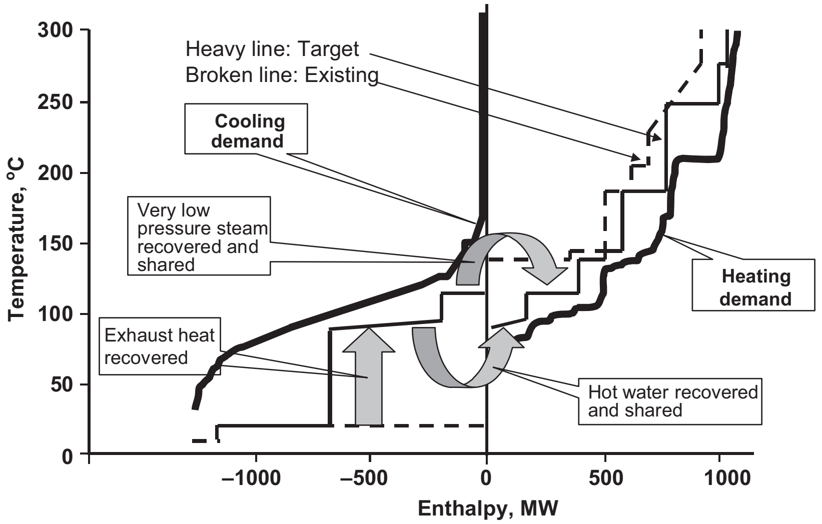


Figure 9.29—SSSP analysis for combined FOC and SCC.

The project successfully achieved its energy savings target and, in recognition of this, the project was awarded a prize by the Director-General of the Agency of Natural Resources and Energy at the 27th Energy Conserving Machinery Awards in January 2007.

Previously, the FOC and SCC sites had been operating independently of each other; this was the first time for them to have energy links. The energy-sharing project, shown in Figure 9.30, consisted of two energy-saving systems and an IT system. The two-energy saving systems were a heat-sharing system and a low-heat power generation system.

The heat-sharing system achieved energy savings of 4,900 kL/year by collecting the exhaust heat from the cooling water coolers in FOC and supplying it to SCC to reduce the fuel consumption of the boilers. The project was monitored by an IT system called an integrated energy monitoring system, as shown in Figure 9.31, which sought the optimal operating conditions and maintained and maximized the combined energy savings for both sites of 4,900 kL/year. The integrated energy monitoring system collected the operating information data and calculated the optimal operating conditions, which could then be viewed independently by both the FOC and SCC operators. The Level- model and two site-specific Level 1 models calculated the optimal operating conditions of the inter-sites energy links. The system automatically started its calculations with real-time data at 1-h intervals throughout the day, taking into account fuel availability, heat and steam requirements, and the power tariffs for each site.

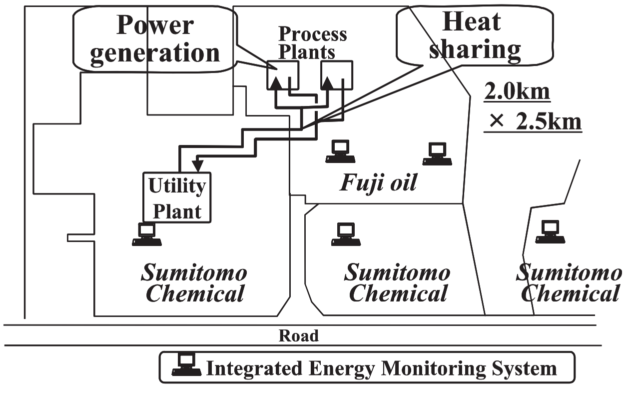


Figure 9.30—Implementation of energy-sharing project.

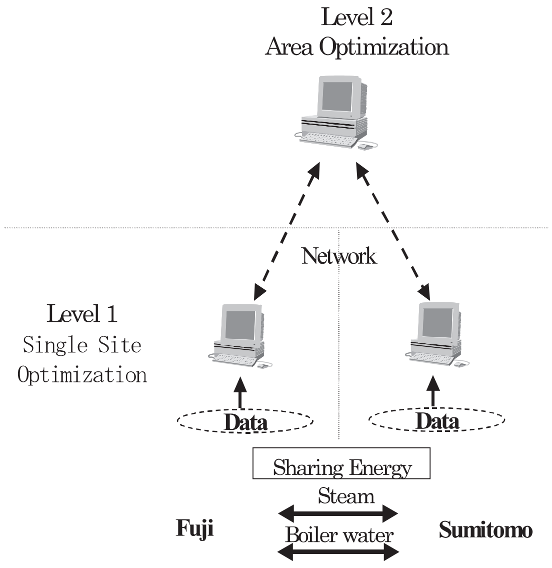


Figure 9.31—Integrated energy monitoring system.

The low-heat power generation system shown in Figure 9.32 utilized the heat of the overhead vapor from the distillation tower in FOC, which used to be cooled by air fin coolers but was changed for the project so that the heat of the overhead vapor exchanged with the high concentration of ammonia solution at the vaporizer. Ammonia gas was generated in the vaporizer at high pressure (3 MpaG), which was then introduced into the turbine generator to produce a maximum 4000 kW of electricity. This achieved an energy saving of 5,600 kL/yr. The exhaust ammonia gas from the turbine was led to a condenser and then the condensed ammonia solution was sent back to vaporizer by a circulation pump. This system has such a high autoregressive performance that, despite being a closed system, unmanned operation could be established.

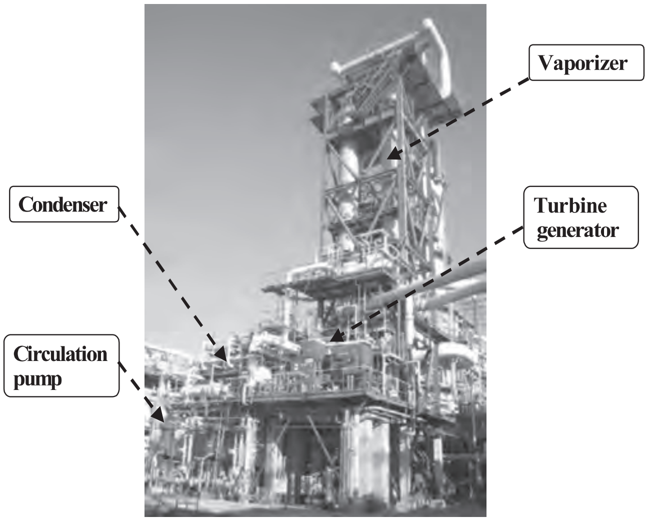


Figure 9.32—Low-heat power generation system.

The total energy saving with the above two systems operating in tandem was 10,500 kL/year with a consequential reduction in CO_2 emissions of 28,000 t/year.

9.7.2 A View of the Future

It is necessary for a forward-looking and enterprising grand design to be established at the earliest possible opportunity. The equipment in many of the large-sized domestic industrial sites in Japan is more than 30 years old, has become less efficient, and needs to be updated, but it is not easy for one company to decide independently on a new investment plan in the present economic situation.

It is believed that the energy-sharing project is an excellent solution to the problem of aging plants. If adopted for widespread use in industrial areas, it would offer many significant benefits to industrial areas by promoting environmental preservation, lowering production costs, and strengthening the international competitiveness.

This research and associated studies have shown that area-wide pinch technology provides an optimal system of energy sharing with a consequential area-wide energy saving. Another possible study in the future would be to consider the benefits provided by area-wide material sharing of hydrogen gas, fuel gas, and so on in industrial sites. The total consumption of such materials if shared by multiple sites would be less than the combined sum of the individual usage of each site. Area-wide material sharing would lead to a reduction in the consumption of raw materials and in waste emissions, which would contribute significantly to the preservation of the global environment.

For the purpose of this study, a project was developed to share energy between the two sites. The next logical step would be to enlarge the scope of the study and provide a large sharing project for multiple sites. In such a case, the role of the integrated energy-monitoring system would become more crucial in maintaining and maximizing the expected energy-saving amount and optimizing the operating conditions for each site. The algorithm of Level 2 would also need to be developed to keep up with any future request for a large energy-sharing project to be provided among multiple sites.

The low-heat power generation system also proved to be very useful in its ability to provide power by utilizing unused lower heat in the refinery and petrochemicals fields. However, as unused lower heat exists in various other fields, including steel, power plants, hot springs, and so on, it is therefore important to develop the low-heat power generation system so that it can be used in a wide range of projects.

REFERENCES

[1] Rana, M.S., Samano, V., Ancheya, J, and Diaz, J.A.I., "A Review of Recent Advances on Process Technologies for Upgrading of Heavy Oils and Residua," *Fuel*, Vol. 86, 2007, pp. 1216–1231.

[2] Threlkel, R., Dillon, C., Singh, U. G., and Ziebarth, M., "Increase Flexibility to Upgrade Residuum Using Recent Advances in RDS/VRDS-RFCC Process and Catalyst Technology," *J. Japan Pet. Inst.*, Vol. 53, 2010, pp. 65–74.

[3] Gruia, A., "Recent Advances in Hydrocracking," Ch. 8., in *Practical Advances in Petroleum Processing*, Hsu, C.S., and Robinson, P. R., Eds., Springer, New York, 2006.

[4] Commercial Hydrocracking Processes: Axens Mild Hydrocracking (MHC), http://www.axens.net/product/technology-licensing/10088/mild-hydrocracking-a-hyc-10.html; UOP MHC Unicracking," http://www.uop.com/mild-hydrocracking-challenges-mature-technology/.

[5] "The Houdry Process," http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_pageLabel=PP_ARTICLEMAIN&node_id=924&content_id=WPCP_007595&use_sec=true&sec_url_var=region1&__uuid=2d80a6b1-7c48-4fd1-93a7-be9376e46d1f.

[6] Fletcher, R.P., "The History of Fluidized Catalytic Cracking: A History of Innovation: 1942–2008," in *Innovations in Industrial and Engineering Chemistry: A Century of Achievements and Prospects for the New Millenium*, Flank, W.H., Abraham, M.A., Matthews, M.A., Eds., ACS Symposium Series 1000, American Chemical Society: Washington, DC, 2009.

[7] Jahnig, C., Martin, H., and Campbell, D., "The Development of Fluid Catalytic Cracking," *Chemtech.*, Vol. 14, February 1984, p. 106–112.

[8] Wrench, R., Wilson, J., Logwinuk, A., and Kendrick, H., *Fifty Years of Catalytic Cracking*, M.W. Kellogg, Wembley, Middlesex, England, 1986, pp. 4–6.

[9] Desai, P. H., Lee, S. I., Jonker, R. J., De Boer, M., Vrieling, J., and Sarli, M.S., "FCC Gasoline Sulfur Reduction," *Fuel Reformulation*, Vol. 43, 1994, pp. 43–44.

[10] Hatanaka, S., unpublished data, 1997.

[11] Hatanaka, S., Sadakane, O., and Yamada, M., "Hydrodesulfurization of Catalytic Cracked Gasoline. 1. Inhibiting Effects of Olefins on HDS of Alkyl(Benzo)thiophenes Contained in Catalytic Cracked Gasoline," *Ind. Eng. Chem. Res.*, Vol. 36, 1997, pp. 1519–1523.

[12] Metcalfe, T. B., "Inhibition by Hydrogen Sulfide of the Hydrodesulfurization of Petroleum Products," *Chim. Ind. Gen. Chim.*, Vol. 102, 1969, pp. 1300–1303.

[13] Hatanaka, S., unpublished data, 2007.

[14] Shimada, K., Sahara, W., Morita, E., and Hatanaka, S., "Computational Modeling of Thiol Formation in FCC Gasoline Hydrodesulfurization," *230th ACS National Meeting*, August 29, 2005, Washington, D.C.

[15] McBride, M.J., and Gordon, S., "Computer Program for Calculating and Fitting Thermodynamic Functions," NASA Reference Publication 1272, 1992.

[16] Muller, C., Michel, V., Scacchi, G., and Come, G. M., "THERGAS: A Computer Program for the Evaluation of Thermochemical Data of Molecules and Free Radicals in the Gas Phase," *Journal de Chimie Physique et de Physico-Chimie Biologique*, Vol. 92, 1995, pp. 1154–1178.

[17] Stein, S.E., Structures Properties Estimation Program, Version 2.0, NIST, Standard Reference Database 25, Gaithersberg, MD, 1994.

[18] Hatanaka, S., Morita, E., and Shimada, K., "Selective Catalytic Hydrocracked Gasoline Hydrodesulfurization," *Science and Technology in Catalysis 2006: Proceedings of the Fifth Tokyo Conference on Advanced Catalytic Science and Technology*, Tokyo, July 23–28, 2006, http://www.parctech.com.

[19] Hatanaka, S., Morita, E., and Shimada, K., "Selective Hydrodesulfurization of Catalytic Cracked Gasoline," *J. Japan Petrol. Inst.*, Vol. 50, 2007, pp. 179–187.

[20] Halbert, T.R., Brignac, G.B., Greeley, J.P., Demmin, R.A., and Roundtree, E.M., "Technology Options for Meeting Low Sulfur Mogas Targets," AM-00-11, *NPRA Annual Meeting*, March 26–28, 2000.

[21] Nocca, J.L., Cosyns, J., Debuisschert, Q., and Didillom, B., "The Domino Interaction of Refinery Processes for Gasoline Quality Attainment," AM-00-61, *NPRA Annual Meeting*, March 26–28, 2000.

[22] Gardner, R., and Schwarz, E.A., "Start-up of First CDHYDRO/CDHDS Unit at Irving Oil's Saint John, New Brunswick Refinery," AM-01-39, *NPRA Annual Meeting*, March 18–20, 2001.

[23] Pitt, R., and Cole, C., *Octane Week*, December, 4, 2000.

[24] Shih, S.S., Owens, P.J., Palit, S., and Tryjankowski, D.A., "Mobil's OCTGAIN Process: FCC Gasoline Desulfurization Reaches a New Performance Level," AM-99-30, *NPRA Annual Meeting*, March 21–23, 1999.

[25] Martinez, N.P., Salazar, J.A., Tejada, J., Antos, G.J., Anand, M., and Houde, E.J., "Meet Gasoline Pool Sulfur and Octane Targets with the ISAL Process," AM-00-52, *NPRA Annual Meeting*, March 26–28, 2000.

[26] Stynes, P.C., Shepherd, T., Thompson, M., Kidd, D., and Covert, C., "Innovation Key to New Technology Project Success Phillips Z-Sorb Becomes Low Sulfur Gasoline Solution," AM-01-43, *NPRA Annual Meeting*, March 18–20, 2001.

[27] Brunet, S., May, D., Perot, G., Bouchy, C., and Diehl, F., "On the Hydrodesulfurization of FCC Gasoline: A Review," *Appl. Catal. A: Gen*., Vol. 278, 2005, pp. 143–172.

[28] Nagamatsu, S., Kogaku, K., Vol. 68, 2004, p. 159.

[29] Song, C., and Ma, X., "New Design Approaches to Ultra-Clean Diesel Fuels by Deep Desulfurization and Deep Dearomatization," *Appl. Catal. B*, Vol. 41, 2003, pp. 207–238.

[30] "Diesel Fuels Technical Review," Chevron, http://www.chevronwithtechron.com/products/documents/Diesel_Fuel_Tech_Review.pdf.

[31] Maxwell, I.E., "Innovation in Applied Catalysis," *Cattech*, Vol. 1, 1997, pp. 5–13.

[32] Dautzenberg, F., "A Call for Accelerating Innovation," *Cattech*, Vol. 3, 1999, pp. 54–63.

[33] Halbert, T., Anderson, G., and Markley, G., *The 15th World Petroleum Congress*, Beijing, 1997.

[34] Abe, J., Nagamatsu, S., and Inomata, M., *Prep. JPI Congress*, Vol. 166, 2000.

[35] Song, C., Hsu, C.S., and Mochida, I., *Chemistry of Diesel Fuels*, Taylor & Francis, New York, 2000.

[36] Johnson, B., Kidd, D., Greenwood, G., and Slater, PN, AM-01-14, *NPRA*, 2001.

[37] Levy, R.E., Pappas, A.S., Nero, V.P., DeCanio, S.J., AM-01-10, *NPRA*, 2001.

[38] Stanislaus, S., Marafi, A., and Rana, M. S., "Recent Advances in the Science and Technology of ULSD Production," *Catalysis Today*, Vol. 153, 2010, pp. 1–68.

[39] Song, C., "An Overview of New Approaches to Deep Desulfurization for Ultra-Clean Gasoline, Diesel Fuel and Jet Fuel," *Catalysis Today*, Vol. 86, 2003, pp. 211–263.

[40] Whitehurst, D. D., Isoda, T., and Mochida, I., "Present State of the Art and Future Challenges in the Hydrodesulfurization of Polyaromatic Sulfur Compounds," *Adv. Catalysis*, Vol. 42, 1998, pp. 345–471.

[41] Babich, I.V., and Moulijn, J. A., "Science and Technology of Novel Processes for Deep Desulfurization of Oil Refinery Streams: A Review," *Fuel*, Vol. 82, 2003, pp. 607–631.

[42] ExxonMobil Refining Technology Brochure of Go-fining, http://www.exxonmobil.com.

[43] UOP Brochure of Advanced Partial Conversion Process (APCU) and HyCycle Unicracking, http://www.uop.com.

[44] Skripek, M., *Petroleum and Coal*, Vol. 37, 1995, p. 4.

[45] CLG marketing brochure of ISOCRACKING process, http://www.chevron.com/products/sitelets/refiningtechnology.

[46] Mukherjee, U.K., Louie, W.S.W., and Dahlberg, A.J., "Process for the Production of High Quality Middle Distillates from Mild Hydrocrackers and Vacuum Gas Oil Hydrotreaters in Combination with External Feeds in the Middle Distillate Boiling Range," Chevron, EP 1319701 A1, 2002.

[47] de Bruyn, L., *6th Bottom-of-The-Barrels Technology Conference*, Barcelona, October 9–10, 2008.

[48] Bonnardot, J., Axens, *6th Bottom-of-The-Barrels Technology Conference*, Barcelona, October 9–10, 2008.

[49] Morel, F., Axens, *5th Bottom-of-The-Barrels Technology Conference*, Athens, October 11–12, 2007.

[50] Tyas, A.R., DuPont, *6th Bottom-of-The-Barrels Technology Conference*, Barcelona, October 9–10, 2008.

[51] Tyas, A.R., *ERTC 13th Annual Meeting*, Vienna, November 17–19, 2008.

[52] Lummus Brochure of Syn Technology, http://www.lummusonline.com.

[53] Allen, L., Economic Environmental Fuels with Syn Technologies, Criterion Catalyst, EAA World Fuels Meeting, Fall 1998.

[54] Street, R. D., Allen, L., Swain, J., and Torrisi, S., "Criterion Catalyst," *Hydrocarbon Engineering*, Vol. 7, 2002, pp. 29–36.

[55] Lee, S. L., *Albemarle Catalyst Courier*, No. 59, Spring 2005, p. 4.

[56] Muller, M., "Two-Phase Distribution Apparatus and Process," UOP, US Patent US6769672 A1, 2004.

[57] Grott, R.J., Bunting, R.L., and Hoehn, R.K., UOP, US Patent 5,837,208, 1998.

[58] McDougald, N.K., Boyd, S.L., and Muldowney, G.P., US Patent 7,045,103 B2, 2006.

[59] Stangeland, B. E., Parimi, K., and Cash, D.R., Chevron USA Inc., US Patent 5,690,896, 1997.

[60] Muller, M., "Mixing Device for Two-Phase Concurrent Vessels," US Patent US7276215, 2007.

[61] Jacobs, G. E., Stupin, S.W., Kuskie, R.W., and Logman, R.A., Fluor Co., US Patent 6,098,965, 2000; and US Patent 6,984,365 B2, 2006.

[62] Den Hartog, A. P., and Van Vliet, W., Shell Oil Co., US Patent 5,635,145, 1997.

[63] Muller, M., Haldor Topsoe A/S, US Patent 5,942,162, 1999.

[64] Seidel, T., Dunbar, M., Johnson, B.G., and Moyse B., *Proceedings of NPRA 2002 Annual Meeting*, AM-02-52, March 17–19, 2002.

[65] Mochida, I., Shin, S., Yang, H., Sakanishi, K., Grudoski, D.A., and Shinn, J.H., *Appl. Catalysis A*, General, Vol. 205, 2001, pp. 101–108.

[66] Mochida, I., Choi, K.H., Kunisada, N., Korai, Y., and Nakano K., *Catalysis Today*, Vol. 86, 2003, pp. 277–286.

[67] Kunisada, N., Choi, K.H., Korai, Y., Mochida, I., and Nakano, K., *Applied Catalysis A*, Vol. 279, 2005, pp. 235–239.

[68] Mochida, I., and Choi, H.K., *J. Japan Petrol. Inst*., Vol. 47, 2004, p. 145.

[69] Yang, H., Chen, J., Fairbridge, C., Briker, Y., Zhu, Y.J., and Ring, Z., *Fuel Process. Technol*., Vol. 85, 2004, pp. 1415–1429.

[70] Nakamura, H., Amemiya, M., and Ishida, K., *J. Japan Petrol. Inst*., Vol. 48, 2005, pp. 281–289.

[71] Egorova, M., and Prins, R., *J. Catalysis*, Vol. 241, 2006, pp. 162–172.

[72] Wade, R., Maesen, T., Vislocky, J., and Torchia, D., *NPRA Annual Meeting*, AM-09-12, San Antonio, TX, March 22–24, 2009.

[73] Gupta, A., US Patent 2005/0006280 A1.

[74] Sie, S.T., and De Vries, A.F., European Patent 0553920 A1, 1993.

[75] Roeseler, C. M., Black, S. M., Shields, D. J., and Gosling, C.D., *NPRA*, 2003, San Antonio, TX, AM-02-17.

[76] Jensen, A. B., and Hommeltoft, S.I., *NPRA*, 2003, San Antonio, TX, AM-03-24.

[77] D'Amico, V. J., van Broekhoven, Nat, E.H.P.J., Nousiainen, H., and Jakkula, J., *NPRA*, 2003, San Antonio, TX, AM-02-19.

[78] D'Amico, V. J., Gieseman, J., Van Broekhoven, E., Van Rooijen, E., and Nousiainen, H., *Hydrocarbon Process*, February 2006, p. 65.

[79] Shimizu, S., and Inomata, J., "Eureka and Gasification—A Breakthrough in Residue Upgrading," *2010 Asia Petroleum Technology Congress*, February 2010.

[80] Ohba, T., Shibutani, I., Watari, R., Inomata, J., and Nagata, H., "The Advanced Eureka Process, Environment Friendly Thermal Cracking Process," *The 19th World Petroleum Congress*, June 2008.

[81] Nishimori, K., "Eureka Process," *Petrotech*, Vol. 29, 2006, pp. 920–923.

[82] Watari, R., Shimizu, S., and Reich, E.A., "Eureka in Combination with Texaco Gasification Refinery Integration," *NPRA Annual Meeting*, San Antonio, March 1997.

[83] Linhoff, B., Townsend, D.W., Boland D., Hewitt, G.F., Thomas, B.E.A., Guy, A.R., and Marsland, R.H., "User Guide on Process Integration for the Efficient Use of Energy," revised 1st ed., The Institute of Chemical Engineering, Rugby, Warks, UK, 1994.

[84] Linnhoff, B., and Hindmarsh, E., "The Pinch Design Method of Heat Exchanger Networks," *Chem. Eng. Sci*., Vol. 38, 1983, pp. 745–763.

[85] Tjoe, T.N., and Linnhoff, B., "Using Pinch Technology for Process Retrofit," *Chem. Eng*., Vol. 28, 1986, pp. 47–60.

[86] Asante, N.D.K., and Zhu, X.X., "An Automated Approach for Heat Exchanger Retrofit Featuring Minimal Topology Modifications," *Comp. Chem. Eng*., Vol. 20, Suppl., 1996, pp. s7–s12.

[87] Dhole, V.R., and Linnhoff, B., "Total Site Targets for Fuel, Co-Generation, Emissions, and Cooling," *Comp. Chem. Eng*., Vol. 17, Suppl., 1992, pp. s101–s109.

[88] Raissi, K., "Total Site Integration," Ph.D. Thesis, UMIST, UK, 1994.

[89] Klemes J., Dhole, V. R., Raissi, K., Perry, S. J., and Puigjaner, L., "Targeting and Design Methodology for Reduction of Fuel, Power and CO_2 on Total Sites," *Appl. Therm. Eng.*, Vol. 7, 1997, pp. 993–1003.

[90] Kimura H., "R-Curve Concepts for Analysis and Optimisation of Cogeneration Systems," 1998, MSc Dissertation, UMIST, UK.

[91] Kenney, W.F., *Energy Conservation in the Process Industry*, Academic Press, San Diego, CA, 1984.

[92] Kimura, H., Zhu, X. X., "R-Curve Concept and Its Application for Industrial Energy Management," *Ind. Eng. Chem. Res.*, Vol. 39, 2000, pp. 2315–2335.

10

Advances in Catalysts for Refining Processes

Isao Mochida[1], Ray Fletcher[2], Shigeto Hatanaka[3], Hiroshi Toshima[4], Shikegi Nagamatsu[5], Makato Inomata[5], Rong He[6], Richard S. Threlkel[6], Christopher J. Dillon[6], Junko Ida[7], Toshio Matsuhisa[7], Shinichi Inoue[8], Shinichi Shimizu[8], and Kazuo Shoji[9]

10.1 INTRODUCTION

The development and use of new catalysts has been a field of significant advances in the practice of petroleum refining in processes ranging from fluid catalytic cracking (FCC) to hydroprocessing to increase the refining efficiency of particularly challenging crude oils in producing the desired distillate fuels with improvements in quality and performance, such as octane and cetane numbers, and compliance with the increasingly strict environmental regulations. The advances in catalysis include a more detailed characterization of catalysts, a more thorough understanding of the chemistry on catalyst surfaces, new catalyst designs and manufacturing for increased activity and selectivity toward desirable products, and increased cycle times for providing more favorable economics for catalytic processes. This chapter provides examples of new advances in catalysis in parallel to the advanced processes discussed in Chapter 7, including processes such as FCC, hydrotreatment of FCC gasoline (catalytic cracked gasoline [CCG]), hydroprocessing of vacuum gas oil (VGO), alkylation, processing of heavy bottoms of crude oils, hydrogen production, and roles of catalyst supports.

10.2 FCC CATALYTIC TECHNOLOGY

The development of FCC catalyst technology has been equally as dramatic as the development of process designs. The first FCC units were operated on clay-based catalysts. A transition occurred to primarily alumina-based catalysts followed by inclusion of zeolites. A brief description of these technologies is as follows:

- *Clay-based catalysts:* Beginning in 1942 and lasting through the early 1950s, most catalysts in use were naturally occurring clays produced by crushing, drying, and sizing. Later, spray drying was introduced by Grace for improved fluidization.
- *Synthetic catalysts:* In the early 1950s, amorphous catalysts with alumina as the primary component were introduced into FCC units. These catalysts gave improved yield selectivities and higher diesel yields. The activities for the clay-based and synthetic catalysts were low at approximately 25–35 wt %, requiring bubbling beds in the reactor vessel for increased contact time. Very high recycle rates of slurry were common.
- *Zeolitic catalysts:* The introduction of zeolite into synthetic catalysts brought about one of the most significant and widespread changes observed in the refining world. Nearly all catalytic crackers in the early 1960s (with the exception of the Orthoflow B) were configured with a very short riser, which lifted the catalyst and oil mixture through a plate grid into a reactor bubbling bed. Once zeolites began commercially appearing in catalysts, these units required reconfiguration to prevent excessive coke make and overcracking of the gasoline.

The unprecedented success of zeolite-based catalysts has been the result of the following characteristics [1]:

- High activity,
- Good activity stability,
- High selectivities to gasoline versus coke and dry gas,
- Thermal and hydrothermal stability,
- Reasonable accessibility,
- Attrition resistance,
- Resistance to poisons (metals, nitrogen, etc.), and
- Acceptably low cost.

Typical FCC catalysts today are composed of zeolite, active alumina, clay, and binder [2]. One of the most significant differences found among various commercially available catalyst systems is related to the binding systems. These binding systems include silica sol, alumina sol, alumina gel, and in situ technologies. In situ technologies are based on the growth of zeolite crystal within spray-dried calcined clay microspheres.

- *Zeolite:* Typical catalysts today contain 30–40 % zeolite with some formulations reaching 50 %. “Activity-boosting” additives are currently available commercially with zeolite concentrations of 60 % or more.
- *Zeolite type:* All Y zeolites begin as basically $Na_{56}[SiO_2]_{136}[AlO_2]_{56}{*}250H_2O$. They are produced via modification and optimization of synthesis conditions, treatment steps, and exchange agents and routes. The zeolite can be dealuminated thermally, chemically, or by using both methods. Furthermore, the silica-to-alumina ratio (SAR) can be optimized to provide the extremes of

---

[1] Kyushu University, Kasuga, Fukuoka, Japan
[2] INTERCAT, Inc., Vleuten, The Netherlands
[3] JX Nippon Oil & Energy Corp., Yokohama, Kanagawa, Japan
[4] Albemarle, Amsterdam, The Netherlands
[5] JGC Corp., Yokohama, Kanagawa, Japan
[6] Chevron, Richmond, CA, USA
[7] Sud Chemie, Shibuya, Tokyo, Japan
[8] Chiyoda Corp., Kawasaki, Kanagawa, Japan
[9] Toyo Engineering Corp., Narashino, Chiba, Japan

maximum zeolitic activity (VGO operations), maximum zeolitic stability (residue cracking operations), plus an innumerable number of intermediate levels.

- *Rare earth:* Rare earth (*38*) is added to the zeolite as an activity enhancer, selectivity modifier, and to improve hydrothermal stability. Rare earth in zeolite concentrations typically vary from 0 to 16 wt %.
- *Active alumina:* Alumina is added to the catalyst to precrack high-molecular-weight molecules present in heavier portions of the feedstock. This precracking function enables further cracking by the zeolite present in the catalyst, increasing the yields of gasoline and liquefied petroleum gas (LPG). The alumina technology present today includes aluminas capable of absorbing vanadium and encapsulating nickel, which are catalyst poisons. Furthermore, catalyst manufacturers are now capable of modifying the pore volumes and acidities of these aluminas, enabling specific cracking of difficult feedstocks. Judicial use of alumina content is required because most aluminas increase coke and dry gas yields.
- *Zeolite-to-matrix ratio:* The relative composition of zeolite and alumina determines the yield selectivities observed by the refiner.

In 1984, Mobil Oil launched a revolutionary new additive, ZSM-5. ZSM-5 is a small-pore zeolite that selectively cracks higher molecular weight olefinic molecules boiling in the gasoline range. ZSM-5 has found wide application in the FCC unit and is used primarily for maximizing propylene yields, but it also has the capability of increasing gasoline octane number.

10.2.1 Future Catalytic Developments

The fluidized catalytic cracker is under continual pressure to transform itself as global motor fuel markets evolve. There has rarely been a period in time in which there have not been substantial efforts being paid to further improving FCC profitability. This continues to be true today. The following are four areas that are currently under intense research for improvement.

10.2.1.1 FCC AS A PLATFORM FOR PETROCHEMICAL FEEDSTOCKS

It is expected that by the middle of this century the world's remaining fossil fuel reserves will become much more precious given the growing global awareness of the effect of carbon dioxide (CO_2) on the environmental health of the planet and the declining availability of easily recoverable reserves [3]. For this reason it is probable that the FCC will transform itself steadily into a feed preparation unit for existing and yet to be discovered chemical processes. The preeminence of today's FCC unit as an engine for the production of motor fuels will likely diminish as the decades pass.

Substantial resources are currently being directed toward increasing the selectivity of the FCC toward producing petrochemical feedstock intermediates. The most obvious example of this trend is continued emphasis on propylene maximization in residue feedstocks. The major engineering companies in the FCC world continue to invest substantial resources to shift the yield selectivity toward propylene through measures such as reduction of hydrocarbon partial pressure, using multiple risers for higher severity, cracking naphtha as a feedstock directly into propylene, etc. Catalyst and additive companies continue to focus efforts on low hydrogen transfer catalytic systems via zeolite and active alumina improvements as well as enhancement of ZSM-5 activity and stability.

10.2.1.2 FCC AS A MAXIMUM DIESEL ENGINE

Given the global trend toward dieselization, engineering and catalyst companies have been placing increasing focus on maximizing diesel yield from the FCC. Research for LCO maximization has been focused on two primary approaches, the first being the reduction of conversion together with enhanced slurry destruction. These efforts are being spearheaded through efforts such as slurry recycling, increasing the catalyst-to-oil ratio, and reducing fresh catalyst intrinsic activity through reduction of the zeolite-to-matrix ratio. Additionally, catalyst manufacturers continue to maximize the intrinsic diffusion capabilities of the catalyst particle for maximal first-pass destruction of residue boiling molecules in the feedstock.

The second approach being taken by some manufacturers has been to experiment with nonstandard FCC catalytic components in the catalyst. This has included experimentation with basic materials as opposed to the standard acidic components. An observed benefit of this novel approach is a reduction in the aromatic content of the LCO, producing improved cetane number. The primary disadvantage of this approach is the low conversion resulting in high slurry yields.

10.2.1.3 THE FCC FOR ULTRA-HEAVY FEEDSTOCK CONVERSION

The exploitation of Alberta's bitumen oil from the vast fields of tar sands is currently at 1.5 million bbl/day. This production rate is expected to increase to 3.5 million bbl/day by 2015 [4–6]. Most of the synthetic crude being produced in Alberta is coked followed by varying degrees of hydrotreating. These synthetic oils currently occupy a minor position in North America's FCC feed slates. The percentage of these crudes reaching the FCC is expected to increase over the next few decades. Despite deep hydrotreating, these hydrocarbon streams remain highly cyclic and therefore pose a challenge to today's catalysts. Substantial improvements in the stability, porosity, and accessibility of today's "state-of-the-art" residue catalysts will likely be required.

UOP is currently active in developing an "FCC-like" process, the Catalytic Crude Upgrading (CCU™) unit, which will be used to partially upgrade ultra-heavy crudes for viscosity reduction, thus eliminating the need for external light hydrocarbon streams as diluents to meet pipeline specifications. The CCU unit produces its own diluent while maximizing the volume retention of crude barrels from ground to pipeline. These crude oils are typically extremely high in vanadium and require a degree of vanadium tolerance well beyond the standard FCC catalytic technology of today. UOP and its partners are currently developing ultra-high vanadium-resistant catalysts.

10.2.1.4 FCC DESIGNED FOR MINIMAL ENVIRONMENTAL IMPACT

The FCC, as with all chemical processes used today, is under increasing pressure to produce fuels and petrochemical intermediates with zero emissions, including CO_2. Current technology [7,8] is able to control sulfur oxide (SO_x) emissions in full combustion units with reductions of 90–95 % common. SO_x reductions in partial burn operations are typically 50–70 %. Research continues on many fronts to improve the SO_x capture efficiency for partial burn operations. Deeper reductions currently require the FCC operator to switch from partial to full burn operation (if applicable), implementation of feed hydrotreating, or utilization of flue gas treatment technologies such as flue gas scrubbers. FCC flue gas nitrogen oxide (NO_x) emission control continues to be an area requiring further research. Typical reduction levels of 50–60 % are achieved with current additive technology [9]. Finally, there is an increasing emphasis on particulate emissions reduction from the FCC unit. Fortunately for the FCC operator of today barrier filter technology exists to nearly eliminate particulate emissions from the FCC unit [10].

10.2.1.5 CONCLUSION

The FCC unit has proven to be one of the most flexible technologies within the oil refining industry for nearly 7 decades. Although the challenges continue to mount, the equilibrium nature of the process lends itself readily to "online" experimentation, thereby enabling the aggressive refiner to maintain the "cutting edge" nature of the operation. Continued research and development is essential for the FCC unit to maintain its central role within the modern high-conversion refinery of today.

10.3 CATALYST LOW-SULFUR GASOLINE PRODUCTION

10.3.1 Introduction

CCG is produced from VGO or atmospheric residue by FCC units and it contains high levels of sulfur. Hydrodesulfurization (HDS) is usually applied for sulfur removal of the petroleum fraction. However, CCG contains 20–40 vol % olefins, therefore the present naphtha HDS process would reduce the octane value because of the hydrogenation (HG) of olefins. Control of the HDS selectivity of the catalyst requires that the HDS active site is different from the olefin HG active site. Several studies on molybdenum catalysts show that the HDS active site is different from the olefin HG active site [11–13].

This section focuses on the features of the selective CCG HDS catalyst. The properties of CCG and the desulfurization processes are presented in Chapter 7.

10.3.2 Active Sites of the Catalyst

To improve the HDS selectivity of CCG, it is necessary to make clear the difference between the HDS active site and the olefin HG active site. Thiophene and butene have been used for the study of the HDS mechanism, and most of these works have indicated that the HDS active site is different from the butene HG active site [11,13,14].

The difference of the active sites was studied on Co-Mo/γ-Al_2O_3 catalyst using the inhibiting effects of hydrogen sulfide (H_2S). As is well known [15], H_2S is adsorbed on the HDS active site having coordinative unsaturation and it competitively inhibits the other sulfur compounds' access to the HDS active site. If olefin reactions are affected by H_2S as HDS is affected, then the structure of the olefin HG active site is considered to be similar to that of the HDS active site. If olefin reactions are not affected by H_2S, then the structure of the active site for olefin reactions may be different from that of the HDS active site. The effects of H_2S on the HDS of thiophene, alkylthiophenes, and benzothiophene (BT) were examined in the H_2 stream with or without H_2S (Table 10.1) [16]. Even with a small amount of H_2S (0.1 vol % in H_2), all thiophenes' HDS was strongly retarded, and the reaction rate constants obtained were 15–20 % of the original. The reactions of diisobutylene, 1-octene, and 1-hexene were examined in the H_2 stream with or without H_2S (Figure 10.1) [16]. With H_2S, the HG of diisobutylene is promoted whereas HG of 1-octene and 1-hexene is retarded. This finding shows that the isoolefin HG active site is different from the HDS active site, and it may be possible to control the selectivity of CCG HDS.

To further clarify the difference between the HDS active site and the isoolefin HG active site, the response of the catalyst activity to the well known promoting effects of cobalt was studied using catalysts with varying cobalt content. The results are shown in Figures 10.2 and 10.3. As is well known [17], thiophene HDS drastically increased with increasing Co/(Co+Mo) ratio. On the other hand, with increasing Co/(Co+Mo) ratio, it is noted that the HG of diisobutylene decreases a little and that of 1-octene largely decreases. The similar decreasing trend has been reported regarding the activity for butene HG on unsupported cobalt-molybdenum sulfide catalyst, in which thiophene HDS and successive butene HG were undertaken at 320°C and atmospheric pressure [18]. They have explained about the phenomena that the addition of cobalt ions blocks

TABLE 10.1—Effects of H_2S on Alkyl-(Benzo)-thiophenes HDS [16]

	H_2S concentration in H_2, vol%	
	0	0.1
Sulfur Compound	**HDS, %**	
thiophene	86.0	27.0
2-methylthiophene	63.8	10.9
3-methylthiophene	75.3	22.3
2, 5-dimethylthiophene	45.3	12.0
2-ethylthiophene	47.2	10.7
benzothiophene	99.4	63.8

Reaction conditions: temperature 160 °C, pressure 1.3 MPa, H_2/feed ratio 1.60 mol/mol, catalyst/feed 0.34 g of cat.min/mol sulfur compounds concentration 2.83×10^{-4} mol/mol.

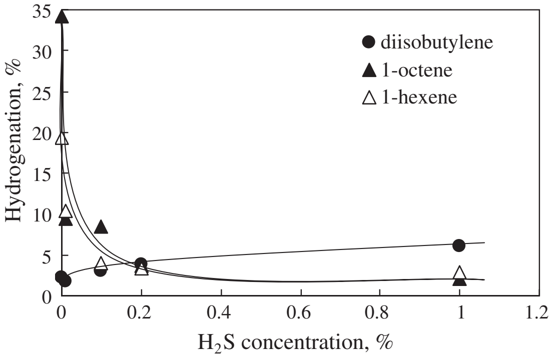


Figure 10.1—Effects of H_2S on olefin HG at a temperature of 150°C, pressure of 1.3 MPa, H_2/feed 0.34 g of cat min/mol, feed toluene 80 mol %, and olefin 20 mol % [16].

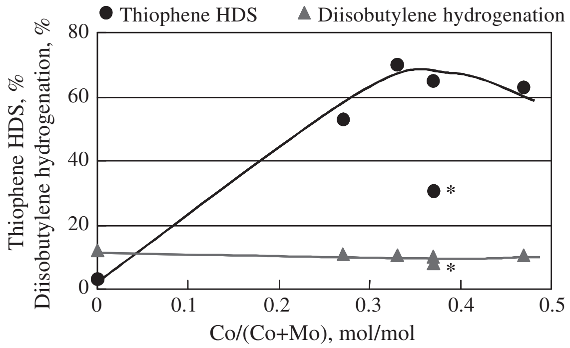


Figure 10.2—Effects of cobalt on HDS and isoolefin HG MoO_3 15.0 mass % (*7.5 mass %), temperature 175°C, pressure of 1.3 MPa, H_2/feed 0.34 g of cat min/mol, feed thiophene 2.83×10^{-4} mol/mol, toluene 80 mol %, and olefin 20 mol % [16].

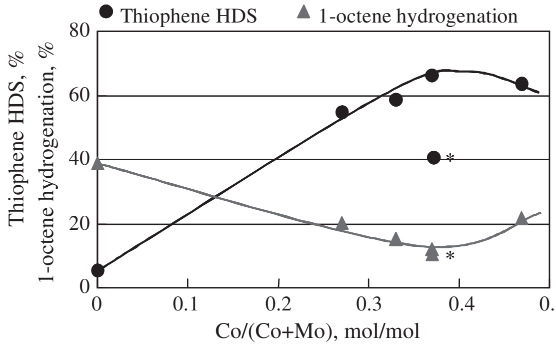
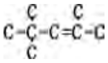


Figure 10.3—Effects of cobalt on HDS and *n*-olefin HGMoO_3 15.0 mass % (*7.5 mass %), temperature 190°C, pressure 1.3 MPa, H_2/feed 0.34 g of cat min/mol, feed thiophene 2.83×10^{-4} mol/mol, toluene 80 mol %, and olefin 20 mol % [16].

the coordinatively unsaturated molybdenum sites on the edges of molybdenum disulfide (MoS_2) and decreases the HG activity. If cobalt blocks the unsaturated molybdenum sites, the small effects of cobalt on isoolefin HG suggest that isoolefin HG proceeds on the unsaturated molybdenum sites not blocked by cobalt. In the case of catalyst having half metal content (*marked), thiophene percentage conversion largely decreases; however, percentage of olefin HG slightly decreases. The mass percentage (7.5 mass %) of molybdenum trioxide (MoO_3) is too small to cover the whole surface of the Al_2O_3. Uncovered Al_2O_3 surface may enhance olefin HG. These results also indicate that HDS and olefin HG proceed at the different active sites.

The studies of the effects of H_2S and cobalt are summarized in Table 10.2. The effects of pyridine modification on the catalyst activity and selectivity of Co-Mo/γ-Al_2O_3 catalyst were investigated by microreactor [19]. Thiophene HDS, diisobutylene HG, and 1-octene HG were studied at 150°C and 1.3 MPa to measure the original activity. Thiophene (2.83×10^{-4} mol/mol)/pyridine (0.01 mol/mol)/toluene, diisobutylene (0.25 mol/mol)/toluene, and 1-octene (0.25 mol/mol)/toluene were passed into the reactor and the inhibition by pyridine spike was studied. The temperature was then increased to 300°C to strip the pyridine and then the temperature was decreased back to 150°C to measure the remaining effects of pyridine. After pyridine was desorbed at 300°C, HDS activity had almost recovered to the initial level. However, the activity for diisobutylene HG still remained much lower than the initial activity. The activity for 1-octene HG recovered to half of the initial activity. The remaining effect of the pyridine spike on isoolefin HG was stronger than that on *n*-olefin HG. These observations strongly support the idea that three different types of active sites are present on the catalyst.

TABLE 10.2—Effects of H_2S and Co on HDS and HG [16]

	H_2S	Co
 HDS	inhibition	promotion
 $C-C(C)(C)-C=C(C)-C$ hydro.	promotion	no effect
$C_4-C-C-C=C$ hydro.	inhibition	inhibition

From these results, one can speculate on the following three types of active sites:

1. *HDS active site:* This site is inhibited by H_2S and promoted by cobalt. *n*-Olefin and isoolefin can approach.
2. *n-Olefin HG active site:* This site is inhibited by H_2S and cobalt. This site has some similarity with the HDS active site.
3. *Isoolefin HG active site:* This site is promoted by H_2S and is slightly inhibited by cobalt. This site strongly interacts with isoolefin, resulting in the formation of an oligomer. This site is totally different from the HDS and *n*-olefin active sites.

These phenomena suggest the possibility of a selective CCG HDS in which the HDS reaction performs with minimizing olefin HG because most of the olefins contained in CCG are isoolefins.

10.3.3 HDS Selectivity Improvement

Cobalt addition test shows that the proper amount of cobalt loaded on γ-Al_2O_3 gives good selectivity for CCG HDS by lowering *n*-olefin HG activity. Cobalt distribution also contributes to the selectivity improvement. Highly dispersed cobalt catalyst was prepared with CyDTA-Co(*trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid-cobalt) [20]. Thiophene HDS and 1-octene HG reaction were examined and the activities were compared with conventional Co-Mo/γ-Al_2O_3 catalyst. CyDTA-Co showed higher HDS activity and lower 1-octene HG activity than the conventional catalyst.

It was found that isoolefins were oligomerized on the isoolefin HG active site [21]. Oligomer may finally be irreversibly deposited on the active site as a coke. If it is possible the coke selectively deactivates that isoolefin HG active site; then this leads to selective CCG HDS.

Three different combinations of the pretreatments were performed on the fresh catalyst. They were sulfiding + aging, sulfiding + aging + coking, and coking + sulfiding + aging. The coking pretreatment was done using a mixture of cyclohexene + 1-methylnaphthalene. The result of CCG HDS is shown in Figure 10.4 [21]. The catalyst with sulfiding + aging gives a higher total HDS percentage than the catalyst with coking. Concerning the HDS selectivity, the catalyst with sulfiding + aging + coking shows higher selectivity than the catalyst without coking. However, the catalyst with coking + sulfiding + aging shows the same selectivity as the catalyst without coking. These results show that coking pretreatment should be done after sulfiding to improve HDS selectivity.

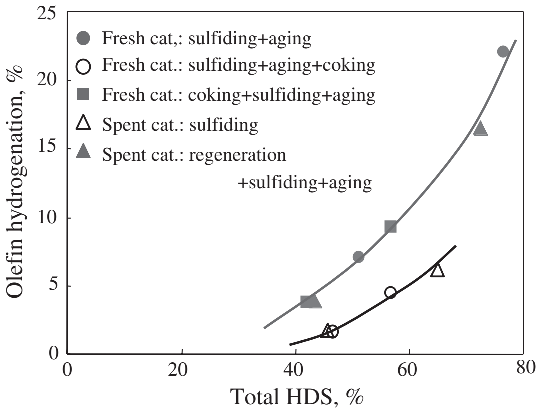


Figure 10.4—Effects of coking pretreatment on HDS selectivity at a temperature of 300°C, pressure of 0.4 MPa, H_2/feed of 85 NL/L, and feed CCG (sulfur 157 ppm [mass] and olefin 36.6 vol %) [21].

The effects of coke were further examined using a refinery spent catalyst, which was used in the diesel fuel HDS process for 1 year. This catalyst, having 8.8 mass % deposited coke, was supplied for CCG HDS activity test. This spent catalyst also shows high HDS selectivity. However, this high selectivity was lost by a regeneration procedure. This result suggests that coke deposit improves the HDS selectivity.

Thiophene HDS was performed over the catalyst with or without aging and coking pretreatment in the presence of diisobutylene and 1-octene [21]. Thiophene HDS is little reduced by the aging pretreatment but is much reduced by the coking pretreatment. The diisobutylene HG percentage is plotted against thiophene HDS in Figure 10.5. Little difference is observed between the selectivity of the catalyst with or without aging. However, it is noted that diisobutylene HG of the catalyst with coking is much lower than that of catalysts without coking.

The 1-octene HG percentage is plotted against thiophene HDS in Figure 10.6 [21]. The 1-octene HG of the catalyst with coking is much higher than that of catalysts without coking. The effects of coking pretreatment on the three different types of active sites are as follows: isoolefin HG active site > thiophene HDS active site > *n*-olefin HG active site. This order also suggests that the coking pretreatment effectively reduces isoolefin HG activity but hardly reduces *n*-olefin HG activity. Because most olefins in CCG are isoolefin, it is considered that CCG HDS selectivity is improved by coking pretreatment.

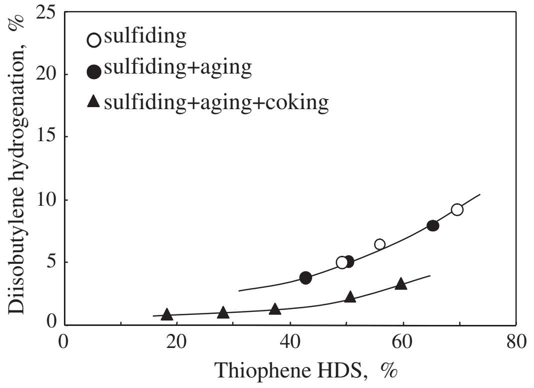


Figure 10.5—Effects of coking on HDS selectivity in the presence of isoolefin at a temperature of 175°C, pressure of 1.3 MPa, H_2/feed of 1.6 mol/mol, feed thiophene of 2.83×10^{-4} mol/mol, toluene of 80 mol %, and olefin of 20 mol % [21].

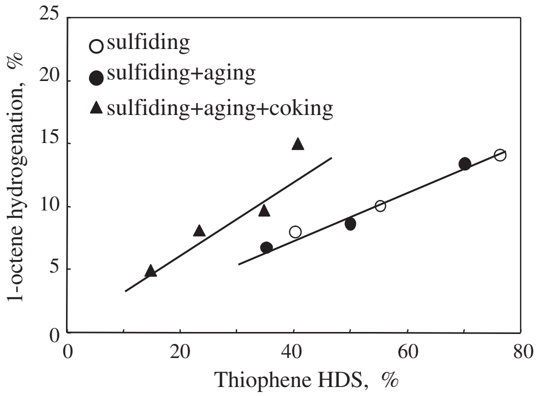


Figure 10.6—Effects of coking on HDS selectivity in the presence of *n*-olefin at a temperature of 190°C, pressure of 1.3 MPa, H_2/feed of 1.6 mol/mol, feed thiophene of 2.83×10^{-4} mol/mol, toluene of 80 mol %, and olefin of 20 mol % [21].

10.3.4 CCG HDS Commercial Catalysts

A Co(Ni)-Mo/-Al_2O_3 catalyst is used in the actual CCG HDS process. Several modifications are made to improve the selectivity. It is supposed that alkaline metals and alkaline earth elements reduce olefin HG activity [22]. Coking is also effective as a pretreatment of the catalyst for selectivity improvement [13]. The patent shows that SCANfining developed by ExxonMobil and Akzo Nobel uses the combination of two catalysts (Table 10.3) [23]. RT-225 is a main selective CCG HDS catalyst. KF-742 is a conventional HDS catalyst and is sometimes used together with RT-225. The information on the catalysis of other processes is scarce, but similar catalysts may be used.

10.4 RECENT ADVANCES IN DEEP HDS CATALYSTS

10.4.1 Catalysts for Deep HDS of Diesel Fuel

The desulfurization technology for diesel fuel has advanced rapidly as oil companies, catalyst manufacturers, engineering companies, universities, and public research institutes all competed with one another to develop catalysts or processes when the regulation on sulfur contents in diesel oil was changed to 500 ppm starting in 1997 as a response to the report by the Central Council for Environmental Pollution Control in 1989 in Japan, requiring oil companies to newly introduce desulfurization systems. This has resulted in a leap of science and know-how on deep HDS and deep HDS catalysts for ultralow sulfur diesel (ULSD) production [24].

TABLE 10.3—Catalysts for SCANfining [23]

	RT-225	KF-742
Support	**Alumina**	**Alumina**
Av. pore dia.	87	72
MoO_3, mass %	4.2	15
CoO, mass %	1.2	4
HDS activity	<0.5	1

The major components of sulfur compounds in diesel fuel are alkyl derivatives of BT and dibenzothiophene (DBTs). HDS is a reaction to remove sulfur from these compounds in the form of H_2S while maintaining the carbon skeleton structures. Furthermore, denitrogenation of organic nitrogen compounds and HG of aromatic compounds also proceed in concurrence with the desulfurization in diesel oil. Because the organic nitrogen compounds in diesel fuel are inhibitors of HDS, denitrogenation is a favorable reaction in a similar fashion to desulfurization. Meanwhile, condensed polycyclic aromatic compounds in diesel fuel are a source of particulate matter (PM) when the diesel fuel is combusted; thus, their HG is also a favorable reaction. However, there is a problem of increased hydrogen consumption in these reactions. It is therefore necessary to conduct deep desulfurization and optimize these reactions to suit the purpose of environmental and economic imperatives.

This section provides an outline of catalyst technology regarding the problems to be solved for ultra-deep HDS and methods to address ultralow sulfur-free diesel fuel with sulfur contents of 10 ppm or lower.

10.4.2 HDS Reactions of Gas Oil

Figure 10.7 shows the results of investigating the sulfur compound distribution in the straight-run diesel fuel (sulfur content 1.4 wt %) and treated gas oil after HDS (sulfur content 380.35 ppmw) using gas chromatography with atomic emission detector (GC-AED) [25]. It is evident that various sulfur compounds including BTs and DBTs are contained in the raw diesel fuel. On the other hand, the product oil after the HDS at 380 ppmw has lost most of the peaks observed for the raw diesel oil with the only remaining peak in the high boiling-point region. In product oil that is more deeply desulfurized at 35 ppmw, it is shown that only 4,6-dimethyldibenzothiophene (4,6-DMDBT) and DBTs with large alkyl group sidechains remain.

In ultra-deep HDS, the concentration of sulfur in diesel oil needs to be reduced to one thousandth. Therefore, nearly all sulfur compounds must be removed from diesel oil by HDS. As seen from the chromatogram for product oil (sulfur content 380.35 ppmw) shown in Figure 10.7, the residual sulfur compounds include mainly refractory sulfur compounds such as 4,6-DMDBT. Thus, it is naturally necessary to keep in mind that HDS of such refractory compounds should be thoroughly performed in deep HDS. Because this 4,6-DMDBT alone is contained as sulfur content of 100 ppmw or higher in feed oil, it needs to be reduced to one tenth that of the feed oil. Table 10.4 presents the relative desulfurization activities of alkyl-BTs examined by Houalla et al. [26]. It becomes more difficult to desulfurize when a methyl group is attached to position 4 or 6 adjacent to the sulfur atom. For example, 4,6-DMDBT has one tenth less reactivity than DBT. It is considered that this is caused by steric hindrances for adsorption of the sulfur atom to the active site of the catalyst because the alkyl substituent is located near the sulfur atom [27]. It is therefore expected that the reactivity can be improved dramatically if it is possible to remove or mitigate the inhibition by this methyl group before the C–S bond cleavage.

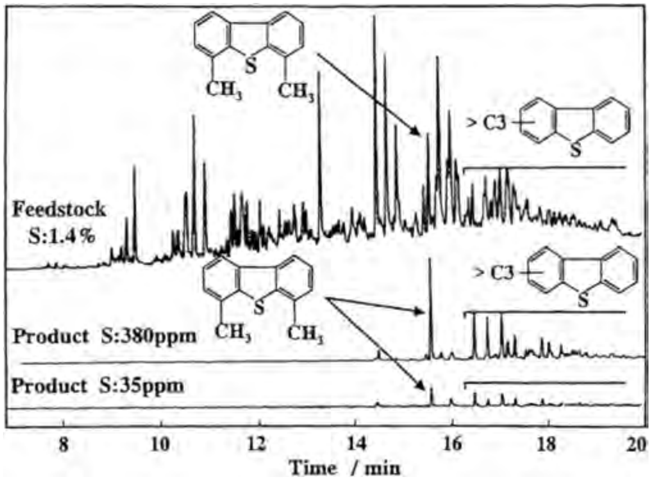
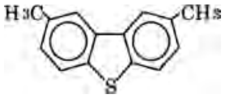
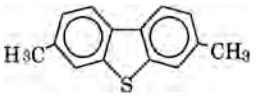
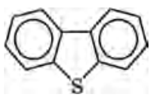
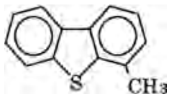
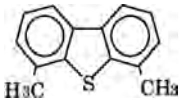


Figure 10.7—GC-AED chromatogram of raw and hydrotreated gas oil [25].

Desulfurization of 4,6-DMDBTs can take a direct route in which the sulfur atom is directly hydrogenated and then desulfurized, a HG route in which it is desulfurized after the aromatic ring is hydrogenated, or an isomerization route in which the methyl group is transferred by isomerization as shown in Figure 10.8. Mochida et al. reported that the HG reaction of the aromatic ring became subject to restriction by thermodynamic equilibrium under high

TABLE 10.4—Relative Activity of Alkyl-DBTs [25]

	Compound	Relative HDS Activity
	2,8-DMDBT	2.6
	3,7-DMDBT	1.5
	DBT	1.0
	4-MDBT	0.16
	4,6-DMDBT	0.1

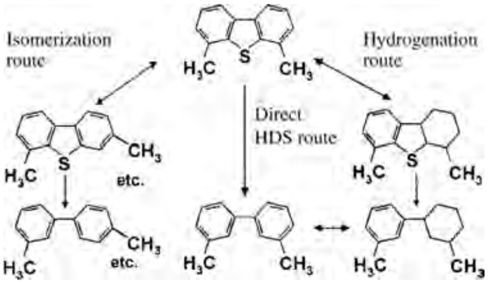


Figure 10.8—HDS reaction pathways of 4,6-DMDBT [28].

temperatures in the HG route for alkyl-DBT, and that HG of DBT for instance is not favored at 330°C or higher regarding thermodynamic equilibrium, with little formation of hydrogenated compounds at temperatures as high as 425°C. They also report that the reaction is not favored for 4,6-DMDBT at 260°C or higher and that there is little formation of hydrogenated compounds at 380°C [28]. In ultra-deep HDS, it is necessary to improve the primary HDS activity in addition to solving the issue of how these reaction paths shall be realized on the catalyst and the issue to mitigate the steric hindrances by methyl groups. As mentioned above, the improvement of catalysts and processes in sulfur-free level is conducted giving attention to the desulfurization mechanism.

Furthermore, it is generally considered that the concentrations of sulfur and nitrogen in the feed oil affect the desulfurization reactivity. Figure 10.9 shows the relationship between the correction factor calculated from sulfur and nitrogen contents in feed oil by the following formula and required desulfurization temperature. It is supposed that the ratio between sulfur content and nitrogen content in feed oil can be used to grasp the reactivity of the feed oil [29].

$$\textit{Correction factor} = (\textit{nitrogen content in feed oil/sulfur content in feed oil})^{2.8} \times (\textit{sulfur content in feed oil})^{2.2} \quad (10.1)$$

This indicates that the nitrogen compounds in feed oil work as reaction inhibitors in deep HDS; thus, denitrogenation of these nitrogen compounds also becomes important in ultra-deep HDS.

10.4.3 Trend of Catalyst Development for Sulfur-Free Diesel Oil

As described in Section 10.4.2, the catalyst needs to be highly active and extend the lifespan by decreasing the reaction temperature so that the refractory sulfur compounds such as 4,6-DMDBT can be selectively desulfurized to achieve a sulfur-free level. There are several catalyst design concepts proposed for these improvements [30]. It is also necessary to develop a catalyst that is resistant to inhibition by H_2S, nitrogen compounds, or ammonia.

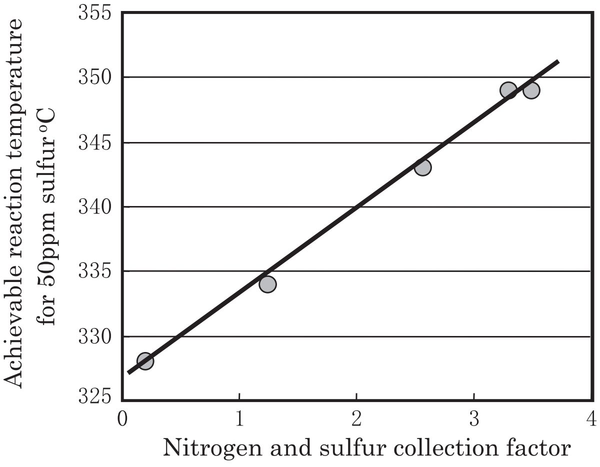


Figure 10.9—Correlation between nitrogen and sulfur collection factor and achievable reaction temperature for 50 ppm sulfur [29].

10.4.3.1 CONTROL OF COMOS PHASE FOR HIGHER ACTIVITY

The CoMo alumina catalyst popularly used in HDS requires presulfiding to be activated before reaction. Before deep desulfurization of the 500-ppm level was implemented, it was assumed that Mo and Co were individually sulfided and existed as MoS_2 and Co_9S_8 on alumina carrier. However, recent advancements in various analytical techniques revealed a unique structure called the CoMoS phase in which molybdenum and cobalt are bonded, which functions as the active site for HDS. As shown in Figure 10.10 [31], it has a unique cluster structure with the fundamental skeleton of the MoS_2 structure and cobalt coordinated on the cluster's edge. In general, the two important points in improving the catalyst activity are increasing the number of active sites and improving the performance of the active sites. It thus means that the number of CoMoS phases should be increased or its performance should be improved to progress to better HDS activity. To conduct the former, the possible methods include an increase in the molybdenum and cobalt content; an increase in the surface area of alumina, which is the carrier for these active metals; and effective formation of the highly diffused CoMoS phase.

Meanwhile, to improve the performance per active site, it is considered that a method to adjust the interaction with the carrier may be effective. It has been recently found that the activity becomes higher as the interaction between the alumina carrier and the CoMoS phase is lower [32]. It is known that some chelating agents are effective in forming this type of CoMoS phase, and there are study reports claiming that P, B, and so forth conventionally known to have activity improvement effects somewhat influence the formation of the CoMoS structure. Therefore, several interesting preparation methods are being contrived.

10.4.3.2 ENHANCEMENT OF METHYL GROUP MIGRATION

Acid sites are necessary for migration of alkyl groups on alkyl aromatics, and various Lewis acids are known to work on this reaction. Acid sites of some zeolite are also known to be effective. Thus, examinations are being made on carriers combining these Lewis acids or zeolite with alumina carrier or using zeolite alone as the carrier. However, strong

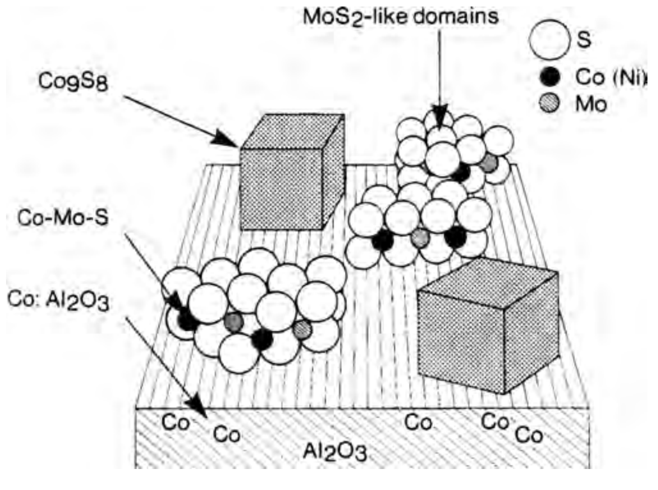


Figure 10.10—Surface structure of sulfided CoMo/Al_2O_3 catalyst proposed by Topsøe and others [31].

acid sites may lead to unfavorable decomposition reactions (reduction of liquid yield) or coke formation reactions (deactivation of catalyst) in addition to the migration of the methyl group, possibly leading to rapid activity deterioration during the initial stages of operation (during SOR). If excessive decomposition or coke formation can be minimized by adding an appropriate acid property, then it may be possible to develop a catalyst that improves catalyst life and promotes methyl group migration.

10.4.3.3 ENHANCEMENT OF HG ACTIVITY

The HG reaction of an aromatic ring to mitigate steric hindrances by methyl groups is expected to be promoted by catalyst metals with good HG activities. Although NiMo, NiW, or precious metal catalysts are normally effective in the HG of condensed polyaromatics, it is known that these catalysts with good HG activities are prone to inhibition of reaction by H_2S, ammonia, and so forth under the reaction conditions. Furthermore, there are negative effects to unnecessarily increase the hydrogen consumption because HG of aromatics that are not related to desulfurization is also facilitated when these catalysts with good HG activities are used. Therefore, some combination of CoMo and NiMo or NiW catalysts has been proposed in the sulfur-free condition.

10.4.3.4 NEW DEVELOPMENTS IN CATALYST SUPPORT MATERIALS

In general, industrial catalysts for HDS comprise Mo or W and Co or Ni on alumina carrier. There are investigation reports indicating that catalysts using titania as the catalyst carrier show better desulfurization activity per unit surface area [33]. Especially regarding HDS of refractory sulfur compound 4,6-DMDBT, some report that it functions better than alumina carrier catalysts. However, because of the disadvantages of titania, including less thermal stability and small specific surface area (~50–60m²/g), there have been few actual cases of industrial manufacturing. The technology to increase the surface area and precisely control the pore size distribution to solve the disadvantages of titania carrier was recently developed [34]. It is an unconventional and interesting catalyst.

10.4.3.5 COMMERCIAL CATALYSTS

The catalysts of catalyst manufacturers and licensers that have been developed and industrialized along one of the concepts explained above are listed in Table 10.5. These catalysts are not limited to those developed for sulfur-free diesel oil but include catalysts for 50-ppm sulfur oil. It is also necessary to select by sufficiently considering the catalyst performance because each has different characteristics (drawbacks and advantages). However, catalyst manufacturers continue to devote their efforts in research and development. It is expected that better catalysts will be manufactured in the near future.

TABLE 10.5—Commercial Catalysts for Deep HDS

Catalyst Manufacturer or Licenser	Catalyst Name
Albemarle	KF-772 KF-757H KF-848 Nebula
ART	SmART (CDX, CDY)
Criterion Catalyst	DC-2318 DC-2531 DN-3330
Halder Topsoe A/S	TK-573 TK-574
IEP Axens	HR-626 HR-526 HR-568 HR-548
Cosmo Oil Co.	C-605A
JGC C&C	CDS-LX6
Nippon Oil Co.	NHS-204

10.5 ADVANCES OF CATALYST TECHNOLOGY IN VGO HYDROTREATING

10.5.1 Advances in Guard-Bed Catalyst

The guard-bed catalyst loading in the reactor top layer is very important to protect the main-bed catalyst against fouling and catalyst poisons, which can severely affect the expected activity and cycle length. The reactor pressure buildup takes place by the accumulation of deposits in the catalyst bed. To remove the effect of deposition on pressure drop buildup and keep good liquid distribution, a grading of catalyst shapes, sizes, and activities is crucial. The foulants that cause the problem in hydrotreating reactors come from several different sources, including the following [35–37]:

- Particulates of widely varying sizes and compositions;
- Gum formation due to reactive molecules such as olefins and oxygenates; and
- Inorganic contaminants, such as iron, nickel, vanadium, arsenic, and silicon.

The particulates include coke fines, iron sulfide, sometimes FCC catalyst fines, and so on and are prospectively removed by grading the catalysts using optimized shape/size and reactivity for the targeted contaminants. Gum formation is a problem commonly seen in commercial hydrotreating reactors, where contaminants of olefins, di-olefins, and oxygenates present in the VGO feed react with the catalyst very rapidly and exothermically, creating problems of reactor fouling, maldistribution, and thermal hot spots. The third type of fouling occurs when inorganic elements such as nickel, vanadium, arsenic, and silicon enter the hydrotreater. These metals are poisons to the hydrotreating catalysts and cause severe deactivation. Hence, poison removal before the main-bed catalysts needs to be properly facilitated. The removal of reactive molecules and inorganic poisons is achieved by a gradual change in the catalyst activity and by applying catalysts with trapping capacity for various metals. A common industrial practice for contaminant control is suitably highlighted by the superior performance achieved by the consecutive use of

- Ketjenfine KG-55 of a specific pentaring alumina (outer diameter [OD] 19 mm, void fraction 62 %)
- Followed by Ketjenfine KF 542-9R/-5R of moderate activity of nickel-cobalt-molybdenum Raschig ring catalysts (9.0/3.5mm and 6.0/2.8mm in OD/inner diameter [ID], void fraction 50 %) for elimination of olefins and oxygenates to prevent gum and coke formation
- Then a nickel-molybdenum alumina Demet catalyst (OD 3–5 mm, void fraction 45 %) for removal of metal poisons.

The higher activity and smaller shaped nickel-molybdenum catalysts at the last Demet position are able to completely remove nickel and vanadium contaminants while maintaining good liquid flow through the catalyst bed [35,36]. The latest development includes the trapping capability of multiple contaminants such as iron, arsenic, and silicon as well as nickel and vanadium. The iron deposition normally originates from corrosion scales, which are of various sizes (0.1–10 mm). However, more difficult to deal with are the organic iron molecules often present in the heavier and high total acid nitrogen (TAN) feeds. These organic iron molecules are very reactive, forming iron sulfide. Iron sulfide in turn accelerates coke formation, through the dehydrogenation reaction at the surface of the catalysts, and the agglomerated catalysts bound with iron sulfide and coke cause serious fouling problems. One of the significant developments for iron trapping capability is Ketjenfine KG-1 [37]. This spherical catalyst (5 mm in diameter) is used for the removal of iron scale and organic iron molecules. The catalyst is designed to trap the iron inside of the pore structure, ensuring maximal iron trapping efficiency and preventing the accumulation of coke on the outer surface of the catalyst particles. Another new development in guard-bed technology is new catalysts that specifically target arsenic and silicon removal. Arsenic is present from several hundreds to thousands of parts per billion in bitumen and some other heavy crudes. Arsenic is a very strong poison for the downstream hydrotreating catalysts; for example, 50 % of catalytic activity can be lost with only 0.1 wt % of arsenic present on the catalyst. Silicon is the contaminant from the crudes and more significantly from the hydroprocessing of coker products. In the coking process, silicon-containing antifoaming agents are used and the decomposed silicon-containing molecules are present in the derived coker products. The poisoning effect of silicon is such that 50 % activity loss can be seen with 12–15 wt % of silicon deposition on the catalyst. Consequently, removal of arsenic and silicon contaminants are of strong interest for optimizing required activity and cycle length as well as nickel and vanadium removal. The latest significant catalytic technology for arsenic, silicon, nickel, and vanadium trapping is Ketjenfine KF 647 and KG 6 [36]. The former catalyst focuses more on silicon trapping and the latter on arsenic trapping, in addition to providing the trapping capacity for nickel and vanadium contaminants. Thus, this kind of multifunctional Demet catalysts plays a very important role for "contaminant management" in the guard-bed reactor and achieving the expected activity and cycle length of the unit. The latest Demet development for common commercial practices is tabulated in Table 10.6.

10.5.2 Advances in Main-Bed Hydrotreating Catalyst

10.5.2.1 CATALYST TECHNOLOGY IN FCC-PT

The hydrotreating of FCC feedstock, to produce a sweetened feed to the FCC unit, can greatly improve the performance of the FCC unit, product selectivity, and product quality. FCC-PT units span a wide range of processing conditions and objectives. Low-pressure units (i.e., 40–60 bar hydrogen partial pressure) primarily address HDS to reduce SO_x emission from the FCC unit and sulfur content in the FCC gasoline. High-pressure units (i.e., 70–100 bar hydrogen pressure) are able to significantly reduce nitrogen, aromatics, and continuous catalytic regeneration (CCR) content of the FCC feed in addition to substantial sulfur reduction. Such high-pressure FCC-PT "sweetening" enables production of much more light fuels of better quality from heavy and hydrogen-deficient feeds. The innovation for VGO hydrotreating catalytic technology has been remarkable in the last decade, often on a par with those observed in the distillate hydrotreating catalytic technology. Cobalt-molybdenum on alumina catalysts has traditionally been used for the HDS objective in low-pressure VGO hydrotreaters. Nickel-molybdenum catalysts have been developed and used for the high-pressure applications to improve the HG activity for more aromatic saturation as well as nitrogen and CCR removal. Historically, either CoMo or NiMo catalysts have been made with alumina support materials of high surface area and acidity. The precursors of NiMo or CoMo metals are then impregnated onto the alumina, dried, and calcined to make the final catalysts. The key technology here is to produce a high activity catalyst by high dispersion of the active metal species of CoMoS or NiMoS or both onto the support materials. The improvement and optimization of support acidity, pore structure, and manufacturing technologies have been the major focus in developing high-activity catalyst via high dispersion of the active species. Such catalysts have much more interaction between the support and metal species and are referred to as Type I catalysts, as tabulated in Table 10.7.

The classic approach for catalyst development had been the improvement of metal species dispersion for the increased active sites. However, Albemarle found in the late 1990s that the metals-support interaction was even more important for improving intrinsic activity. Albemarle and Nippon Ketjen commercialized a new, superior CoMo catalyst called Ketjenfine 757 by applying a proprietary and patented production technology in 1998. This catalyst achieved very deep HDS in distillate and VGO hydrotreating applications [38–48]. Ketjenfine 757 was developed for the first time using a new catalyst design concept (i.e., highly dispersed active sites of an optimized metals-support interaction to improve the intrinsic activities), thereby providing an overall higher catalytic activity. Albemarle named such

TABLE 10.6—Albemarle's Guard-Bed Technology for Multiple Contaminant Control [35–37]

	KF 647	KF 648	KF 841	KG 6
Function	Hydrogenation Demet	Hydrogenation Demet	Hydrogenation Demet	Arsenic trap
Removes	Ni, V, As, Si	Ni, V	Ni, V	Ni, V, As
Composition	NiMo	NiMo	NiMo	NiMo
Shape	Quadralobe	Quadralobe	Quadralobe/cylinder	Quadralobe
Diameter (mm)	1.3/2.6	1.3/2.6	1.3/2.1/2.6	2.6
Av. length (mm)	3.5/5.0	3.5/5.0	3.5/5.0	5.0
Sock density	510	510	625–695	530

TABLE 10.7—Albemarle's Type I and Type II Latest Catalytic Technologies [38,39]

Product	Size/Shape	Composition/ Type	Characteristics
KF 752	1.5E, 2E, 3Q	CoMo Type I	Moderate HDS activity catalyst
KF 756	1.5E, 2E, 3Q	CoMo Type I	Higher HDS Type I catalyst
KF 757	1.5E, 2E, 3Q	CoMo Type II STARS	High HDS Type II catalyst
KF 767	1.5E, 2E, 3Q	CoMo Type II STARS	Higher HDS Type II catalyst
KF 770	1.5E, 2E, 3Q	CoMo Type II STARS	Much Higher HDS Type II catalyst
KF 901	1.5E, 2Q	NiCoMo Type I	Moderate HDS and HDN Type I catalyst
KF 905	1.5E, 2Q	NiCoMo Type II STARS	Higher HDS and HDN Type II catalyst
KF 841	1.3Q, 3Q	NiMo Type I	Moderate HDN activity
KF 846	1.3Q, 3Q	NiMo Type I	High HDN activity catalyst
KF 848	1.3Q, 2Q	NiMo Type II STARS	High HDN Type II catalyst
KF 857	1.3Q, 2Q	NiMo Type II STARS	Higher HDN Type II catalyst
KF 860	1.3Q, 2Q	NiMo Type II STARS	Higher HDN Type II of high stability

HDN = hydrodenitrification.

new catalytic active sites as Super Type-II Active Reaction Sites (STARS™) [38,39]. The highly dispersed Type II sites of optimized support-metals interaction in STARS ™ technology can achieve at least 30 % higher activity than the classic Type I catalysts. As shown in Figure 10.11, the Type II catalyst shows a highly dispersed single-layer MoS_2 of curvature structure. The reaction turnover frequency at Type II sites was found to be significantly increased, showing an activity benefit of 60 % or even higher (Figure 10.12) at the deeper HDS conditions as compared with the classic Type I technology. Ketjenfine 848 is a high-activity NiMo catalyst of Type II technology that is available.

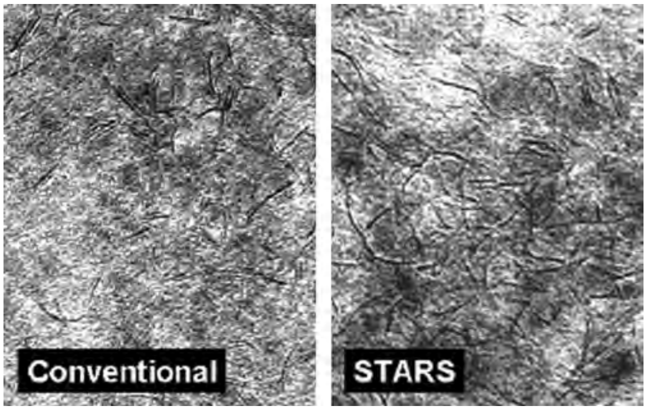


Figure 10.11—Transmission electron microscopy micrographs of conventional and STARS catalysts.

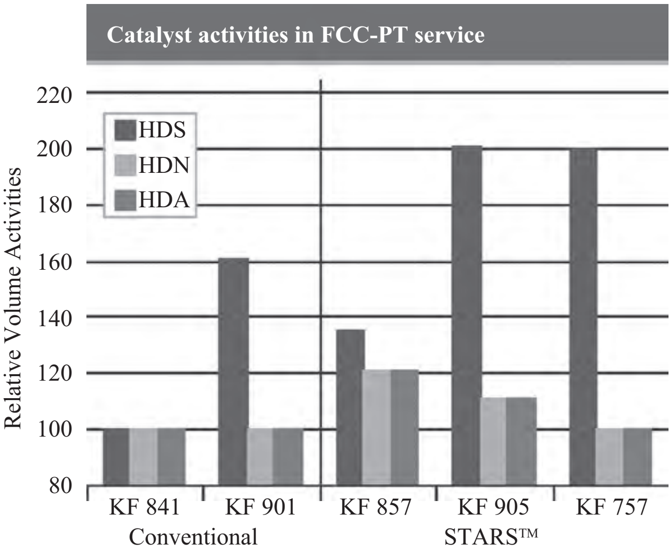


Figure 10.12—Volumetric activities in FCC-PT VGO service [38,39].

The Type II catalytic development was also accompanied by optimization work in the catalyst activation and its required application. The best optimized liquid sulfiding procedure and conditions were identified to maximize the intrinsic activity of the Type II catalytic activity sites [41]. To enable refinery gas-phase sulfiding in certain units, a specific liquid treatment of PROTECT™ is also applicable to Type II STARS ™ catalytic technology for catalyst activation/startups that cannot use a liquid-phase activation procedure [41]. The rejuvenation technology called REACT™ was also developed to allow refiners the opportunity for multiple use of a given Type II catalyst in which activity recovery of more than 90 % can be routinely achieved [41]. Thus, the catalytic development in VGO hydrotreating has been principally advanced and improved through the new concept of optimizing metals-support interaction under a highly dispersed state and the application technologies of optimal sulfiding and reactivation for multiple use of a given catalyst. The Type II STARS technology is one of the greatest achievements in the hydrotreating catalytic technology developments in the last several decades. The technology has provided the step-out performance increase required by the market via a new catalytic concept and helps the refineries achieve the ultralow sulfur regulation in gasoline and diesel products.

There are several other catalytic advances published concerning catalyst characteristics [49–54]. The University of Aarhus and Haldor Topsøe succeeded in obtaining the atomic scale of Co-Mo-S structure present in the hydrotreating catalyst by means of scanning tunneling microscopy (STM) [49]. They clarified that the presence of the cobalt promoter atom causes the MoS_2 nanocluster shape to change from a triangular to a hexagonally truncated form. This morphological transformation drives the preference of the cobalt atom to be presented at the sulfur edge of MoS_2 and changes the electronic environment of the neighboring sulfur atoms for improved HDS activity. Haldor Topsøe claimed that the new BRIM active site of metallic character is created on the top of MoS_2 slabs close to the edge and plays an important role for prehydrogenation for the succeeding HDS reaction. They mentioned that the optimal balance of BRIM sites together with Type I and Type II sites is the key technology for improved catalytic activity and subsequently developed several new BRIM catalysts on the market [50,51]. Criterion published that high dispersion of Type II catalytic active sites of easier sulfidability is crucial for activity improvement [52]. They claim that highly dispersed Type II sites of smaller slab size and less stacking structure can be made by a specific catalyst preparation technique, and it can then enable a 100 % sulfidable MoS_2 structure of resultant high activity. They also suggested that the optimal balance of Type I and Type II can be important for stability and longer cycle length as well as the SOR activity [53]. Thus, an in-depth understanding of the active site structures and their functionalities has progressed, thereby leveraging the extensive catalytic activity improvement seen in the last decade.

10.5.2.2 CATALYST TECHNOLOGY IN A HYDROCRACKING PRETREATER

Hydrocracking (HC) is another VGO process to produce naphtha and diesel fractions. Because the nitrogen in the feed causes substantial inhibition to the acid sites of zeolitic or silica-alumina catalysts or both in the HC reactor, nitrogen removal is required in a HC pretreater (HC-PT). Thus, a higher hydrodenitrification (HDN) activity HC-PT catalyst is able to improve the performance of the HC process through allowing more feed barrels or difficult feedstocks or both of lower cost to be processed. KF 848 was the first STARS ™ Type II NiMo catalyst of improved HDN activity for the HC-PT service and achieves 30–50 % higher HDN relative to the conventional Type I catalyst used previously in the HC-PT application. The latest development in this STARS catalyst market has brought even higher HDN activity catalysts than described above [45,46].

Albemarle, Nippon Ketjen, and ExxonMobil jointly developed the unprecedented high-activity catalyst Nebula™ in 2001 [43,44,55,56]. The Nebula™ breakthrough technology reaches previously unattainable levels of desulfurization, denitrogenation, and aromatic saturation in kerosene, distillate, and VGO applications. The Nebula™ concept represents, in the author's opinion, the greatest single step forward since the beginning of hydroprocessing catalyst development in the 1950s, as amply illustrated in Figure 10.13. Nebula™ also shows great benefits in the demanding commercial applications of HC-PT as shown in Figure 10.14.

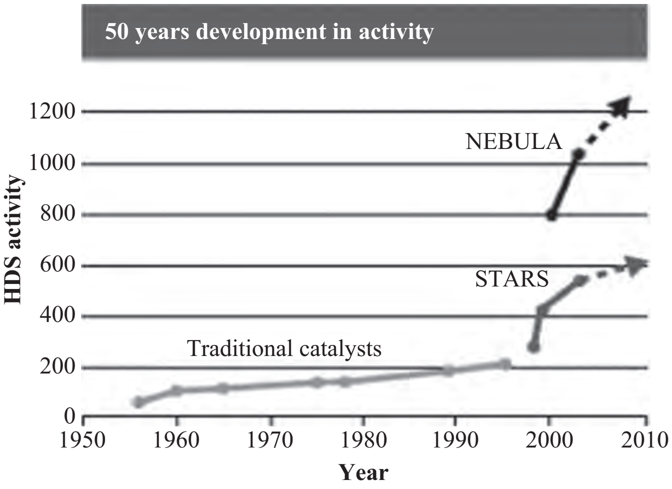


Figure 10.13—Catalytic activity of conventional, STARS, and Nebula technologies.

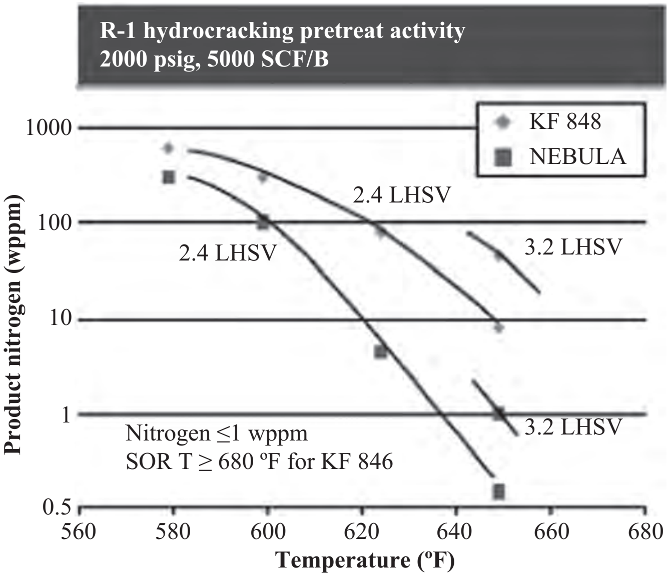


Figure 10.14—HDN activity in HC-PT with KF 848 and Nebula.

10.5.2.3 CATALYST TECHNOLOGY IN MILD HYDROCRACKING

Mild hydrocracking (MHC) is a hydroprocessing application for partially converting VGO to primarily middle distillate products while achieving the needed HDS activity. MHC is typically a low to medium conversion process (ca. <50 %), usually being operated at relatively moderate pressure conditions of approximately 40–70 bar hydrogen partial pressure, typically with a single reactor. The product quality of the distillate depends strongly on the feed properties and unit pressure—such products usually need further hydrotreating to then be suitable for the clean fuel pool. The product VGO makes an excellent FCC feedstock, and as a consequence, some FCC-PT units of moderate pressure are operated in MHC mode to produce more distillate at a higher temperature while providing a good FCC feedstock. The catalysts for MHC operation need CoMo or NiMo or both on alumina-, amorphous silica-alumina-, or zeolitic-containing support for the enhanced cracking activity of reasonable stability [41,57]. Table 10.8 shows Albemarle's latest MHC catalyst portfolio. These catalysts have demonstrated the expected HDS, HDN, conversion to distillate, and satisfactory stability in various commercial applications. The latest commercial practice has started to apply Type II catalytic technology to the MHC application for better performance and stability for longer cycle length.

10.6 CATALYSTS FOR BOTTOM-OF-THE-BARREL UPGRADING: RDS/VRDS AND OCR/UFR CATALYSTS

10.6.1 Introduction

The bottom-of-the-barrel (i.e., atmospheric residue [AR, 345ºC+] or vacuum residue [VR, 565ºC+]) is of limited direct use because of its high specific gravity; low

TABLE 10.8—Albemarle's Fulfilled MHC Catalytic Technology

Product	Size/ Shape	Composition/ Type	Characteristics
KF 1014	1.5E, 3E	NiMo amorphous	Moderate activity—distillate selective
KF 1015	1.5E, 3E	NiMo amorphous	Moderate activity—distillate selective
KF 1022	1.5E	CoMo amorphous	Moderate activity—distillate selective
KF 1023	1.5E	NiMo amorphous	Moderate activity—distillate selective
KC 2301	1.5E, 2E	NiMo zeolitic	High activity—distillate selective
KC 2601	1.5E, 3E	NiMo zeolitic	High activity—distillate selective
KC 2602	1.5E, 3E	CoMo zeolitic	High activity—distillate selective

hydrogen-to-carbon ratio; and high concentrations of sulfur, nitrogen, nickel, vanadium, and other impurities. The residuum desulfurization (RDS) or vacuum residuum desulfurization (VRDS) process, in combination with the on-stream catalyst replacement (OCR) or upflow reactor (UFR) process possibly present upstream, can achieve greater than 98 % hydrodemetalization (HDM), greater than 95 % HDS, greater than 70 % HDN, and further upgrade residuum via microcarbon residue (MCR) reduction (HDMCR) of greater than 70 % and VR conversion of up to 60 liquid volume (LV) % [58,59]. The upgraded residuum can be used as low-sulfur fuel oil or as feed to residuum FCC (RFCC) and delayed coker units [60,61]. Typical ranges of feed and product properties of the OCR/UFR-RDS process are summarized in Table 10.9.

The early RDS units contained catalysts adapted from VGO hydrotreating catalysts to remove sulfur and generate low-sulfur fuel oil. Because of the deposition of metals in feed on the surface and in the small pores of these catalysts as sulfides, the HDS activity fouls rapidly when metal concentration in the feed exceeds 10–20 ppm [62]. The catalyst system used in the RDS/VRDS process now consists of layered catalysts so that the residuum is sufficiently demetalized by catalysts of high HDM activity before contacting catalysts of high conversion activities (i.e., HDS, HDN, and HDMCR). The layered catalyst system allows effective handling of residuum of high metal content for an extended period of time and can be tailored to emphasize specific catalytic functions depending on the feed properties and the end use of the upgraded residuum. For example, HDS and HDMCR functions are more important for low-sulfur fuel oil production and delayed coker feed generation, whereas HDM, HDMCR, and HDN functions are of more emphasis for RFCC feed generation.

TABLE 10.9—Typical Feed and Product Properties of OCR/UFR-RDS Processes

	AR Feed	RDS Product
API	10–20	16–23
Sulfur (wt %)	2–5	0.25–0.70
CCR (wt %)	8–17	3–7
Nickel + vanadium (ppm)	40–160	5–25

The length of a RDS/VRDS run is limited by the metal capacity of the catalyst system and the metal concentration of the residuum processed [63]. In practice, the needs of a refiner are met by balancing the metal capacity of a catalyst system with its upgrading capability to meet a regular maintenance turnaround schedule. The commercialization of the OCR process in 1991 using a spherical HDM catalyst that can be replaced onstream enables refiners to retrofit existing RDS units for handling heavier residuum feed of higher metal content while maintaining or improving run length.

Residuum hydrotreating catalyst development efforts at Chevron over the past few decades have led to the commercialization of many catalysts (Table 10.10). The heavy investment in technology continues at Advanced Refining Technologies (ART), a joint venture between Chevron and Grace Davison since 2001. Currently, ART supplies more than half of residuum hydrotreating catalysts worldwide.

10.6.2 General Catalyst Functionality and Deactivation Mechanism

Residuum consists of asphaltenes (large polynuclear aromatic compounds insoluble in paraffinic hydrocarbons) surrounded by resins in micelle form to remain dispersed in saturates and aromatics [64]. The metals (nickel, vanadium, etc.) are typically present as high-molecular-weight organometallic

TABLE 10.10—Resid Hydrotreating Catalysts Introduced since RDS/VRDS Commercialization

Year	HDM Catalyst	HDS Catalyst
1969		GC-101
1974		ICR 105
1975		GC-100, 102
1979		GC-105, 106, 107
1981	ICR 121	
1982	ICR 122	
1984	GC-125, 130	
1985		GC-102, 107
1987		ICR131
1988	ICR132	
1990	ICR 133, 122H	ICR 135, 145, 146
1991	ICR 138	ICR 137
1995		ICR 148
1996	ICR 149	
1997	ICR 151	
1999		ICR 153
2000	ICR 161	
2001	ICR 167	
2004	ICR 165	ICR170, 171

compounds (such as metalloporphyrins) in the asphaltene and resin fractions of residuum. In contrast, most of the sulfur is often present as lower molecular weight compounds in the aromatic and resin fractions [65]. This difference in distribution between metals and sulfur, combined with the fact that the deposition of metals in the feed as sulfides on catalyst is irreversible, makes physical properties of residuum hydrotreating catalysts as important as chemical properties for their performance, as discussed later in this section.

Residuum hydrotreating catalysts typically consist of γ-alumina support impregnated with active metals (i.e., molybdenum promoted with nickel or cobalt or both). These active metals are initially present as oxides on the alumina support and are converted to corresponding sulfides in situ. The metal sulfides are the catalytically active phases in the reaction environment. The molybdenum loading is typically sufficient so that the molybdenum sulfide phase is formed at high coverage and high dispersion on the alumina support. The nature of active sites involved in reactions occurring in residuum hydrotreating is highly complex because of the large variety of molecules in the feed. Studies conducted with much lighter oils and model sulfur compounds suggest that the edge sites of the MoS_2 slab decorated by cobalt or nickel are involved in the HDS reaction [66]. It is possible that other parallel reactions such as HDN and HDMCR may involve different sites.

The activity (HDM, HDS, etc.) and life of residuum hydrotreating catalysts are strongly affected by their physical properties, including surface area, pore volume, and pore size distribution [63,67]. In general, physical properties that favor HDM activity are undesirable for HDS activity and vice versa. This point is illustrated in Figure 10.15, which shows the inverse correlation of HDM and HDS activity with pore size. As the average pore size increases, so does the diffusion rate of high-molecular-weight organometallic compounds inside of the catalyst pellet, leading to better HDM activity. On the other hand, the larger pore size of HDM catalysts also means lower surface area for supporting active metals, which results in lower conversion activity. Conversely, conversion catalysts have smaller pores and higher surface area. The higher surface area in conversion catalysts allows better dispersion of MoS_2 slabs at higher molybdenum loading on the alumina support to form more active sites. The smaller mesopores are large enough for most of the lower molecular weight sulfur compounds to access the active sites inside of the conversion catalyst pellets. Conversion catalysts have limited HDM activity because of the much-hindered diffusion of large organometallic molecules inside of the catalyst pellets.

To better manage the large-pore (HDM) versus small-pore (conversion) dilemma, a typical RDS/VRDS catalyst system is layered such that the HDM activity is higher toward the inlet where the metal concentration in residuum is the highest. Conversion activity is higher toward the outlet so that residuum of decreasing metal concentration trickles down the reactor, contacting increasingly more active conversion catalysts.

The deactivation of the RDS/VRDS catalyst system proceeds through a characteristic initial rapid deactivation period, middle-of-run slow deactivation period, and end-of-run ultimate deactivation period (Figure 10.16). The average catalyst temperature of a RDS/VRDS unit is raised to meet a product specification (usually sulfur content). Figure 10.16 shows the temperatures required for meeting sulfur target versus metals deposited on the catalyst system as a measure of run length. During the initial period of contact with residuum, the rapid buildup of coke on catalyst (up to 20 wt %) leads to loss of catalyst surface area and pore volume. The asphaltene fraction in residuum is a major contributor to coke formation. Metal deposition has also been suggested to contribute to the initial rapid deactivation period [67]. The slow deactivation in the middle of the run is primarily due to accumulation of metal sulfides, which reduces catalyst porosity and surface area. The buildup of metal sulfides eventually reduces the mesoporosity to the extent that heteroatom-containing molecules are excluded from the catalysts, leading to the ultimate deactivation.

Analysis of spent catalysts reveals that the extent of penetration of metal sulfide deposits into the catalyst pellets decreases significantly as the pore size decreases from the top (HDM section) to the bottom (HDS section) of the catalyst bed. Metal sulfide deposits are spread fairly uniformly over the cross-section of an HDM catalyst pellet near the reactor inlet. On the conversion catalyst near the reactor outlet, most metal sulfide deposits are concentrated near the edge of the catalyst pellet. This high concentration of metal sulfide deposits near the catalyst edge is responsible for pore mouth plugging, which causes the ultimate deactivation.

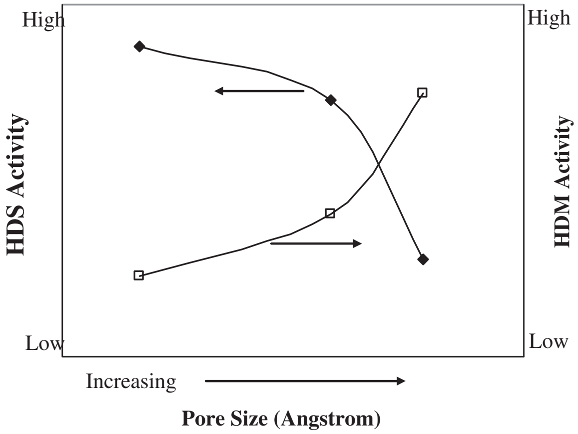


Figure 10.15—HDS and HDM activity trade off as pore size changes.

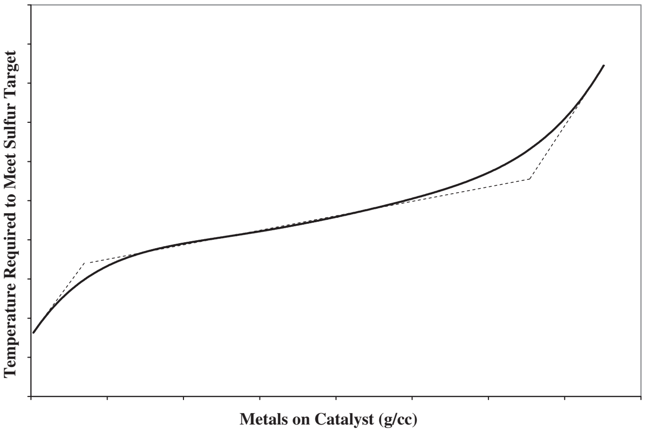


Figure 10.16—Typical deactivation curve for RDS catalyst system.

10.6.3 Practical Considerations for Residuum Hydrotreating Catalysts

The HDM catalysts used in RDS/VRDS processes often have several grades of nominal diameters. At the reactor inlet, catalyst size gradually decreases so that particulates present in residuum are filtered out over several layers. This catalyst grading practice reduces the tendency of particulates to cause excessive pressure drop increase, especially in the bed containing the catalyst of the smallest size. The physical grading technique is based on extensive refinery experience, dating back to when Chevron first developed top-bed grading technology to minimize the effect of high levels of insoluble iron in some California crudes on refinery operations [62].

The spherical catalysts for the UFR/OCR process are designed following principles similar to HDM catalysts for RDS/VRDS. However, these spherical catalysts have specific density requirements to maintain the plug flow of catalyst down the OCR reactor. The plug flow of catalyst and the countercurrent feed flow maximize catalyst effectiveness by exposing the most metal-loaded and least active catalyst to the fresh residuum before being removed from the reactor. It is also critical for these spherical catalysts to have high resistance to attrition because fines generated from the moving bed operation can change the flow regime inside of the reactor and contaminate other processes downstream of the OCR unit. The spherical γ-alumina support materials for UFR/OCR catalysts are formed from pseudoboehmite via a Grace proprietary process.

The γ-alumina support materials for RDS/VRDS catalysts are formed from pseudoboehmite by peptization, extrusion, and high-temperature calcination. The extrudates typically have a multilobe cross section. This shape provides a higher ratio of external surface area per unit volume such that higher diffusion rate, higher contaminant metals tolerance, and lower pressure drop buildup rate can be achieved compared with cylindrical extrudates [63,68]. The pseudoboehmite raw materials are custom manufactured at Grace by precipitation of acidic and basic solutions of aluminum salts, followed by washing and drying under complex operation conditions [69].

10.6.4 Developments and Improvements

The backbone of the RDS/VRDS catalyst system has traditionally included three catalysts: ICR132 of excellent metal removal activity and high metal capacity, ICR137 of good conversion activity (i.e., HDS, HDMCR, and HDN) and high metal tolerance, and ICR131 of high conversion activity and moderate metal tolerance.

To meet the demand for a catalyst system capable of handling heavier feedstock, HDM catalysts of higher metal removal activity and metal capacity and conversion catalysts of higher sulfur, nitrogen, and MCR removal activity are both desired. Better engineering of conversion and HDM activity tradeoff can also contribute to higher cumulative HDS and HDM activity for the full system.

A new HDM catalyst, ICR161, has very high HDM activity to better protect the conversion catalysts and extra metal capacity to delay the onset of ultimate deactivation in the HDM bed. Another new HDM catalyst, ICR167, improves HDS and HDMCR activity of HDM section without significantly reducing metal capacity. The ICR161/167 combination has higher HDM activity, metal capacity, and HDS activity than traditional HDM catalyst ICR132, as shown in Figure 10.17.

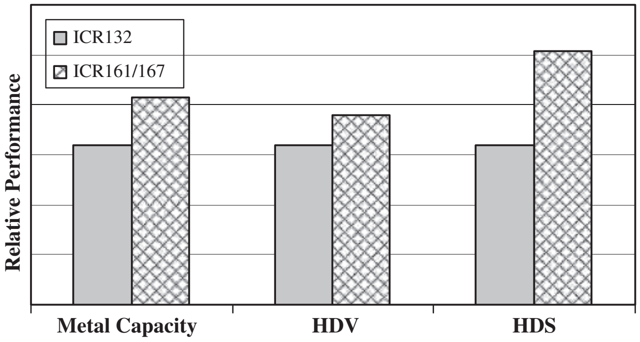


Figure 10.17—Improved performance of new HDM catalysts vs. traditional HDM catalyst.

A new conversion catalyst, ICR170, is used at the front end of the conversion bed to increase tolerance of the conversion catalyst bed to metal leakage from the HDM section without significantly reducing the HDS activity. The metal capacity of ICR170 is 20 % higher than that of traditional conversion catalyst ICR131. Figure 10.18 shows the HDMCR, HDS, and HDV activities of ICR170, 131, and 137. The HDS and HDMCR activities of ICR170 are better than those of ICR137 with a slight compromise in HDV activity. Another conversion catalyst, ICR171, of very high conversion activity is suitable for applications requiring very low product sulfur (0.1–0.5 wt %). This deep conversion catalyst is used at the end of the conversion bed where metal concentration has been sufficiently reduced. The HDS and HDMCR activities of ICR171 are superior to those of the deep conversion catalysts ICR153 and 135 with some tradeoff in HDV activity, as shown in Figure 10.19.

The main focus of OCR/UFR catalyst development has been to improve physical properties of the spherical support.

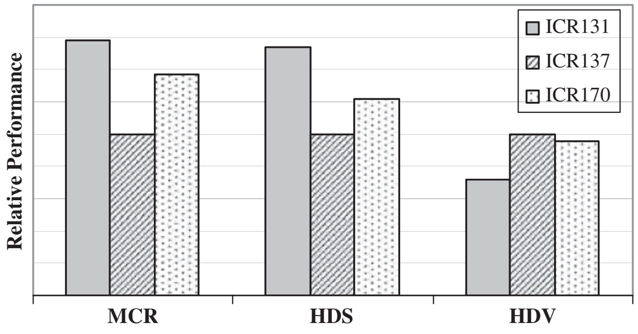


Figure 10.18—Comparison of HDMCR, HDS, and HDV activities of three conversion catalysts.

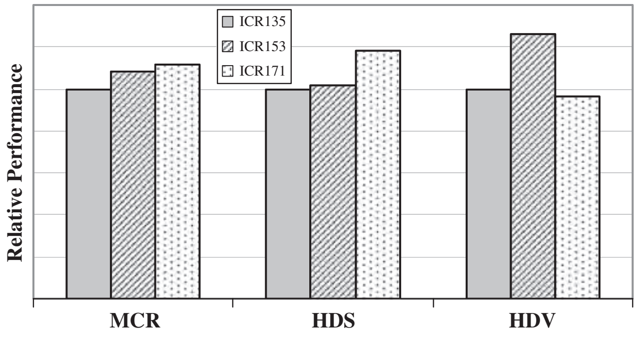


Figure 10.19—New deep conversion catalyst of superior HDMCR and HDS activities.

The original ICR138 has been expanded into three grades of increasing size to improve reactor hydrodynamics and accommodate feedstock with a wider range of properties. The new OCR/UFR catalyst ICR165 commercialized in 2004 has enhanced HDS function compared with ICR138.

10.6.5 Design of RDS/VRDS Catalyst System

The extensive range of ART residuum hydrotreating catalysts allows great flexibility in designing an RDS/VRDS catalyst system for various feedstocks depending on the end use of the upgraded residuum. The design of a layered catalyst system is a compromise between conversion activity and metal capacity. A good kinetic model considering feed reactivity and deactivation rate relative to metal and coke buildup is essential for the task. Extensive pilot plant studies have been conducted at Chevron to quantify feedstock reactivity differences on various residuum hydrotreating catalysts. These differences are largely due to the different distribution of heteroatoms in asphaltenic and nonasphaltenic fractions of residuum from various sources around the world.

By varying the selection and relative volume of HDM and conversion catalysts, catalyst systems can be designed to accommodate refiners processing residua of a wide range of contaminant levels. Two illustrative catalyst systems of different HDS deactivation pattern relative to metal capacity when processing an AR of Middle Eastern origin are shown in Figure 10.20. A refiner that needs to meet very strict sulfur specification and uses light residuum feed is likely to prefer catalyst system A, which limits the level of metals in residuum that the refinery can process without suffering earlier-than-planned shutdown. Refiners with less strict sulfur target are likely to prefer catalyst system B with extra metal capacity for processing heavier feedstock of lower cost.

10.6.6 Summary

A new generation of residuum hydrotreating catalysts has been developed as a result of research and development efforts at ART that builds on the expertise in residuum hydrotreating accumulated over the past few decades at Chevron. These advances in catalyst technology lead to a net gain of impurity removal capability and capacity in OCR/UFR-RDS/VRDS processes, allowing more challenging feedstock to be processed. Meanwhile, the new additions to the extensive family of residuum hydrotreating catalysts provide more flexibility in customizing a catalyst system to meet/exceed specifications for downstream applications.

Residuum hydrotreating catalyst technology is continuously challenged by the increasing level of impurities in residuum feedstock. The industrial trend of increasing demand for high-value petroleum products [70,71] and decreasing demand for fuel oil from residuum also plays an important role in guiding next-generation catalyst developments.

10.7 SOLID ACID CATALYSTS FOR MOTOR FUEL ALKYLATE

Replacing toxic liquid acids (e.g., hydrofluoric and sulfuric acid) with solid acid catalysts is a challenging goal for isoparaffin alkylation technology because of the rapid deactivation of solid acid catalysts. Although zeolite catalysts (e.g., USY zeolite and zeolite β with sufficient acidity for alkylation) have shown appropriate activity, most have life measured in hours or even minutes. The catalyst design concept for solid alkylation is to exhibit (1) high activity to enhance alkylation reactions and limit side reactions, and (2) the stability and regenerability characteristics to be repeatedly fully recovered at near-reaction conditions.

Solid acid catalysts applied for the Alkylene™ process, the Alkyclean™ process, and the Fixed-Bed Alkylation (FBA™) process are shown in Table 10.11.

TABLE 10.11—Solid Acid Catalysts Applied for the Alkylation Processes

Process	Licensor	Catalyst
Alkylene™	UOP	Supported metal catalyst
Alkyclean™	ABB Lummus Global	Supported noble metal zeolite
	Akzo Nobel Catalysts	
FBA™	Topsøe	Supported liquid catalyst

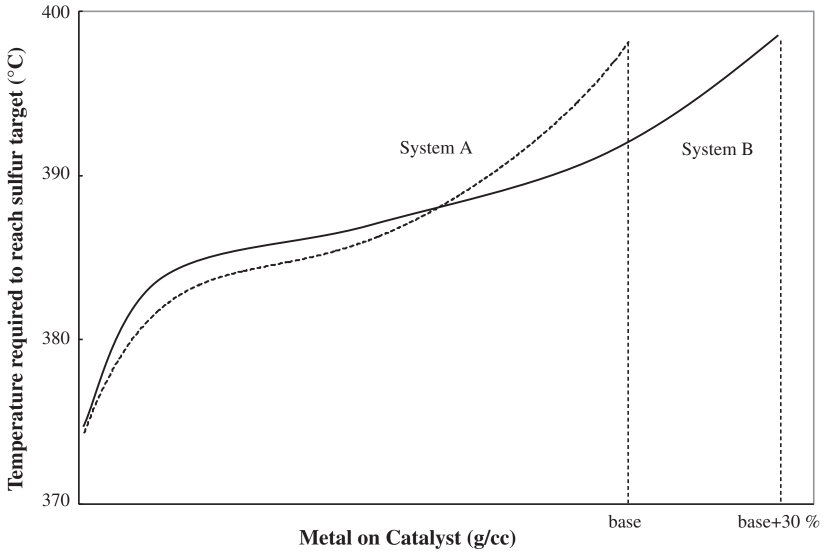


Figure 10.20—The design of an RDS catalyst system is a compromise between conversion activity and metal capacity.

10.7.1 Alkylation Chemistry

The reaction is initiated by the formation of tertiary butyl carbenium ions ($i\text{-C}_4{+}$) on the acid sites of the solid catalyst as shown in Figure 10.21. The alkylation of C_4 olefins with this $i\text{-C}_4{+}$ on the catalyst surface forms $i\text{-C}_8{+}$ (carbenium) ions. Hydride transfer from another isobutene molecule forms a C_8 paraffin product and another carbocation that will propagate the reaction. In this mechanism, a high isobutene-to-olefins ratio in the reaction environment and high hydrogen transfer reaction rates favor the formation of trimethylpentane (TMP), which has a high octane value and is the more desirable C_8 product when compared with dimethylhexane.

When reaction time is increased, isomerization equilibrium favors the formation of lower octane dimethylhexane. The optimal contact time to maximize alkylate product quality is critical. Lower temperature and higher isobutene-to-olefin ratio (I/O) in the reaction environment increase overall selectivity toward TMP over lower octane side reaction products.

10.7.2 Catalyst for Alkylene™

The supported metal catalyst was developed based on UOP's extensive expertise in developing supported platinum catalysts such as the CCR platforming process [73]. Metals on the catalyst hydrogenate and strip unsaturated, high-molecular-weight hydrocarbons blocking active sites on the catalyst surface by contacting the catalyst with hydrogen and isobutene. The catalyst has optimal particle size and pore distribution to allow for good mass transfer into and out of the catalyst. The catalyst, which has high physical strength, has been demonstrated to have very low attrition rates by extensive physical testing.

10.7.3 Catalyst for FBA™

The FBA™ process applies a unique fixed-bed reactor coupled with a liquid superacid catalyst adsorbed on a particulate porous solid [74]. The various components such as liquid superacid, reaction intermediates, and hydrocarbons interact with the porous solid according to their individual polarities as follows; fresh liquid acid > spent liquid acid > intermediates (ester type intermediates) > hydrocarbons. The catalyst zone slowly migrates through the supported bed in the direction of the hydrocarbon flow. The migration of the catalyst zone is closely coupled to the alkylation chemistry and to the interaction between various components and the catalyst. The liquid hydrocarbon phase passes through the fixed bed in plug flow. The olefins in hydrocarbons react with the acid to form an ester. The ester is less strongly adsorbed on the solid support than the acid and moves downstream into the olefins' lean and acid rich environment with the hydrocarbon flow. In a reaction zone of low olefin concentration and higher acid activity, the ester reacts with isobutene to form alkylate and an acid molecule, which prevents olefin oligomerization.

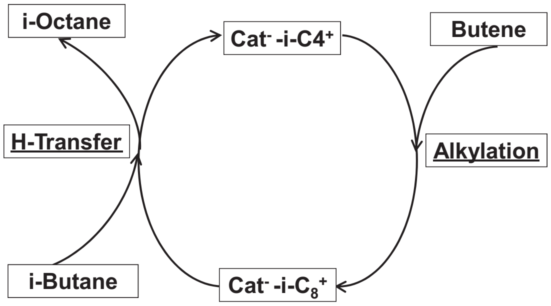


Figure 10.21—Alkylation reaction mechanism [72].

The spent acid, having a weaker interaction with the support than the active acid, moves downstream of the acid zone and is removed for recovery outside of the reactor system. Thus, the catalyst activity can be maintained without interruption of the alkylation operation. FBA™ pilot plant results with different feedstocks are shown in Table 10.12. The research octane number (RON)/motor octane number (MON) of the alkylate from the FBA™ process using FCC-derived mixed butylenes as a feedstock was 95/92 at an I/O of 14 and reactor inlet temperature of 8°C. The product quality reflects the variation in feed quality and operating conditions. Increasing the inlet temperature from 8 to 31°C results in a decrease in product quality of 2–3 RON and 1–2 MON. Half reduction in feed I/O from 14 to 7 lowers the RON by 2 and the MON by 1 octane number. A lower feed I/O reduces utility costs and improves the process economics.

10.7.4 Catalyst for Alkyclean™

The noble zeolite-based catalyst that contains no halogens has acid sites with sufficient strength for alkylation and exhibits the required activity, stability, and regenerability characteristics [72]. In Akzo's patents, the solid acid catalyst is Y zeolite or zeolite β with 0.01–2 wt % of Group VIII noble metal, especially palladium or platinum [75].

TABLE 10.12—FBA™ Pilot Plant Results with Different Feedstock and Product Quality Sensitivity to Reactor Inlet Temperature and I/O [74]

	Feed 1		Feed 2		Feed 3
Feedstock, wt %					
Propane	0.1		0.2		17.7
1-Butene	2.3		15.6		9.3
2-Butene	63.4		29.2		18.5
Isobutene	0.3		19.8		7.3
Pentenes	0		0.4		5.2
Isobutene	0.7		26.7		19.3
Other paraffins	33.2		7.7		22.6
Butadiene	0		0.4		0.1
Operating conditions					
I/O	15	14	14	7	15
Reactor inlet temperature, °C	5	8	31	8	5
Product quality					
RON	98	95	92	93	93
MON	95	92	91	92	91

Moreover, the catalyst is resistant to potential feed impurities, such as water, oxygenates, sulfur compounds, and butadiene. The catalyst is regenerated with dissolved H_2 under regeneration conditions close to reaction conditions by switching the fixed-bed reactor. The durability of the catalyst was demonstrated over hundreds of cycles of rejuvenation and multiple moderate temperature regeneration.

Table 10.13 shows the effect of various regeneration procedures on the life of the regenerated catalyst. The catalyst activity can be repeatedly fully recovered by vapor phase stripping with H_2 at 230°C. However, such a regeneration procedure is not practical because the heating up and cooling down periods required at the start and end of a regeneration cycle take too much time. Catalyst can be regenerated in the liquid phase with dissolved H_2 at regeneration conditions that are close to alkylation reaction conditions.

10. 8 CATALYSTS FOR HYDROGEN PRODUCTION

10.8.1 Steam Reforming Catalysts

A highly active steam reforming catalyst, named ISOP catalyst, was developed by Toyo Engineering Corporation (TOYO) for hydrogen and synthesis gas (syngas) production from light natural gas, the reaction activity of which is 3–4 times higher than current market catalysts that have similar activities to one another.

TABLE 10.13—Effect of Various Regeneration Procedures on the Life of Regenerated Catalyst [75]

	Temperature (°C)	Pressure (Bar)	Time (h)	Catalyst Life (h)
Fresh catalyst				10
H_2 gas*	230	21	1	10
H_2 gas*	230	21	1	10
H_2 gas*	230	21	1	10
i-C_4 liquid with dissolved H_2	90	21	66	6.5
i-C_4 liquid with dissolved H_2	115	30	18	4

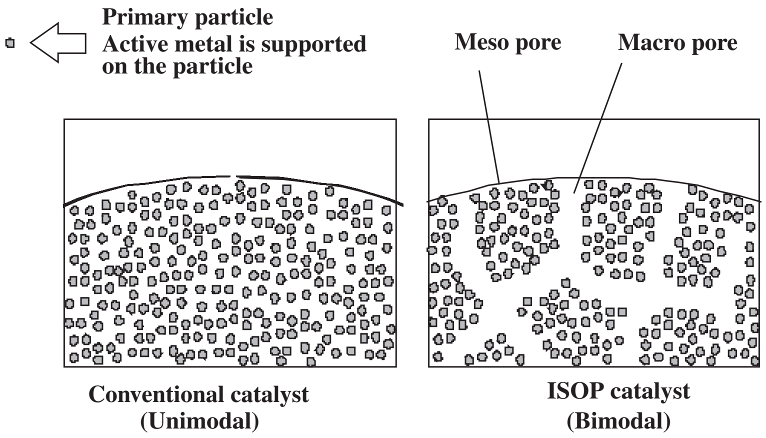
*Repeated regeneration

TOYO has licensed the manufacturing right of the ISOP catalyst to Sued-Chemie Catalyst Japan Ltd. and Sued-Chemie Catalyst, Inc. of the United States. The commercial track records in the ISOP catalyst are more than 15 years for fuel cell plants and more than 10 years for large-scale industrial plants. The ISOP catalyst has been authorized by Kellogg Brown & Root (KBR), one of the renowned licensors of the ammonia process in the world, and has been in commercial operation in Japan, Bangladesh, Germany, and Indonesia.

Ni/Al_2O_3 with alkaline or Ni/MgO constitutes other currently available conventional catalysts for large-scale plants. The pore structures of these catalysts become similar to each other because of sintering of supports in operations at elevated temperatures (500–800°C) whereas their fresh properties are quite different from each other [76]. These catalysts have commonly large diffusional resistance (e.g., the effectiveness factor at the reformer inlet is 0.2 and that at the outlet is typically 0.05), and every catalyst shows a similar apparent activity within a few hundred hours of operation. On the other hand, ISOP catalyst prepared by thermally stable components has a bimodal pore structure having mesopore, or micropore in a case, and macropore together as shown in Figure 10.22 so that the effectiveness factor increases without any sacrifice of nickel dispersion.

The concept on the increasing activity is shown in Figure 10.23. The macropore in the bimodal structure contributes to increasing the effective diffusivity (Dev) into active sites. Further, nickel was designed to be supported so as to disperse more finely and retain the finer condition [77].

ISOP catalyst developed under this concept is 3–4 times as active as conventional catalysts on the basis of reaction rate. ISOP catalyst in the spoke shape, which has a large geometric surface area per catalyst particle, was partially charged in a 1500 t/day-class ammonia plant after confirming the high performance in a pilot plant [78]. The catalyst has shown for more than 3 years the expected temperature decrease on the reformer tube, which is a sign of the high activity. Observed activities of ISOP catalyst in the ammonia plant agree with those observed in the pilot and laboratory experiments at a 95 % confidence limit range as shown in Figure 10.24.



Conventional catalyst (Unimodal)

ISOP catalyst (Bimodal)

Figure 10.22—Schematic structure of catalysts.

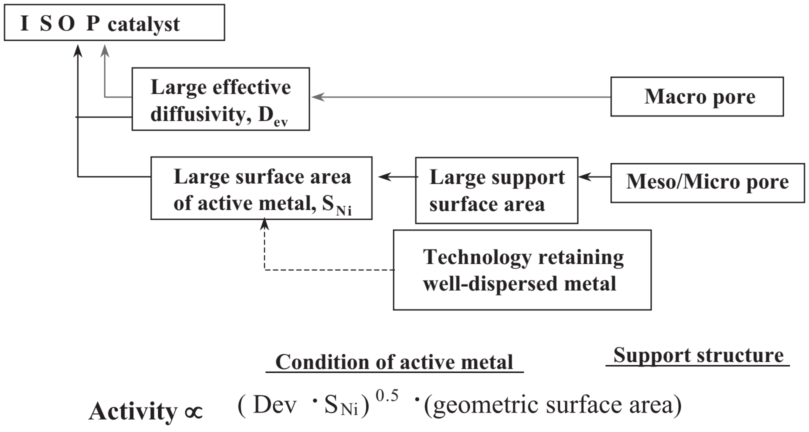


Figure 10.23—Concept of high activity in ISOP catalyst.

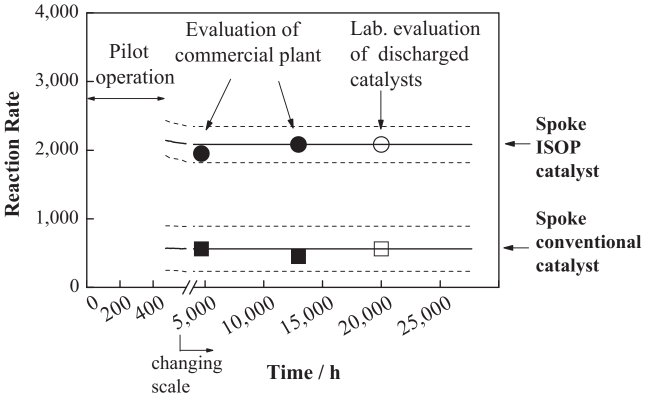


Figure 10.24—Activity of ISOP catalyst (Solid lines are estimated activities from pilot operations. Dotted lines indicate 95 % confidence limit range).

Commercial catalysts should have proper performance properties (Table 10.14). The conventional catalyst charged in the ammonia plant, which has the lowest level of acid amount, is the most coking-resistant in conventional catalysts for the light natural gas. ISOP catalyst and the conventional one were discharged from each tube at a periodic scheduled shutdown after 2 years of operation. An amount of deposited carbon in ISOP catalyst is approximately one third that in the conventional catalyst, which verified that the ISOP catalyst is more resistant to the coking in the commercial operation. The larger coking resistance of ISOP catalyst is understood because of a lower concentration of coke precursor on the well-dispersed nickel because the coking reaction is competitive to the steam reforming reaction (i.e., a gasification reaction of hydrocarbons).

TABLE 10.14—Commercial Performance of ISOP Catalyst in Comparison with Conventional Catalyst

Activity	3–4 times higher
Coking resistance	Higher, one third of deposited carbon in 2 years operation
Mechanical strength	Higher, before and after operation
Sulfur resistance	Equivalent
Steam resistance	Equivalent

The mechanical strength of the conventional catalysts is approximately 400 N before use. ISOP catalyst retained a higher strength than the value of the conventional one in the 2 years of operation.

On sulfur resistance, ISOP catalyst proved in the operation that no special treatment is required other than an ordinary desulfurization system (e.g., CoMo + ZnO).

10.8.2 Benefits of ISOP Catalyst in Box-Type Reformer

ISOP catalyst reduces the plant's capital and operating costs. Because the steam reformer is operated at high temperatures from an equilibrium requirement, there were implicit prospects that no successful result would be obtained by increasing catalyst activity because of slow heat transfer. However, precise simulating studies from a plant-designing viewpoint verified benefits with highly active ISOP catalyst.

The active catalyst proceeds via endothermic reaction much more and decreases the tube metal temperature. Figure 10.25 shows two different, but typical, tube temperature profiles in a top-firing furnace for an ammonia plant. The maximal peak temperatures are at 20–30 % in the down-tube position. In both cases the ISOP catalyst (thicker lines) decreases the peak temperatures by approximately 30°C compared with the case using a conventional catalyst (thinner lines). The temperature decrease of the tube makes the temperature difference larger between the flue gas and the tube wall, which increases the heat transfer much more: The heat transfer due to radiation is proportional to the difference in the temperatures, each raised to the fourth power. Further, the higher activity makes the approach to equilibrium smaller, which requires a lower temperature at the outlet to obtain an expected production rate. The lower temperature requires less fuel. These effects by the ISOP catalyst achieve 1.6–2.0 % saving of reformer fuel.

The higher activity also extends the life of the reformer tube in existing plants [78]. Although the effect is highly dependent on an original design and its operating conditions, a decrease of 20°C of the tube temperature can extend the tube life by 2.5 times; a 30°C decrease can theoretically extend tube life by 3.7 times. On the other hand, an increase in production is expected when the tubes are operated at the same high temperatures in the same manner.

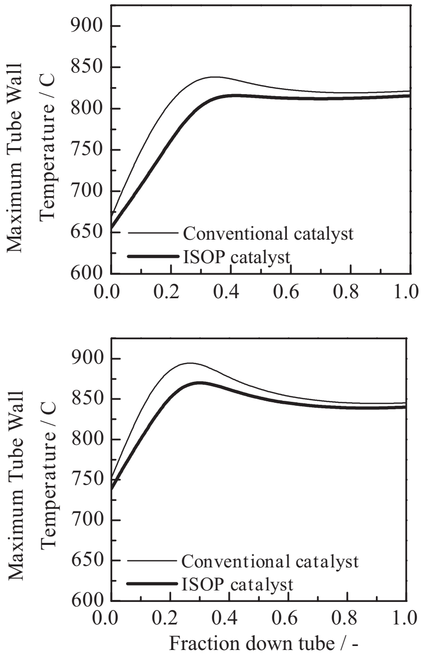


Figure 10.25—Tube wall temperature profiles in typical steam natural gas reformers.

For newly built plants, the highly active catalyst can reduce the capital cost. The temperature decrease makes thinner tubes applicable [78], which provides a large cost reduction.

10.8.3 Benefits of ISOP Catalyst in Heat-Exchanger Reformer

The box-type reformers have established their position in industries with long experience. However, they have a disregarded demerit of large firing duties that require complicated and expensive heat recovery systems. To improve this problem, heat-exchanger reformers with shell-and-tube structure have been proposed in combination with a conventional box-type reformer or an autothermal reformer. These reformers enable higher heat efficiency; however, they are structurally so complicated that a compact design is strongly required.

A highly active catalyst is a breakthrough technology to solve this problem. ISOP catalyst reduces the reformer in size and cost. A design example of a heat-exchanging reformer for methanol production is shown in Figure 10.26 The figure shows that the reformer using ISOP catalyst can produce a similar amount of syngas with a 40 % less tube number than that using a conventional catalyst. In the case of applying ISOP catalyst, the process gas temperature decreases (thicker line) and the temperature difference increases. Now, particular attention is paid to the case in which an increasing ratio of the temperature difference using ISOP catalyst with the heat-exchanging reformer is much larger than the case with the box-type reformer. In the heat-exchanging reformer, the temperature difference is essentially small because of a lower temperature of the heating fluid than that by the burner heating in the box-type reformer. The larger temperature difference requires the smaller area of the heat transfer, which can be expressed in increasing heat flux as shown in the middle figure of Figure 10.26. The reduction of the heat transfer area directly leads to the cost reduction of the shell-and-tube structured reformer.

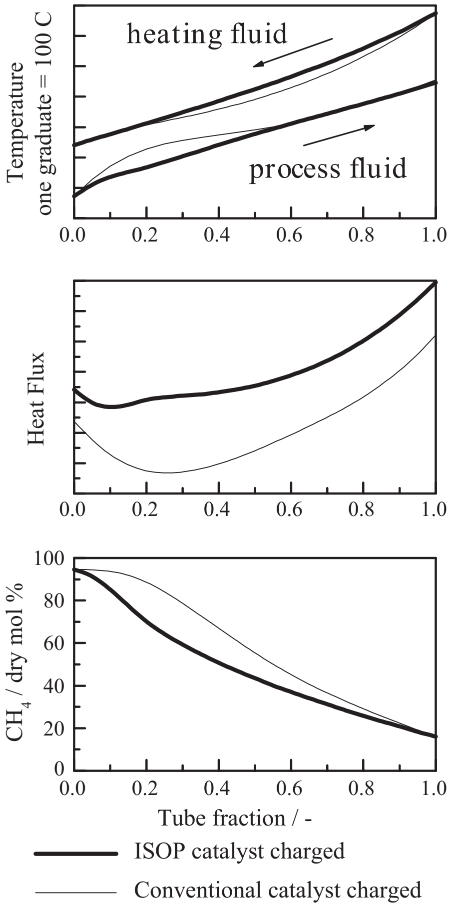


Figure 10.26—Profiles of temperature, heat flux, and methane concentration in a heat-exchanging reformer. The number of tubes when ISOP catalyst is used is 40 % less than that when a conventional catalyst is used.

10.8.4 Recent Development in Water-Gas Shift Catalysts for Applications in Polymer Electrolyte Fuel Cells for Household Power Units

In this section, the recent development in water-gas shift (WGS) catalysts, particularly for applications in polymer electrolyte fuel cells (PEFCs) for household power systems, is reviewed. The difficulty of meeting the stringent operating requirements with the conventional copper-zinc (Cu-Zn)-type catalyst led to the development of the noble metal-based WGS catalysts in search of a new replacement. However, at least for this particular application, use of noble metal-based WGS catalysts for various reasons seems to be far from the practical use. Instead, the reinvestigation of the "old" Cu-Zn-type catalyst in this "new" WGS operating environment led the way to the development of the newly improved Cu-Zn catalyst.

The WGS reaction was originally developed to increase hydrogen yield while decreasing carbon monoxide (CO) concentration from synthesis gas, which was required for ammonia production. The synthesis gas produced from a steam reforming reaction usually contains several to 10 vol % CO, at which level ammonia synthesis catalysts are poisoned; therefore, a high degree of CO removal must be achieved. The WGS reaction is a reversible and exothermic reaction (Eq 10.2) to the right, implying that a lower CO concentration (higher CO conversion) at equilibrium is favored at lower temperatures.

$$CO(g) + H_2O(g) \leftrightarrow CO_2\ (g) + H_2\ (g)\ \Delta H = -41.2\ \text{kJ/mol} \quad (10.2)$$

Industrially, the WGS reaction is performed in two steps where a high-temperature shift (HTS) reaction is followed by a low-temperature shift (LTS) reaction. The former reaction is performed at approximately 300–450°C and the corresponding catalyst must have a high durability in this temperature range. The major HTS catalyst used today is the Fe_2O_3-Cr_2O_3-type metal oxide catalyst, which has been basically unchanged for nearly a century [79]. The active component of this catalyst is Fe_3O_4, and the role of chromia is to prevent sintering of Fe_3O_4.

In the 1960s, the Cu-ZnO base LTS catalyst was developed and replaced the old scrubbing method, which used a copper ammonium formate aqueous solution for removal of carbon oxides [79]. The LT-WGS reaction is performed between approximately 180 and 250° C, and the active component of the LTS catalyst is copper metal whereas zinc oxide (ZnO) acts as the support for the copper. This catalyst is sensitive to thermal sintering, exposure to air is dangerous because of its pyrophoricity upon reduction, and condensation of steam must be avoided because catalyst activity is drastically reduced in wet conditions [80].

These problems are usually not much concern for typical chemical plants unless unforeseen events happen during the operation of the reactors. However, applications in PEFCs, particularly for household power systems, require a daily startup and shutdown (DSS) followed by purging of the combustible gases with air or steam. Low durability of Cu-ZnO catalysts under oxidizing conditions in the presence of steam has led researchers in the field to investigate other catalytic systems such as noble metal-based catalysts to replace the commercial Cu-ZnO catalyst from the PEFC applications. Section 10.8.5 summarizes the recent advancements in such catalysts.

10.8.5 Noble-Metal-Based WGS Catalysts

Platinum (Pt)- [81–95], rhodium (Rh)-, ruthenium (Ru)-, palladium (Pd)- [89,96], and iridium (Ir)- [91,92] based catalysts have been investigated over various support metal oxides for a LTS reaction in the last decade. Among the many noble metals studied, Pt-based catalysts supported on reducible metal oxides offer promising results. In this reaction, activation of H_2O is more difficult than CO activation because H_2O is thermodynamically more stable than CO [97]. In the conventional Cu-ZnO system, the activation of H_2O takes place via oxidation of Cu to CuO. However, in a Cu-free system (e.g., Pt), it is known that PtO_x is thermodynamically unstable at the operating temperatures of WGS; therefore, a chemical interaction of H_2O with Pt cannot be expected [98]. Over noble-metal-based catalyst systems, mechanistic investigations to address questions including H_2O activation, CO adsorption, and surface intermediates have been performed by many researchers. It is generally accepted that there are two types of reaction mechanisms over the noble-metal-based systems: (1) associative (surface formate formation) and (2) regenerative redox. In the associative mechanism, hydroxyl groups on the support surface and CO react to form surface formate species followed by its decomposition into H_2 and CO_2 assisted by gaseous water [99–101]. In the redox mechanism, oxygen is supplied by the lattice oxygen in the support, which reacts with CO adsorbed on the metal to form CO_2. The oxygen vacancy is regenerated by H_2O, forming H_2 [98,102,103].

Azzam et al. studied Pt/CeO_2 and Pt/TiO_2 using in situ Fourier transform infrared (FTIR) spectroscopy and transient kinetic studies to elucidate possible mechanisms for Pt/CeO_2 and Pt/TiO_2. In the Pt/CeO_2 system, surface formate was seen to form on the support, which reacted with gaseous H_2O to form CO_2, H_2, and hydroxyl groups (redox mechanism). In Pt/TiO_2, the reaction possibly proceeded via redox and the formate route with redox regeneration. It was concluded that the reducibility of support and the stability of formate and carbonate species together determine the reaction pathways for WGS [84].

Panagiotopoulou et al. [89] investigated Pt, Rh, Ru, and Pd catalysts over partially reducible metal oxide supports. They reported that Pt and Pd showed relatively high activity and that Rh and Ru had intermediate activity. The researchers calculated the activation energy (E_a) of M/CeO_2 and M/TiO_2 (where M represents various metals) and found that the values of E_a did not depend on the nature of the metallic phase but only on the nature of the support. This evidence suggested that the key contribution factor for the activation energy originates from a reaction step associated with the metal oxides. Furthermore, they also suggested that the reducibility of the support possibly influences the redox mechanism or formation of surface formates by affecting the surface hydroxyl groups.

Iida et al. studied Pt supported on TiO_2 (rutile and anatase), ZrO_2, and Al_2O_3 using various spectroscopic and temperature programming techniques including transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and FTIR. It was found that Pt/TiO_2 was much more active than Pt on ZrO_2 and Al_2O_3 although the dispersion of Pt over TiO_2 was lower than that on ZrO_2 and Al_2O_3. Between Pt supported on rutile TiO_2 and anatase TiO_2, the former had a higher dispersion. XPS revealed that the Pt was slightly negatively charged compared with Pt^0, which may indicate the donation of electrons from TiO_2 to Pt. Because this feature was not observed over ZrO_2 or Al_2O_3, TiO_2 was seen to have more effect in the electronic state of Pt than other supports. From the TPD profiles of CO adsorption, it was shown that the strength of Pt-CO bonding on TiO_2 support was weaker than other supports. This suggested that the adsorbed CO on TiO_2 was more reactive than those on other supports. It was concluded that the support and Pt interactions could have a large effect on the activity of the WGS reaction [82].

Although the initial activity of Pt-based catalysts was closer (or higher in some cases) to the conventional Cu-ZnO system under certain conditions, many found that it became unstable with time-on-stream [85,88,96]. Azzam et al. [85] found that Pt/CeO_2 deactivated because of formation of stable carbonate species on the ceria surface. Because carbonate is known to be unstable over TiO_2 [104], deactivation by this route would be less problematic for Pt/TiO_2 and would offer an attractive solution over Pt/CeO_2. However,

Pt/TiO_2 also deactivated with time despite higher initial activity of Pt/TiO_2 than Pt/CeO_2. The cause of deactivation was determined to be the sintering of Pt. Pt sintering was seen to occur when traces of formaldehyde were formed under the reaction conditions. A separate formaldehyde adsorption experiment on a reduced catalyst confirmed a decrease in Pt dispersion from 55 to 30 %. It was suggested that the presence of formaldehyde in combination with the presence of defect titania enhances Pt mobility on TiO_2 and causes Pt sintering [95].

One of the attempts to overcome this problem was to incorporate promoters in the Pt-based catalytic system [81,86–88,91,92,94]. Zhu et al. [88] reported that sodium addition to Pt/TiO_2 improved the stability of Pt/TiO_2 catalyst by preventing Pt sintering. Farrauto and coworkers [94] have used molybdenum (Mo) and rhenium (Re) as the promoters over Pt/ZrO_2 and improved its activity by 3-fold. The addition of these promoters had a positive effect on the thermal stability of the catalyst, possibly because of formation of Pt-Re-Mo alloy under the reaction conditions. They reported that this system is currently working in commercial units.

Sato et al. studied the effect of Re addition to TiO_2-supported Pt, Pd, and Ir catalysts. Catalyst activity was found to increase with the addition of Re over all catalysts. Turnover frequency (TOF) data of H_2 formation were obtained over Pt, Pd, and Ir catalysts with varying particle sizes. It was shown that although H_2 formation rate became steady with a Re:Pt ratio greater than 1:1, TOF kept increasing with higher Re:Pt ratio, suggesting a formation of bimetallic clusters between Pt and Re. On the contrary, for Ir-Re catalyst, the addition of Re resulted in formation of highly dispersed nanoparticles and the increase in TOF was not observed. The effect of Re on activation energy was also studied and it was found that the Re addition decreased the activation energy on Pt/TiO_2 and Pd/TiO_2 but increased on Ir/TiO_2. FTIR experiments with a successive introduction of H_2O and CO on reduced Pt-Re/TiO_2 catalyst showed the formation of surface formate species, which was seen to decompose accompanied by the evolution of H_2 and CO_2 upon reintroduction of H_2O. It was suggested that the role of Re was to stabilize the formate species and accelerate the rate of H_2 formation [91]. Spectroscopic data suggest that Re is at least partially in an oxidic state (ReO_x) under the reaction conditions [85–87,91,92]. Another possible role of Re suggested is that ReO_x provides an additional pathway for H_2O sorption/activation, which improves activity [85].

10.8.6 Cu-Zn-Al-Type Catalysts

In the last few years, new Cu-Zn-Al-type catalysts, which have higher resistance against hydrothermal conditions compared with the conventional Cu-ZnO type, have been reported [105,106]. The effect of DSS accompanied by steam purging on conventional Cu-ZnO catalyst was investigated with respect to Cu coordination number, crystallite size, electronic state, number of surface Cu particles by in situ XRD, X-ray absorption fine structure (XAFS), and nitrous oxide (N_2O) chemisorption. Reaction tests were performed at $H_2/CO/CO_2/H_2O = 5:1:1:3$ at a GHSV of 2500 h^{-1}. Characterization of the catalyst, which underwent 50 cycles of DSS treatment with cooling under condensed steam atmosphere between each cycle, was performed after in situ reduction of the sample at 250°C for 1 h in a H_2 stream. The XRD pattern on the conventional Cu-Zn catalyst showed that the introduction of water over freshly reduced surface at 250°C was enough to increase Cu crystalline size from 1.7 to 4.5 nm. It was also shown that the Cu was oxidized to Cu_2O and CuO in steam [105]. New Cu-Zn-Al-type catalyst was shown to have a higher resistance to hydrothermal conditions compared with the conventional Cu-Zn catalyst. In situ XRD pattern along with XAFS revealed that $ZnAl_2O_4$ (spinel) was formed under the reaction conditions only on the new Cu-Zn-Al catalyst. Growth in crystallite size for Cu was almost negligible (11.1 nm → 12.8 nm) after 50 cycles of DSS treatment in the new Cu-Zn-Al catalyst whereas the growth for the conventional Cu-ZnO catalyst was much larger (12.4 nm → 25.0 nm) [106]. It seems that this new synthesis method enables the formation of Zn spinel under the reaction conditions over which Cu sintering can be minimized because of the hydrothermally stable nature of spinel. These findings are very interesting and may offer an attractive solution to the current problem faced in WGS catalysts for PEFC applications today.

A unique operation regimen used in PEFCs for household power systems, in which the system is started up in the morning and shut down at night with air or steam purging in between, led researchers to seek a better WGS catalyst in noble-metal-based catalysts. However, overall cost of the PEFC power unit is still high, and reducing the catalyst cost is one of the difficulties faced today. Use of the noble metals, particularly Pt, may be cost-prohibitive although technical hurdles could be overcome. On the other hand, the new type of Cu-Zn-Al catalyst, which forms $ZnAl_2O_4$, seems to be promising with respect to cost and performance. To successfully and widely introduce PEFC household power systems in the market, development not only in catalyst formulation but also in operation methodology is necessary to effectively bring down the overall cost of the system.

10.9 CURRENT ROLES OF SUPPORTS IN CATALYST DEVELOPMENT IN PETROLEUM REFINING

The petroleum refining industry currently faces heavier crude, stringent regulation of petroleum products, a very high price of crude oil, and spread of the refining industry over the world as the major issues. Such issues require further improvement of the catalysts and processes, although the basic schemes of refining technology have stayed essentially unchanged in recent decades regarding the basic principles, catalytic species, and processes. More severe operating conditions and multistage processing compensate for insufficient functions of the catalysts. Hence, there is room to improve the functions of the catalysts.

The basic guidelines for catalyst development include novel combination of catalysts with different functions and novel combination of the catalysts and supports. Such combinations require the development of more detailed structural concepts of solid catalysts to improve their activity, selectivity, durability, and mechanical strength. The new structural concept of solid catalysts involves

- Nanoparticles with definite size and crystallization of the catalytic species and support,
- Arrangement of nanoparticles in the nearest and next-nearest neighbors,

- Three dimensional arrangement of catalytic function in the real catalyst grain (pellets or cylinders),
- Physical access to the nanoparticles,
- Chemical interaction among nanoparticles, and
- Molecular transfer and conversion over the series of active sites distributed on the particle surfaces.

In catalytic refining, for the reactions in fluid phase over solid catalysts, the feed molecules must move from the bulk phase to the grain surface; diffuse into the pore on the surface of the particles, which may spread into the center of the grain; go through particular catalytic reactions on the active sites; and return to the bulk phase. In such a series of steps, feed molecules behave in monomolecular or clustered forms. Hence, the mass transfer of feed molecules in the liquid and pore to meet the active site on particular positions of the molecule is strongly affected by their solubility. In addition, the solvolytic reactions of partner molecules may take place to control the adsorption, desorption, and reactivity of the feed and the products.

10.9.1 Roles of the Catalyst Supports

The roles of catalyst supports can be addressed under three main considerations:

1. *Larger effective surface area of the catalytic species:* The catalyst support is most classically expected to provide the larger effective surface of the catalytic species dispersed on the surface of the support. This role of the support is expanded to the conserving of the solid state of the catalytic species, allowing the smaller pressure drop at the flows of the feed and the product and easy separation from the catalytic materials. Thus, the support is expected to have a larger surface area and stronger interaction to better disperse the catalytic species. However, the smaller pores to increase the surface are not necessarily favorable because the catalytic species may not get into the pores whereas the feed and the products may suffer diffusion limitations to meet the catalytic species in such pores or leaving the pores after the reaction. Too strong of an interaction between feed or product molecules and catalyst surfaces may deactivate the catalytic species because such an interaction can change the chemical properties of the catalytic species.
2. *Bifunctional roles of the support:* Some supports are acidic, for example, while the support and catalytic species possess activity for HG or dehydrogenation reactions. In such a case, the feed can be subjected first to dehydrogenation, subsequently to acidic isomerization, and finally to HG. Such a series of catalytic reactions proceed successively over the particular combination of the catalyst and supports. Thus, the support is expected to function not only as a carrier of the catalytic species for a particular reaction but also as a catalyst for another reaction. Such a combination of the catalyst and support provides bifunctional catalysts. Some supports can strongly adsorb the feed or products that are transferred to catalyst surfaces. The adsorption of reactants accelerates the catalytic reaction. The transfer of reactants from the catalyst to the support is defined as "spillover." The transfer in the reverse direction is termed "reverse spillover."
3. *Chemical modification for catalytic species:* The supports can be acidic/basic, oxidative/reductive, or coordinative against the catalytic species, which is chemically modified by such a support. This modification can sometimes, but not always strengthen the catalytic functions of the supported species. For example, TiO_2 is reported to be such a support. TiO_2 is first found to very strongly trap the noble metals such as platinum to reduce its catalytic activity when they are heat-treated at higher temperatures. A strong metal support interaction such as in this case is not desirable. However, an adequate temperature of the heat treatment was found to enhance the catalytic activity through favorable metal support interaction. Cobalt tetraphenyl porphyrin is reported to give radical species when supported on TiO_2 of large surface area when appropriately heat-treated. Such a combination promotes some catalytic reactions such as NO decomposition and decomposition of hydrogen peroxide. Such roles of supports suggest ways to enhance the catalytic activity and to provide new functions through interaction of the catalytic species and the support. Adequate treatments as well as the careful selection of the catalyst and support are essential to develop novel catalysts. Some examples of the catalytic development in the refining technologies based on support selections are reviewed below.

10.9.2 Catalyst Supports for HDS

Deep HDS has been required to meet the environmental regulations on gasoline and diesel to achieve less than 10-ppm sulfur content. The HDS mechanism and catalysts have been studied extensively. The problem in deep HDS of diesel fuel is to rapidly desulfurize the refractory sulfur species such as 4,6-dimethyl dibenzothiophene at temperatures below a certain limit where the catalyst deactivation and cracking of the feed would not occur. The HDS of sulfur species in diesel fuel is known to occur according to the following five schemes, shown in Figure 10.27:

1. Direct HDS,
2. HG before HDS,
3. Isomerization before HDS,
4. Demethylation, and
5. C-S bond scission.

Because of steric hindrance due to the two methyl groups at particular positions of 4,6-dimethyl dibenzothiophene, direct HDS is strictly inhibited. Hence, the schemes 2–5 are postulated for HDS of refractory sulfur species. For example, in scheme 2, HG of one phenyl group is desired, and for scheme 3, migration of the methyl group on the phenyl ring is designed. Thus, a byfunctioned catalyst for acidic isomerization and subsequent HDS is utilized. A combination of acidic zeolite as an acidic catalyst for HDS using $CoMoS/Al_2O_3$ is proposed. A problem with this catalyst is the rapid deactivation due to coke formation on the zeolite. The problem must be overcome by adjusting the reaction conditions to limit undesired reactions. Weaker acid catalysts do not allow the desired isomerization reactions.

A second approach is to enhance the HG of phenyl groups in the presence of H_2S at fairly high concentrations. Acidic support has recently been found to enhance the HG activity. Thus, several acidic supports are reported to be effective for HDS of refractory sulfur species, including Al_2O_3-SiO_2, Al_2O_3-B_2O_3, Al_2O_3-zeolite, TiO_2-SiO, and TiO_2-Al_2O_3. Some acidic supports are highly acidic whereas the acidic reactions of the feed are not wanted. Hence, the direct

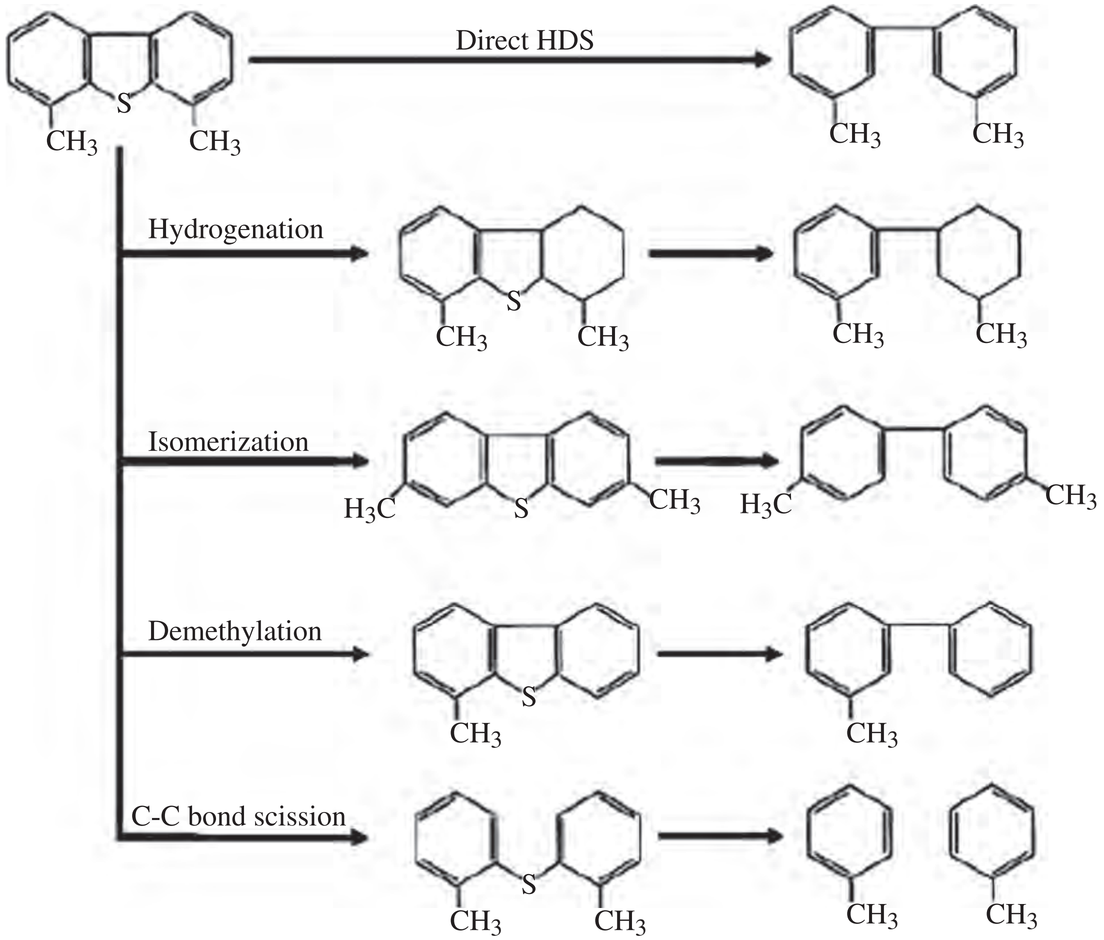


Figure 10.27—Schemes of HDS in diesel fuels.

interaction of the feed and acidic support must be avoided or the acidic site must be restricted to the HDS catalyst. The present authors proposed an alumina coating of zeolite to function as such a support.

Another important role of an acidic support is to enhance the desorption of adsorbed H_2S on the catalyst active site. Hence, the catalyst can be active under high H_2S partial pressures, which are often brought about by the feed of very high sulfur content.

There still remains in deep HDS of highly aromatic feed containing refractory diesel fuel fraction. Catalytic species should overcome the inhibition of aromatic partners for the hydrogenative HDS of the refractory sulfur species.

10.9.3 Supports for Deep and Selective HDS of Gasoline

Deep HDS of straight-run gasoline is relatively easy because gasoline does not contain any refractory sulfur species. Hence, milder conditions to achieve the zero-sulfur goal become a research target. In contrast, cracked gasoline, a product from FCC and thermal cracking, contains significant amounts of olefins and benzenes that increase the octane number. Thus, the issue is to achieve deep HDS without HG of olefins and benzenes, whereas olefins are very reactive for HG. Hence, the key point is how to suppress the HG of olefins, keeping the high direct HDS activity. As described in this section, the support helps control such an activity. Carbon supports are supposed to reduce the HG activity. Concerning the acidic function of the support on the HG activity, the carbon on the alumina support may moderate the acidity to control the HG activity of the supported CoMoS. This approach leads to a better performance of the HDS catalyst for treating cracked gasoline.

10.9.4 Support of HDM Catalyst

Crude currently tends to be heavier and contain higher concentrations of metal, nitrogen, and sulfur species. Hence, extensive HDM is expected to be performed to remove V and Ni, which exist as ions in porphyrin complexes in petroleum. The roles of the catalyst in HDM are

- Decoagulation of asphaltene structure to allow for the contact of metal ions to the active sites of HDM catalyst through partial HG, defining the effectiveness of HDM;
- Supplying H_2S through HDS of reactive sulfur species;
- Eliminating metal ions on the surface of HDM catalyst in the form of sulfides; and
- Trapping and storage of metal sulfide to continue the HDM process to increase HDM capacity.

HDM catalyst has been developed to impregnate NiMo on alumina of large pore and large surface area. The roles of NiMo and alumina can be allocated into 1 and 2 for NiMo and 3 and 4 for alumina, respectively. Roles of 1 and 2 can be replaced by solvent and recycling H_2S to the HDM step as proved by Shell patent, respectively. The alumina of HDM catalyst has been proven to carry metal sulfide; hence, the activity of NiMo is restored while the elimination of metals progresses. It is not clarified yet how metallic species can move on the alumina surface to form sulfide particles.

On the basis of such a mechanistic consideration, novel HDM catalyst can be developed. Ni is much less reactive than V in petroleum. The reasons are the high stability of Ni porphyline and the location in the asphaltene. More research is necessary to achieve extensive removal of V and Ni as well as higher HDM capacity of the catalyst.

10.9.5 Nanoscopic Views on Catalyst and Support

Supported catalytic species have been recognized to be dispersed in particle sizes of approximately 1–100 nm on the support surface. Reducing the particle size of catalytic species and accurate measurement of particle sizes have been targeted in catalyst research and preparation. Observation and control of the catalyst structure even at the atomic level have been attempted. The support is assumed to provide the site for the precursor and final form of the catalyst on a much larger area where the functional groups on the support surface can play important roles. In the course of catalyst development for deep HDS, binary oxides of acidic supports were considered to improve the activity and selectivity of the catalysts, such as Al_2O_3-SiO_2 and Al_2O_3-USY. In such cases, where the sulfide particles are located on either oxide or where the adjacent site is located to modify the sulfide catalyst become important. Acidic support certainly enhances the HG activity as described above. The contact of feed or product molecules with moderately acidic support surface may be allowed without much harm. However, highly acidic zeolite catalyst such as USY should not interact directly with the feed because this interaction may cause cracking and/or coking. This would lead to unwanted cracked products and the deactivation of the catalysts. The present authors proposed to coat the zeolite with alumina to prohibit the direct interaction, but alumina coating can modify the sulfide catalyst by applying the acidity of the zeolite layer underneath. The thickness of alumina coating must be carefully controlled for optimal performance. Nanosized control of alumina coating is a key factor.

Alumina-silica support consists of nanoparticles, in which alumina particles may carry the sulfide catalyst and silica particles surround the alumina particles to enhance the acidity at contact areas. Hence, the size of alumina must be large enough to carry the sulfide and as small as possible for the highest degree of modification with the surrounding silica particles. The silica particle must be as small as possible to modify the alumina particles through large contact areas. Thus, the binary components of the support are designed and prepared on the basis of nanosized geometry. The upgrading of heavier crude is now attempted by using nanoparticles of MoS or FeS as catalysts.

REFERENCES

[1] Venuto, P., and Habib, E., *Fluid Catalytic Cracking with Zeolite Catalysts*, Marcel Dekker, Inc., New York, 1979, p. 30.

[2] Flank, W.H., Abraham, M.A., Matthews, M.A., and Fletcher, R., *Innovations in Industrial and Engineering Chemistry*, American Chemical Society, Washington, DC, 2008, pp. 231, 237.

[3] Flank, W.H., Abraham, M.A., Matthews, M.A., and Fletcher, R., *Innovations in Industrial and Engineering Chemistry*, American Chemical Society, Washington, DC, 2008, p. 247.

[4] *Oil Sands Industry Update*, Alberta Economic Development, Edmonton, Alberta, Canada, June 2006.

[5] *Oil Sands Technology Roadmap—Unlocking the Potential*, Alberta Chamber of Resources, Edmonton, Alberta, Canada, January 30, 2004.

[6] Kelly, S., and Wise, T., "Markets for Canadian Oil Sands Products," paper presented at the *National Petrochemical Refiners Association Annual Meeting*, Salt Lake City, UT, March 19, 2006.

[7] Butler, E., Groves, K., Hymanyk, J., Malholland, M., Clark, P.A., and Aru, G., "Reducing Refinery SO_x Emissions," *Petrol. Technol. Quart.*, Q3, 2006.

[8] Mulholland, M., Aru, G., and Clark, P., "SO_x 25," *Hydrocarbon Eng.*, Vol. 9, 2004.

[9] Radcliffe, C., "Reducing FCC Unit NO_x Emissions," *Petrol. Technol. Quart.*, 2008, http:// www.eptq.com/view_edition.aspx?intContentID=21&intEID=68.

[10] Evans, M., Fletcher, R., Lakhani, H., Sawyer, J., and Schuttenburg, K., "An Alternative to FCC Fluegas Scrubbers," paper presented at the *National Petrochemical Refiners Association Annual Meeting*, San Antonio, TX, March 22–24, 2009, Paper AM-09-38.

[11] Bouwens, S.M.A.M., Vissers, J.P.R., Beer, V.H.J., and Prins, R.J., "Phosphorus Poisoning of Molybdenum Sulfide Hydrodesulfurization Catalysts Supported on Carbon and Alumina," *J. Catal.*, Vol. 112, 1988, pp. 401–410.

[12] Arteaga, A., Fierro, J.L.G., Grange, P., and Delmon, B., "CoMo HDS Catalysts: Simulated Deactivation and Regeneration. Role of Various Regeneration Parameters," in B. Delmon and G.F. Froment, Eds., *Catalyst Deactivation 1987*, London, Elsevier Science Publishers, 1987, p. 59.

[13] Okamoto, Y., Tomioka, H., Imanaka, T., and Teranishi, S., "Surface Structure and Catalytic Activity of Sulfided MoO3Al2O3 Catalysts: Hydrodesulfurization and Hydrogenation Activities," *J. Catal.*, Vol. 66, 1980, pp. 93–100.

[14] Satterfield, C.N., and Roberts, G.W., "Kinetics of Thiophene Hydrogenolysis on a Cobalt Molybdate Catalyst," *AIChE J.*, Vol. 14, 1968, pp. 159–164.

[15] Hagenbach, G., Courty, Ph., and Delmon, B., "Catalytic Effect of Palladium on Hydrogen Reduction of Metal Oxides," *J. Catal.*, Vol. 23, 1971, pp. 295–300.

[16] Hatanaka, S., Yamada, M., and Sadakane, O., "Hydrodesulfurization of Catalytic Cracked Gasoline. 2. The Difference between HDS Active Site and Olefin Hydrogenation Active Site," *Ind. Eng. Chem. Res.*, Vol. 36, 1997, pp. 5110–5117.

[17] Kasahara, S., Koizumi, N., Iwahashi, J., and Yamada, M., "Effects of Fe, Co, Ni on Hydrodesulfurization Activity of Sulfided Mo/Al_2O_3 (Part 1)," *J. Japan Petrol. Inst.*, Vol. 38, 1995, pp. 345–352.

[18] Inamura, K., and Prins, R., *Proceedings of the 2nd Tokyo Conference on Advanced Catalytic Science and Technology*, Aug. 21, Paper 70, 401 (1994).

[19] Hatanaka, S., Sadakane, O., and Okazaki, H., "Hydrodesulfurization of Catalytic Cracked Gasoline," *J. Japan Petrol. Inst.*, Vol. 44, 2001, pp. 36–42.

[20] Sakamoto, N., Ito, H., Honma, T., and Yamada, M., *Japan Petroleum Institute Conference*, Hakodate, D22, P185, 1992.

[21] Hatanaka, S., Yamada, M., and Sadakane, O., "Hydrodesulfurization of Catalytic Cracked Gasoline. 3. Selective Catalytic Cracked Gasoline Hydrodesulfurization on the Co-Mo/γ-Al_2O_3 Catalyst Modified by Coking Pretreatment," *Ind. Eng. Chem. Res.*, Vol. 37, 1998, pp. 1748–1754.

[22] Mey, D., Brunet, S., Canaff, C., Maugé, F., Bouchy, C., and Diehl, F., "HDS of a Model FCC Gasoline over a Sulfided CoMo/Al_2O_3 Catalyst: Effect of the Addition of Potassium," *J. Catal*, Vol. 227, 2004, pp. 436–447.

[23] "Two-Stage Hydrodesulfurization Process," U.S. Patent 5,985,136, 1999.

[24] Stanislaus, S., Marafi, A., and Rana, M.S., "Recent Advances in the Science and Technology of Ultra Low Sulfur Diesel (ULSD) Production," *Catal. Today*, Vol. 153, 2010, pp. 1–68.

[25] Fujikawa Takashi, *Chem. Eng.*, Vol. 11, 2003, p. 37.

[26] Houalla, M. et al., *Prepr. Amer. Chem. Soc. Div. Petrol. Chem.*, Vol. 22, 1977, p. 941.

[27] Ma, X., Sakanishi, K., and Mochida, I., "Hydrodesulfurization Reactivities of Various Sulfur Compounds in Diesel Fuel," *Ind. Eng. Chem. Res.*, Vol. 33, 1994, pp. 218–222.

[28] Farag, H., Whitehurst, D.D., Sakanishi, K. and Mochida, I., "Carbon versus Alumina As a Support for Co-Mo Catalysts

Reactivity towards HDS of Dibenzothiophenes and Diesel Fuel," *Catal. Today*, Vol. 50, 1999, pp. 9–17.

[29] *Evaluation of Reactivity for Ultra-Low Sulfur Gas Oil*, PEC Report, 2001.

[30] *Development of Reduction Technology for Pollutants in Petroleum Refining*, NEDO Report, 2004.

[31] Topsøe, H. and Clausen, B.S., "Importance of Co-Mo-S Type Structures in Hydrodesulfurization," *Catal. Rev. Sci. Eng.*, Vol. 26, 1984, pp. 395–420.

[32] Eijsbouts, S., and Inoue, Y., *Stud. Surf. Catal.*, Vol. 92, 1995 pp. 429.

[33] Dzwigaj, S., Louis, C., Breysse, M., Cattenot, M., Belliere, V., Geantet, C., Vrinat, M., Blanchard, P., Payen, E., Inoue, S., Kudo, H., and Yoshimura, Y., "New Generation of Titanium Dioxide Support for Hydrodesulfurization," *Appl. Catal. B*, Vol. 41, 2003, pp. 181–191.

[34] Inoue, S., Muto, A., Kudou, H., and Ono, T., "Preparation of Novel Titania Support by Applying the Multi-Gelation Method for Ultra-Deep HDS of Diesel Oil," *Appl. Catal. A*, Vol. 269, 2004, pp. 7–12.

[35] Rascona, I., et al., *Albemarle's Catalyst Courier*, Vol. 50, December, 2002.

[36] Brevoord, E., *Albemarle's Catalyst Courier*, Vol. 43, March 2001.

[37] "Grading and Guard Catalysts," http://www.albemarle.com/Products-and-Markets/Catalysts/HPC/Grading-and-Guard-Catalysts-151.html.

[38] Dufresne, P., et al., *Albemarle Catalyst Courier*, Vol. 38, December, 1999.

[39] Gerritsen, L.A., *Albemarle Catalyst Courier*, Vol. 41, September, 2000.

[40] Reid, T., *Albemarle's Catalyst Courier*, Vol. 49, September, 2002.

[41] "Hydrotreating," http://www.albemarle.com/Products-and-Markets/Catalysts/HPC/Hydrotreating-156.html.

[42] *Albemarle's Catalyst Courier*, Vol. 57, Autumn 2004.

[43] Brevoord, E., "Next Step to Cleaner Diesel Fuels," *Albemarle's Catalyst Courier*, Vol. 59, Spring 2005, pp. 10–11.

[44] Lee, S.L., "Latest Developments in Albemarle Hydroprocessing Catalysts," *Albemarle's Catalyst Courier*, Vol. 63, Spring 2006, pp. 8–9.

[45] Mayo, S., "Ketjenfine (KF) 905 STARS Demonstrates High Activity and Stability in FCC-PT Service," *Albemarle's Catalyst Courier*, Vol. 66, Winter 2006, pp. 10–11.

[46] Leliveld, B., "STARS Ketjenfine 860—Exceptional New Catalyst for Hydrocracking Pretreat," *Albemarle's Catalyst Courier*, Vol. 67, Spring 2007, pp. 6–7.

[47] Leliveld, B., "New Ketjenfine 770 STARS to Improve Ultra-Low Sulfur Diesel Production," *Albemarle's Catalyst Courier*, Vol. 73, Autumn 2008, pp. 4–6.

[48] Toshima, H., "*Advances in Upgrading Heavy Oils and Coker Gas Oil Through Hydroprocessing*," SCOPE 2007, Albemarle Corporation, Baton Rouge, LA.

[49] Lauritsen, J.V., Helveg, S., Lægsgaard, E., Stensgaard, I., Clausen, B.S., Topsøe, H., and Besenbacher, F., "Atomic Scale Structure of Co-Mo-S Nanoclusters in Hydrotreating Catalysts," *J. Catalysis*, Vol. 197, 2001, pp. 1–5.

[50] Topsøe, H., et al., *NPRA Annual Meeting*, AM-05-18, San Francisco, March 13–15, 2005.

[51] Skyum, L., et al., *ERTC 13th Meeting A6*, Vienna, Nov. 17–19, 2008.

[52] Remans, T.J., et al., "Catalytic Solutions for Sustainable ULSD Production," *European Catalyst and Technology Conference, Prague*, February 2003.

[53] Carlson, K.D., et al., *ERTC 13th Meeting A4*, Nov. 17–19, 2008.

[54] Campbell, T., et al., *NPRA Annual Meeting*, AM-05-16, San Francisco, March 13–15, 2005.

[55] Plantenga, F., *Albemarle's Catalyst Courier*, Vol. 47, March 2002.

[56] Mayo, S., Presented at the *NPRA Annual Meeting*, San Francisco, CA, March 13–15, 2005, Paper AM-05-14.

[57] Boot, L., et al., *Albemarle's Catalyst Courier*, Vol. 50, December, 2002.

[58] Brossard, D.N., "Chevron Lummus Global RDS/VRDS Hydrotreating-Transportation Fuels from the Bottom of the Barrel," in R. A. Meyers, Ed., *Handbook of Petroleum Refining Process*, 3rd Ed., McGraw-Hill, New York, 2004, p. 8.1.

[59] Earls, D.E., "Chevron Lummus Global On-Stream Catalyst Replacement Technology for Processing High-Metal Feeds," in R.A. Meyers, Ed., *Handbook of Petroleum Refining Process* , 3rd Ed., McGraw-Hill, New York, 2004, p. 10.1.

[60] Reynolds, B.E., and Silverman, M.A., "VRDS/RFCC Provides Efficient Conversion of Vacuum Bottoms into Gasoline," paper presented at the *Japan Petroleum Institute Petroleum Refining Conference*, Tokyo, Japan, 1990.

[61] Reynolds, B.E., and Brossard, D.N., "RDS/VRDS Hydrotreating Broadens Application of RFCC," *ATI Quarterly*, 1995/1996.

[62] Hung, C., Olbrich, H.C., Howell, R.L., and Heyse, J.V., "Chevron's New HDM Catalyst System for a Deasphalted Oil Hydrocracker," in *Proceedings of the AICHE Spring National Meeting*, 1986.

[63] Howell, R.L., Hung, C., Gibson, K.R., and Chen, H.C., "Catalyst Selection Important for Residuum Hydroprocessing," *Oil & Gas J.*, Vol. 83, 1985, pp. 121–128.

[64] Speight, J.G., *Petroleum Chemistry and Refining*, Taylor & Francis, London, 1997.

[65] Reynolds, J.G., "Characterization of Heavy Residua by Application of a Modified Separation and Electron Paramagnetic Resonance," *Liquid Fuels Technol.*, Vol. 3, 1985, pp. 73–105.

[66] Topsøe, H., and Clausen, B.S., "Active Sites and Support Effects in Hydrodesulfurization Catalysts," *Appl. Catal. A*, Vol. 25, 1986, pp. 273–293.

[67] Tamm, P.W., Harnsberger, H.F., and Bridge, A.G., "Effects of Feed Metals on Catalyst Aging in Hydroprocessing Residuum," *Ind. Eng. Chem. Process Des. Dev.*, Vol. 20, 1981, pp. 262–273.

[68] Richardson, R.L., Riddick, F.C., and Ishikawa, M., "New Shaped Catalyst Gives Two-Year Run on Mixed Resids.," *Oil & Gas J.*, Vol. 77, 1979, p. 95.

[69] Pearson, A., "Aluminum Oxide (Alumina), Activated," in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York, 2003, Vol. 2, pp. 391–403.

[70] Reynolds, B.E., Rogers, J.L., and Broussard, R.A., "Evolution of Resid Conversion Options," paper presented at the *NPRA Annual Meeting*, San Antonio, TX, 1997.

[71] Reynolds, B.E., Cash, D.R., and Armstrong, M.J., "VRDS for Conversion to Middle Distillate," paper presented at the *NPRA Annual Meeting*, San Francisco, CA, 1998.

[72] D'Amico, V., Gieseman, J., Van Broekhoven, E., Van Rooijen, E., and Nousiainen, H., *Hydrocarbon Processing*, February, 2006, p. 65.

[73] Roeseler, C.M., Black, S.M., Shields, D.J., and Gosling, C.D., paper presented at the *NPRA Annual Meeting*, San Antonio, TX, 2003, paper AM-02-17.

[74] Jensen, A.B., and Hommeltoft, S.I., paper presented at the *NPRA Annual Meeting*, San Antonio, TX, 2003, paper AM-03-24.

[75] U.S. Patent 584997, 5739074.

[76] Numaguchi, T., Hirano, A., Shoji, K., and Yoshida, S., "Evaluation of Activity and Carbon Deposition of Steam Methane Reforming Catalysts," *J. Japan Petrol. Inst.*, Vol. 39, 1996, pp. 203–210.

[77] Numaguchi, T., *Catalysts & Catalysis*, Vol. 43, 2001, p. 287.

[78] Shoji, K., Hirota, Y., and Numaguchi, T., "Development of Highly Active Nickel Catalyst for Steam Natural Gas Reforming," *Stud. Surf. Sci. Catal.*, Vol. 121, 1999, pp. 449–452.

[79] Satterfield, C., *Heterogeneous Catalysis in Industrial Practice*, 2nd Ed., Kriger, Malabar, FL, 1996.

[80] Ladebeck, and Wagner, *Handbook of Fuel Cell Technology*, Wiley, West Sussex, UK, 2003.

[81] Iida, H., Tahara, K., Higashi, H., and Igarashi, A., *Adv. Tech. Mat. Mat. Proc. J.*, Vol. 4, 2002, p. 62.

[82] Iida, H., and Igarashi, A., "Characterization of a Pt/TiO_2 (Rutile) Catalyst for Water Gas Shift Reaction at Low-Temperature," *Appl. Catal. A*, Vol. 298, 2006, pp. 152–160.

[83] Iida, H., Kondo, K., and Igarashi, A., "Effect of Pt Precursors on Catalytic Activity of Pt/TiO_2 (Rutile) for Water Gas Shift Reaction at Low Temperature," *Catal. Comm.*, Vol. 7, 2006, pp. 240–244.

[84] Azzam, K.G., Babich, I.V., Seshan, K., and Lefferts, L., "A Bifunctional Catalyst for the Single-Stage Water-Gas Shift

Reaction in Fuel Cell Applications. Part 1. Effect of the Support on the Reaction Sequence," *J. Catal*., Vol. 251, 2007, pp. 153–162.

[85] Azzam, K.G., Babich, I.V., Seshan, K., and Lefferts, L., "A Bifunctional Catalyst for the Single-Stage Water-Gas Shift Reaction in Fuel Cell Applications. Part 2. Roles of the Support and Promoter on Catalyst Activity and Stability," *J. Catal*., Vol. 251, 2007, pp. 163–171.

[86] Iida, H., Someya, M., Kondo, K., and Igarashi, A., *Sci. Tech. Catal*., Vol. 55, 2006, p. 265.

[87] Azzam, K.G., Babich, I.V., Seshan, K., and Lefferts, L., "Role of Re in Pt-Re/TiO_2 Catalyst for Water Gas Shift Reaction: A Mechanistic and Kinetic Study," *Appl. Catal. B*, Vol. 80, 2008, pp. 129–140.

[88] Zhu, X., Hoang, T., Lobban, L.L., and Mallinson, R.G., "Significant Improvement in Activity and Stability of Pt/TiO2 Catalyst for Water Gas Shift Reaction Via Controlling the Amount of Na Addition," *Catal. Lett*., Vol. 129, 2009, pp. 135–141.

[89] Panagiotopoulou, P., and Kondarides, D.I., "Effect of the Nature of the Support on the Catalytic Performance of Noble Metal Catalysts for the Water-Gas Shift Reaction," *Catal. Today*, Vol. 112, 2006, pp. 49–52.

[90] Panagiotopoulou, P., Christodoulakis, A., Kondarides, E.I., and Boghosian, S., "Particle Size Effects on the Reducibility of Titanium Dioxide and Its Relation to the Water-Gas Shift Activity of Pt/TiO_2 Catalysts," *J. Catal*., Vol. 240, 2006, pp. 114–125.

[91] Sato, Y., Terada, K., Soma, Y., Miyao, T., and Naito, S., "Marked Addition Effect of Re upon the Water Gas Shift Reaction over TiO_2 Supported Pt, Pd and Ir Catalysts," *Catal. Comm*., Vol. 7, 2006, pp. 91–95.

[92] Sato, Y., Soma, Y., Miyao, T., and Naito, S., "The Water-Gas-Shift Reaction over Ir/TiO2 and Ir-Re/TiO_2 Catalysts," *Appl. Catal. A*, Vol. 304, 2006, pp. 78–85.

[93] Iida, H., and Igarashi, A., "Difference in the Reaction Behavior between Pt-Re/TiO_2 (rutile) and Pt-Re/ZrO_2 Catalysts for Low-Temperature Water Gas Shift Reactions," *Appl. Catal. A*, Vol. 303, 2006, pp. 48–55.

[94] Ruettinger, W., Liu, X., Xu, X., and Farrauto, R.J., *Top Catal*., Vol. 51, 2008, p. 60.

[95] Azzam, K.G., Babich, I.V., Seshan, K., and Lefferts, L., "Single Stage Water Gas Shift Conversion over Pt/TiO_2—Problem of Catalyst Deactivation," *Appl. Catal. A*, Vol. 338, 2008, pp. 66–71.

[96] Wang, W., Gorte, R.J., and Wagner, J.P., "Deactivation Mechanisms for Pd/Ceria during the Water-Gas Shift Reaction," *J. Catal*., Vol. 212, 2002, pp. 225–230.

[97] Henderson, M.A., *Surf. Sci. Rep*., Vol. 46, 2002, p. 1.

[98] Takanabe, K. Aika, K.-I., Seshan, K., and Lefferts, L., "Sustainable Hydrogen from Bio-Oil—Steam Reforming of Acetic Acid As a Model Oxygenate," *J. Catal*., Vol. 227, 2004, pp. 101–108.

[99] Jacobs, G., Graham, U.M., Chenu, E., Patterson, P.M., Dozier, A., and Davis, B.H., "Low-Temperature Water-Gas Shift: Impact of Pt Promoter Loading on the Partial Reduction of Ceria and Consequences for Catalyst Design," *J. Catal*., Vol. 229, 2005, pp. 499–512.

[100] Goguet, A., Shekhtman, S.O., Burch, R., Hardcare, C., Meunier, F.C., and Yablonsky, G.S., "Pulse-Response TAP Studies of the Reverse Water-Gas Shift Reaction over a Pt/CeO2 Catalyst," *J. Catal*., Vol. 237, 2006, pp. 102–110.

[101] Choung, S.Y., Ferrandon, M., and Krause, T., "Pt-Re Bimetallic Supported on CeO2-ZrO2 Mixed Oxides as Water-Gas Shift Catalysts," *Catal. Today*, Vol. 99, 2005, pp. 257–262.

[102] Gorte, R.J., and Zhao, S., "Studies of the Water-Gas Shift Reaction with Ceria-Supported Precious Metals," *Catal. Today*, Vol. 104, 2005, pp. 18–24.

[103] Hilaire, S., Wang, X., Luo, T., Gorte, R.J., and Wagner, J., "A Comparative Study of Water-Gas Shift Reaction over Ceria Supported Metallic Catalysts," *Appl. Catal. A*, Vol. 215, 2001, pp. 271–278.

[104] Wang, J.A., Cuan, A., Salamones, J., Nava, N., Castillo, S., Moran-Pineda, M., and Rojas, F., "Studies of Sol-Gel TiO_2 and Pt/TiO_2 Catalysts for NO Reduction by CO in an Oxygen-Rich Condition," *Appl. Surf. Sci*., Vol. 230, 2004, pp. 94–105.

[105] Kawashima, Y., Umeki, T., and Okumura, K., presented at the *99th Catalysis Society of Japan Meeting*, Kobe, Japan, 2007, Abstract No. 99.

[106] Umeki, T., Takatsu, K., Nakai, S., Kawashima, Y., and Okumura, K., presented at the *102nd Catalysis Society of Japan Meeting*, Nagoya, Japan, 2008, Abstract No. 102.

11

Natural Gas Conditioning and Processing

Calogero Migliore[1]

11.1 INTRODUCTION

Natural gas is the fastest growing form of energy in the world. Annual global consumption is expected to reach 160 trillion f^3 (4.5×10^{12} m^3) by 2020. Natural gas is a more environmental-friendly energy source compared with oil and coal. It is increasingly being utilized for power generation and is already extensively used for industrial and household consumption as well as for the production of advanced petrochemical derivatives. These facts describe the importance and perspectives of natural gas as a future major energy commodity, holding the promise of being the energy source of the 21st century.

The development of the natural gas industry has been very much influenced by the physical characteristics of natural gas. Oil, being a liquid at ambient temperature, can be contained and transported relatively easy using simple and less-expensive technologies; natural gas is more complex and generally more expensive to store and transport because of its physical nature, which requires high pressures, very low temperatures, or both.

Getting gas to the market has always been problematic and has prevented the development of many fields. Most natural gas industry developments have thus been based on indigenous resources. Natural gas was initially traded based on transmission through pipelines between neighboring countries. It was only with the success of the transport trials as liquefied natural gas (LNG) in the 1960s that long-distance trade between nonbordering countries was established.

Transportation is a major aspect of the gas industry to ensure the supply of gas to the users. The main objective of a natural gas supply system is to produce gas from an underground field, move it to a processing facility where the gas is processed to an acceptable quality, and then move it to customers for its final use. This cannot happen without there being a continuous link from the producing field to the consumer of the gas. This involves the natural gas value chain concept.

Currently there exist two chains in the gas industry. One scheme involves a conventional arrangement in which natural gas is transmitted all of the way from the field to the city gate or consumer facility in high-pressure pipelines. The other one is the LNG scheme, which involves the liquefaction of the gas, its transportation in bulk carriers, the regasification at the point of delivery, and the transportation to the final users also through high-pressure pipelines.

This chapter will review the processing facilities involved in both existing schemes and their contribution with respect to the natural gas value chain concept. New proposed gas value chains and other technologies to monetize natural gas will be also discussed.

11.2 PROPERTIES OF NATURAL GAS

11.2.1 What Is Natural Gas?

Starting from its origin, it is generally accepted that natural gas derives from the microbial degradation of organic matter that was buried in the sands of what was before seashore. Many of the source rocks of significant gas deposits appear to be associated with the worldwide occurrence of carboniferous coal (roughly 286,000,000 to 360,000,000 years of age) [1].

In general, where oil and gas occur together, three layers of fluid exist with water at the bottom, then oil, and gas on top. Gravitational and capillary forces largely control the distribution of these fluids' accumulation. Typical fluid distributions resulting from the equilibrium of these forces are shown schematically by sectional views of a dome trap in Figures 11.1 and 11.2. Also illustrated in the figures are the possible modes of occurrence of the natural gas in the reservoir: associated free gas, associated solution gas, and nonassociated free gas.

In a reservoir in which crude oil (liquid phase) and natural gas (free gas phase) occur together (Figure 11.1), there is also an associated natural gas in solution with oil. This gas will flow out of the liquid phase once the pressure drops below the saturation pressure in the reservoir or in the surface at the production facilities.

A reservoir of only natural gas is shown in Figure 11.2. The gas in this kind of reservoir is nonassociated gas because no crude oil coexists in the reservoir. Depending on the amount of condensable hydrocarbons C_3–C_5+ present, these natural gas reservoirs can be divided into three groups: dry gas, wet or rich gas, and retrograde gas or condensate gas reservoirs. In a retrograde or condensate gas reservoir, initially all hydrocarbons are present in a single gas phase in the reservoir, but condensation will occur during pressure depletion.

Natural gas is a compressible fluid. There are many implications of this for the safe and economic supply of gas, but the most important is the energy content per volume unit. At atmospheric pressure and ambient temperature, natural gas has a very low energy content, whereas oil, being an incompressible fluid at those conditions, has a high energy content. Therefore, oil is transported and stored using relatively simple and less-expensive technology; in contrast, natural gas must be transported and stored at high pressure or in its liquefied form (LNG) to achieve an energy content that makes the cost of the infrastructure economically viable.

Methane is the main constituent of natural gas. The remainder may contain various amounts of the higher hydrocarbon gases, such as ethane, propane, butane, and pentane, and nonhydrocarbon gases, such as carbon dioxide

---

[1] Repsol Technology, Madrid, Spain

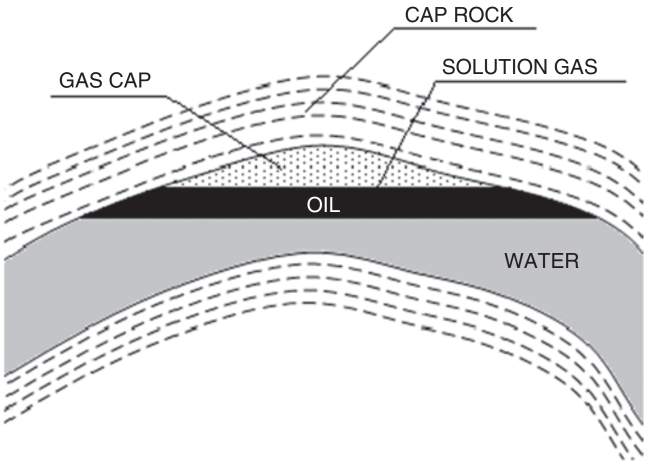


Figure 11.1—Schematic diagram of an associated gas reservoir.

(CO_2), nitrogen, hydrogen sulfide (H_2S), and helium. Table 11.1 shows the composition of a typical natural gas.

Some of the natural gases produced contain acid gases (CO_2 and H_2S) at levels that require treatment. Gases containing CO_2 or H_2S are known as sour gases; if they are free of them, then they are known as sweet gases. CO_2 must be kept below certain limits, normally below 3 % by volume, because it can cause corrosion in pipelines in combination with water. H_2S is also highly corrosive and it is toxic. It must normally be reduced to approximately 5 mg/m^3.

11.2.2 Thermodynamic Properties—Equation of State

Thermodynamic properties may be predicted by correlating pressure (P), volume (V), and temperature (T). The state of matter under a given set of physical conditions follows physical laws. The mathematic representations of these laws are known as equations of state (EOS), which correlate PVT data on a mole basis as follows:

$$\Phi(PVT) = 0 \quad (11.1)$$

There are many EOS available today that have been developed over the years. In this section, only the two most basic available EOS will be mentioned—the ideal gas law and the real gas equation using compressibility factor—and the two most popularly used EOS for natural gas systems—the Soave-Redlich-Kwong (SRK) and the Peng-Robinson (PR) equations.

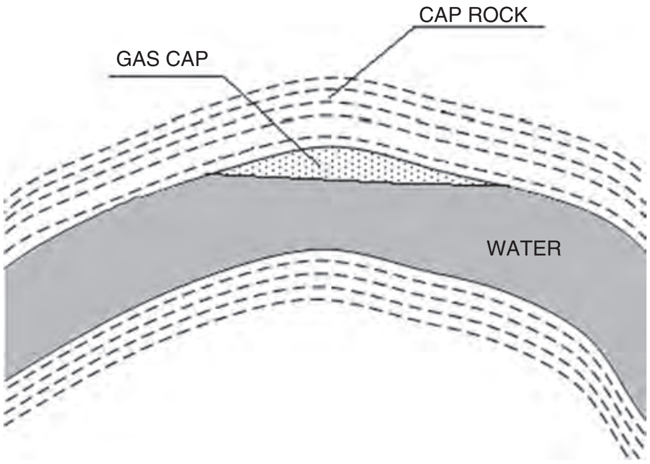


Figure 11.2—Schematic diagram of a nonassociated gas reservoir.

TABLE 11.1—Composition of a Typical Natural Gas

Component	Vol %
Methane	85.10
Ethane	8.70
Propane	2.90
Butanes	0.90
Pentanes$^+$	0.15
H_2S	Trace
CO_2	1.75
N_2	0.50
Helium	None

11.2.2.1 IDEAL GAS LAW, REAL GAS BEHAVIOR, AND COMPRESSIBILITY FACTOR

The simplest EOS is the ideal gas law. The concept of an ideal gas is a hypothetical approach, but is very useful to explain real gas behavior. An ideal gas is the one that follows:

- The molecules occupy no volume (the size of molecules is zero).
- There are no interaction forces between molecules.
- Collisions between molecules are elastic (no energy loss during collision).

Following the ideal gas law, the state of a gas is determined by its pressure, volume, and temperature according to the equation

$$PV = nRT \quad (11.2)$$

where P and T are the absolute pressure and temperature of the gas, n is the number of moles, and V is the volume occupied by the gas. R is the universal gas constant.

At low pressure (e.g., pressure up to ≈ 60 psia, ≈ 400 kPa), the ideal gas law is moderately accurate for most gases. However, generally speaking, real gases do not exhibit ideal behavior. They deviate from ideal behavior because of the following reasons:

- Molecules occupy a finite volume.
- There exist intermolecular forces exerted between molecules.
- Molecular collisions between molecules are not elastic.

The compressibility factor Z allows correcting for nonideal gas behavior. It is a very useful thermodynamic property to account for a real gas approach. The simplest form of an equation of state using the correction factor Z is the following:

$$PV = nZRT \quad (11.3)$$

Therefore, in this case, Z is the ratio of the volume occupied by the real gas to the volume occupied if it were ideal. Z varies with pressure, temperature, and gas composition.

11.2.2.2 CUBIC EOS

Cubic EOS are the simplest expressions that can, in principle, represent the vapor- and liquid-phase volumetric behavior of pure fluids. The most widely used for natural gas are the SRK (11.4) and the PR (11.5) equations. Both equations were designed specifically to yield reasonable vapor pressures to perform satisfactory for vapor/liquid equilibrium calculations.

$$P = \frac{RT}{v-b} - \frac{\alpha\, a}{v(v+b)} \tag{11.4}$$

$$P = \frac{RT}{v-b} - \frac{\alpha\, a}{v(v+b)+b\,(v-b)} \tag{11.5}$$

where α, a, and b are system parameters. Parameters a and b are determined from the critical temperature (Tc) and critical pressure (Pc). Parameter α is determined from a correlation based on experimental data that use a constant called the Pitzer acentric factor (ω). Pitzer's acentric factor is a measure of the configuration and sphericity of the molecule, a measure of the deformity of the molecule.

For single-phase hydrocarbon gas systems at a pressure above 10 bar, the SRK and PR equations show similar performance, although PR is generally better in predicting cryogenic systems.

For mixtures, both equations introduce the use of binary interaction parameters (k_{ij}). These are empirical factors that represent the interaction between a pair of dislike molecules. The interaction parameters for SRK and PR are unlikely to be the same because of their empirical character.

11.2.3 Heating Value

The heating value of natural gas is the energy released as heat after the complete combustion of a mass unit of gas. It is a prime characteristic of natural gas because gas combustion is the main final use of this fuel, either to provide heat (primary energy) or power, when used in gas engines. It is also a key quality factor in gas trading. Methane, the main component of natural gas, has a heating value of 37.71 MJ/m^3 at 15°C and 1 atm; this value is obtained by cooling down the combustion products to 15°C. If water remains as vapor, then the energy recovered is known as the net heating value or lower heating value (LHV). If water is condensed, the recovered energy is known as the gross heating value or higher heating value (HHV). Table 11.2 shows the high heating value of the components of natural gas.

11.2.4 Wobbe Index

The wobbe index (WI) or wobbe number gives a measure of the relative heat input into a burner at a fixed gas pressure of any fuel gas. It is defined as

$$\mathrm{WI} = \frac{HHV}{\sqrt{d}} \tag{11.6}$$

where d is the relative density of gas (air = 1).

The WI is the combination of the heat input and the flow of gas into a burner. The heat input is directly proportional to the heating value, and the flow of gas into a burner is inversely proportional to the square root of the relative density.

The WI is a measure of the burning character of a natural gas. WI is important for calculating the amount of air to be drawn into a simple burner such as those used in a typical domestic appliance. Raising the WI will increase the carbon monoxide (CO) production because the amount of air remains the same in the burner but the requirement for complete combustion has been increased. Conversely, a reduction in the WI will lead to a loss of heat service and flame instability.

TABLE 11.2—HHV of the Components of Natural Gas

Component	HHV (MJ/Sm^3)
Methane	37.7
Ethane	66.1
Propane	93.9
Butanes	121.6
Pentanes$^+$	>149.4
H_2S	23.8
CO_2	0
N_2	0
Helium	0

The WI and impurity levels define the suitability of a natural gas for a particular market, and more specifically to a particular appliance.

11.3 NATURAL GAS CONDITIONING

11.3.1 Introduction

Natural gas from the reservoir normally contains water and various contaminants such as nitrogen (N_2), CO_2, H_2S, and other sulfur compounds such as carbonyl sulfide (COS) and mercaptans (RSH), aromatics, mercury, and sometimes helium. Purification processes for natural gas are hence of primary importance.

The presence of contaminants can result in damage to process facilities or failure to meet sale or environmental specifications; therefore, they have to be removed to a certain degree. The current trend of applying more severe emission and environmental standards requires gas streams to be purified to even more stringent levels. In addition, lower limits can also be set for plant operation reasons, especially in liquefaction plants: water, CO_2, and aromatics can freeze on heat exchanger surfaces, reducing efficiency and causing blockages; as far as mercury is concerned, it attacks aluminum, the main construction material for cryogenic heat exchangers. Typical specifications for impurities contained in the liquefaction section feed gas are listed in Table 11.3. In high-pressure pipelines, water is removed before compression to prevent corrosion, freeze-ups, and hydrate

TABLE 11.3—Typical Impurity Specifications in Gas to Liquefaction Section

Component	Limit (max)
Water	1 ppmv
Total sulfur	30 mg/SCM
H_2S	3–5 ppmv
CO_2	50 ppmv
Mercury	0.01 mg/SCM
Benzene	1 ppmv
Pentenes and heavier	0.1 mol %

Figure 11.3—Amine unit at the YPF La Plata Refinery (Argentina). *Source*: Picture courtesy of YPF.

formation; dew point control processes are also frequently used to avoid condensate formation during transportation.

The main processes for natural gas treatment are discussed in the next sections.

11.3.2 Acid Gas Removal (Gas Sweetening)

Acid gases (CO_2 and H_2S) can be removed from feed gas by different treatment technologies such as chemical and physical absorption processes, amongst others. Examples of chemical absorption are the conventional or activated amine process and the hot potassium carbonate process; examples of physical absorption are the proprietary solvent processes such as Sulfinol™[2] and Selexol™[3].

The acid gas treatment unit is also referred to as acid gas removal unit (AGRU) or sweetening unit because the resulting product no longer has the sour, foul odors of RSH and H_2S.

11.3.2.1 AMINE PROCESSES

Amine processes are very common in refineries, petrochemical plants, and natural gas processing plants (Figures 11.3 and 11.4). The simplified process flow diagram (Figure 11.5) illustrates the major equipment in an amine treatment process. The raw sour gas is fed to the bottom of an absorber equipped with structured or random packing or trays. The gas is sweetened by the amine solution in countercurrent flow. The solution from the absorber is heated up against regenerated solution directly or after flashing. Afterward, the resultant "rich" amine solution is fed to the regenerator and regenerated by reboiling. The acid gas, or off-gas, is sent to a sulfur recovery unit if the volumes of sulfur that can be recovered are sufficiently large to justify the investment or the environmental restrictions require high levels of sulfur recovery; if not, the off gases are just flared or incinerated. The cooled regenerated amine solution, or "lean" amine, is recirculated back to the head of the absorber column.

Some operating conditions and other considerations to be taken into account in an amine unit are

- Reboiler duty/temperature constraint because of solvent degradation.
- Absorber conditions: temperature from 35°C to 50°C and pressure from 35 to 205 bar (3500 to 20,500 kPa).
- Lean amine temperature from 20°C to 55°C to be optimized to increase solvent selectivity.
- Regenerator conditions: temperature ranges from 115°C to 130°C (bottom) and pressure from 1.4 to 2.0 bar (140 to 200 kPa).

There are many different amines used for gas sweetening.

- Monoethanolamine (MEA)
- Diethanolamine (DEA)
- Methyldiethanolamine (MDEA)
- Diisopropylamine (DIPA)
- Diglycolamine (DGA)
- High-load DEA (activated) and formulated MDEA

Selection of a particular amine process depends on feed gas composition and product gas specifications and takes into account the specific characteristics of each amine. For instance, CO_2 and H_2S selectivity is very dependent on the selected amine: primary and secondary amines (e.g., MEA,

---

[2] Sulfinol™ belongs to Shell Global Solutions International BV, The Hague, The Netherlands.

[3] Selexol™ belongs to Dow Chemical Company. The Selexol technology is currently owned by Union Carbide Corporation.

Figure 11.4—Amine unit at YPF La Plata Refinery (Argentina). *Source*: Picture courtesy of YPF.

DEA, and DIPA) react directly with H_2S and CO_2; tertiary amines, of which the most used is MDEA, is more selective to H_2S than CO_2.

The acid gas removal capacity of the circulating solution, or solvent strength, is another critical parameter of the process. It depends on amine concentration, which is usually limited by corrosion considerations. Thus, MEA (a primary amine) solution is limited to 15–20 wt % whereas for DEA (a secondary amine), concentration is limited to 30 wt %; MDEA can operate at much higher concentrations

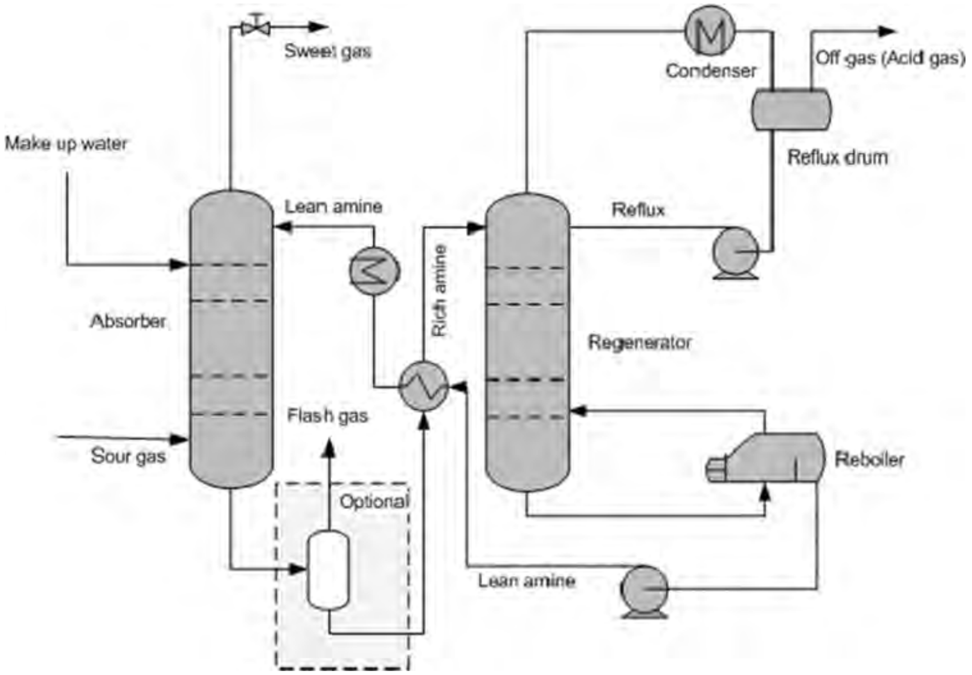


Figure 11.5—Typical amine process configuration.

such as 50 wt % with low corrosion potential. Considerable additional treating capacity is available with the formulated MDEA solvents using the same concentration, 50 wt %.

MDEA-based solvents are currently the most used in the gas industry. They have received a great deal of attention because of MDEA's selective reaction with H_2S in the presence of CO_2 (preferential removal of H_2S from a sour gas stream while rejecting or delaying the recovery of most of the accompanying CO_2 until a subsequent processing step). Thus, the contact time between the solvent (MDEA) and sour gas is designed to allow removal of the H_2S up to the required degree and at the same time to minimize CO_2 coabsorption. Increased selectivity for H_2S over CO_2 expands the regeneration capacity of the amine unit, reduces the energy required for the process, and improves the H_2S quality of the acid gas.

The selectivity of MDEA and related solvents can be influenced by

- *Contact temperature:* Colder processing (less than 32°C) or hotter processing (greater than 50°C) results in improved selectivity.
- *Contact pressure:* lower pressure improves selectivity.
- *Feed gas CO2/H2S ratio:* higher ratios of CO_2 to H_2S favor selectivity.
- Total acid gas load.
- Location of lean amine feed point on the absorber tower.

MDEA-based solvents have numerous advantages over primary and secondary amines.

- Selective removal of H_2S from the gas stream while kinetically limiting CO_2 absorption.
- Increase in sulfur plant efficiency and capacity because of the H_2S-enriched gas feed.
- Less degradation. Unlike MEA, DEA, or DGA, MDEA does not form amine CO_2 degradation products that enhance corrosion at elevated temperatures in the regenerator.
- Less corrosion.
- Lower amine circulation rate and pumping power. Acid gas pickup of up to 0.5 mole/mole MDEA is available without the need for costly metallurgy upgrades.

Finally, the desirable characteristics of basic MDEA have been extended by various manufacturers with the addition of chemical enhancers to create high-performance formulated MDEA products [2]. An example of this is Dow Chemical's solvent Ucarsol®[4], which has very high versatility and selectivity to remove CO_2 and H_2S. Some benefits of using a formulated solvent are smaller and more efficient plants, reduced energy consumption, lower capital cost, and lower contaminant levels in treated gas.

11.3.3 Other Acid Gas-Treating Processes

Hot potassium carbonate is used to remove CO_2 from a mixture of gases by absorption and then stripping the solution by pressure reduction without additional heating. The flow scheme of the hot potassium carbonate process shares some features with amine processes; however, in the hot potassium carbonate system, the gas-liquid contactor operates at high temperature, which saves a considerable amount of heat exchange in the process.

The Sulfinol process has been used in most LNG plants where Shell has been involved. Over 200 Sulfinol units have been licensed worldwide, including natural gas, synthesis gas, and refinery gas treatment. The solvent is a mixture of Sulfolane and DIPA, Sulfinol D. Another option is Sulfinol M, which uses MDEA instead of DIPA to minimize hydrocarbon absorption with the acid gas. The addition of Sulfolane increases the physical solubility of H_2S, CO_2, and organic sulfur compounds in the solvent. Approximately 80 % of the RSH in the sour gas stream are removed at this step; they are then further reduced in the molecular sieve unit.

The Selexol process uses a physical solvent made of a mixture of dimethyl ethers of polyethylene glycol to remove acid gases from synthetic or natural gas. The process solvent is regenerated either thermally, by flashing, or by gas stripping. The Selexol process is ideally suited for the selective removal of H_2S and other sulfur compounds or for the bulk removal of CO_2.

A common feature of physical solvent processes such as Sulfinol and Selexol is hydrocarbon coabsorption, which is usually a disadvantage because of

- The loss of valuable hydrocarbons into the acid gas (less sales)
- Contamination potential of the acid gas stream to the sulfur recovery unit by formation of COS, carbon disulfide (CS_2), and C (carbon or soot) [3].

Membrane separation is based on the principle of selective gas permeation. When a gas mixture is introduced to a membrane system, gas components dissolve into the membrane material and diffuse through it. Solubility and diffusivity are different for each gas component. CO_2, water vapor, and H_2S are easily permeable gas components, whereas methane, ethane, and other hydrocarbons permeate very slowly. This kind of process is typically applied for CO_2 bulk removal; for example, in natural gas treatment to meet pipeline specifications and for production of a CO_2-rich stream for enhanced oil recovery (EOR) injection.

11.3.3.1 ADSORPTION PROCESSES

Pressure swing adsorption (PSA) is based on the cyclic physical adsorption of the contaminant at a high pressure followed by desorption at low pressure. Typical applications of the PSA process are the separation of CO_2 from methane for upgrading of landfill gas, upgrading of biogas from digesters, and production of natural gas from poor-quality reserves. Molecular sieves efficiently remove low concentrations of polar or polarizable contaminants such as H_2O, methanol, H_2S, CO_2, COS, RSH, sulfides, ammonia, aromatics, and mercury down to trace concentrations. Extractive distillation can be used to separate H_2S from CO_2 but has a high energy cost [3].

11.3.3.2 SULFUR RECOVERY AND TAIL GAS TREATING

Sulfur recovery is used to reduce the sulfur emissions following legislation. The Claus sulfur recovery process consists of two steps:

1. *Thermal step:* The H_2S is first partially oxidized at high temperature (1000–1400°C) with air, forming SO_2. Afterward, the Claus reaction takes place ($2H_2S + SO_2$ to $3/XS_x + 2H_2O$), producing elemental sulfur, with 60–70 % of the total sulfur being produced in this step.

---

[4] Ucarsol® belongs to The Dow Chemical Company, TX.

2. *Catalytic step:* The remaining H_2S and SO_2 go to the catalytic section at lower temperatures (200–350ºC) for further conversion to elemental sulfur.

A tail gas unit manages the tail gas from the Claus process with the remaining sulfur compounds. There are three main options for tail gas treating:

1. Additional Claus catalytic process
2. Recovery of the sulfur compounds and its recycle to the Claus unit
3. Tail gas H_2S selective oxidation to sulfur

11.3.3.3 DEHYDRATION

11.3.3.3.1 Overview

The main reason for removing water vapor from natural gas streams is that it becomes liquid or solid under low-temperature and high-pressure conditions. Thus, liquid water in natural gas pipelines causes various flow problems such as corrosion, slug flow, or hydrate formation, which results in plugging or flow restrictions. Water is also removed to meet sales gas specifications. In cryogenic facilities, water can freeze and produce blockages. All of these problems reduce the availability and efficiency of pipelines and process equipment.

There are some cases when gas pipelines need to be operated with the presence of liquid water although the temperature is below the hydrate formation point. In those cases, hydrate inhibitors are necessary; alcohols or glycols such as methanol, diethylene glycol (DEG), or monoethylene glycol (MEG) are typically injected to depress hydrate and freezing temperatures. The three main types of processes to dehydrate natural gas are condensation, absorption, and adsorption.

11.3.3.3.2 Dehydration by Condensation

Dehydration by condensation consists in cooling natural gas and separating water as a condensate. In this process, MEG is injected not to “dehydrate” the gas (see *Dehydration by Absorption*) but rather to improve the water separation and prevent hydrates from forming.

11.3.3.3.3 Dehydration by Absorption

The main use of this dehydration process is to reach water dew point specification to avoid water condensation in pipelines. The hydrocarbon dew point of the gas is related to its natural gas liquids (NGL) content, so it remains the same as for the feed gas.

Glycols are typically used for applications in which water dew point depressions on the order of 15–49°C are required. DEG, triethylene glycol (TEG), and tetraethylene glycol (TREG) are all used as liquid desiccants. TEG is the most common for natural gas.

In general terms, the unit configuration consists of a simple absorber/regenerator system (see Figure 11.6). The gas enters at the bottom of the glycol absorber equipped with structured packing or trays. As the gas rises, the water is removed (absorbed) by the decreasing TEG concentration. Concentration of the lean glycol entering at the top of the absorber is the main variable that determines the water dew point specification that can be reached and therefore the efficiency of the process. The rich glycol that leaves the absorber is sent to a flash drum and then to a regeneration section. The lean glycol leaving the regeneration section is finally returned to the absorber closing the loop. Like the amine process, a lean-rich heat exchanger is used to heat up the rich glycol solution to conserve energy.

11.3.3.3.4 Dehydration by Adsorption

Dehydration by adsorption is used to obtain very low water content (0.1 ppm or less), levels required in NGL extraction and LNG production plants. It is based on solid desiccant

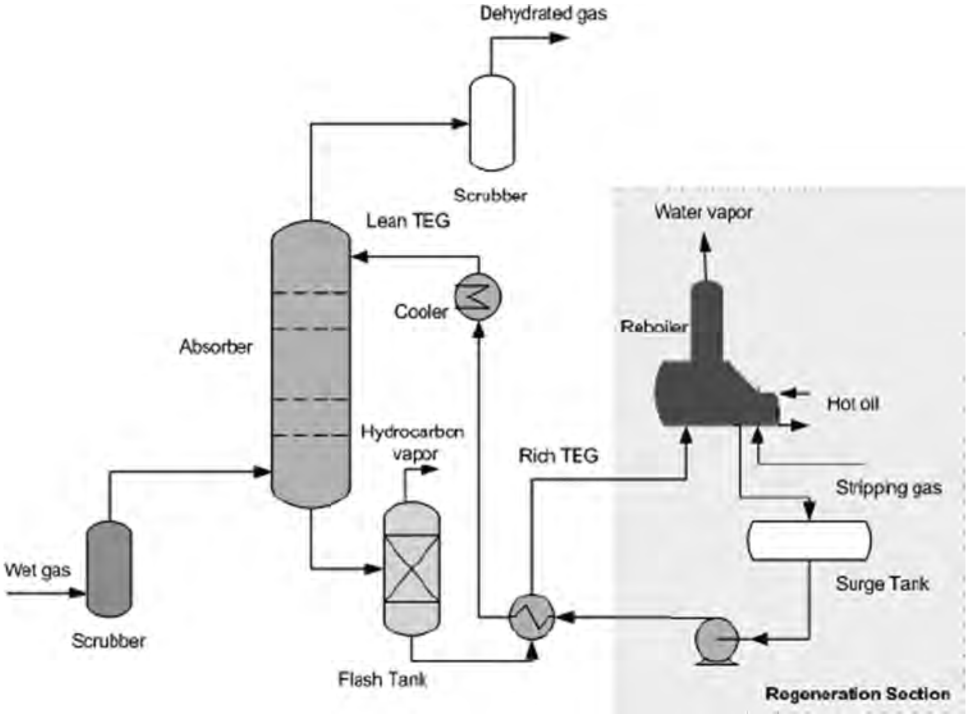


Figure 11.6—TEG dehydration unit.

TABLE 11.4—Typical Adsorbents for Dehydration [4]

Desiccant	Outlet Water Dew Point (°C)
Alumina	–73
Silica gel	–60
Molecular sieves	Less than –100

materials called adsorbents. The most common adsorbents are alumina, silica gels, and molecular sieves. Table 11.4 shows the dew point achievable with each of them.

The dehydration process based on adsorption consists of several vessels filled with adsorbent (adsorption beds). In LNG and NGL extraction plants, each bed is commonly made up of four layers of material: inert ballast balls, a guard layer, a water adsorption layer, and inert ballast balls again. Table 11.5 shows the material commonly used in each of the different layers.

The most used desiccant for the water adsorption layer is zeolite 4A, which is used in different sizes and shapes. The guard layer of silica gel or alumina adsorbs any entrained water liquid droplets and solvent traces. The inert ballast balls prevent desiccant movement and aid in gas distribution [4]. A typical life cycle considered for adsorbent materials is 2–4 years.

Figure 11.7 shows a typical water adsorption unit composed of three vessels, two of them operating in water adsorption mode whereas the other one is being regenerated. Once a bed has been in adsorption mode for approximately 16 h, it switches to regeneration mode for approximately 8 h. The regeneration is composed of two main stages:

1. *Heating step (up to 260–280°C):* The regeneration gas flow is normally approximately 5–15 % of the process flow and can be heated by a dedicated heat source or by integrating the dehydration unit with another unit of the plant.
2. *Cooling step:* Once the bed has been regenerated, then it is cooled down to normal adsorption temperature by the regeneration gas (without heating).

In liquefaction and NGL extraction plants, the dehydration unit is placed downstream of the AGRU because sweet natural gas from the AGRU absorber is always saturated with water. Typical process conditions of the dehydration unit in these types of plants are shown in Table 11.6.

The source and destination of the regeneration gas can vary depending on the end flash gas (EFG)/boil-off gas (BOG) flow rates, the impurities present in the feed gas, and the fuel gas system configuration. Typically, the regeneration gas is sweet dry gas and is sent to the fuel gas system.

TABLE 11.5—Typical Molecular Sieve Bed Configuration

Layer	Material
Inert ballast balls	Alumina, mullite, or ceramic
Guard layer	Silica gel or alumina
Water adsorption layer	Zeolite 4A—large size
	Zeolite 4A—small size
Inert ballast balls	Alumina, mullite, or ceramic

11.3.3.4 SULFUR COMPOUND REMOVAL

A primary contaminant found in most raw natural gas streams is sulfur, in the form of H_2S, elemental sulfur and often in various other organic forms (RSH, COS, etc.).

Sulfur compounds are known poisons for most gas and refinery processes, even when present at very low levels (often below detection levels at many facilities), and are significant contributors to atmospheric pollution.

As a general rule, when the integrity, operation, and maintenance of the facility are not compromised, it is recommendable, in terms of cost and contaminant removal effectiveness, to treat the most concentrated stream. Thus, the heaviest sulfur components are usually removed from the heaviest streams of the NGL fractionation process. On the other hand, lighter sulfur components, such as H_2S, are removed from the gas streams [5,6].

The molecular sieves are commonly used as a dry regenerative process to treat propane or butane streams and can also be used for treatment of mixed LPG streams. With the appropriate type of sieve material, the product can be treated to meet water content, volatile sulfur, and corrosion (copper strip test) specifications in one single process.

11.3.3.5 MERCURY REMOVAL

Another impurity that can be present in a natural gas stream is mercury, primarily in elementary form and in very small amounts. Chlorides and other species can also be present.

Mercury combines with aluminum to form a mercury-aluminum amalgam. When the amalgam is exposed to air, the aluminum is oxidized, and the oxide flakes away. Mercury is again available to form amalgam and the process is repeated again and again. A small amount of mercury can "eat through" a large amount of aluminum over time. For this reason, and considering that aluminum is one of the construction materials used in some of the main pieces of equipment in a LNG facility, mercury must be removed to levels below 0.01 mg/Sm^3 before entering the liquefaction train.

The mercury removal unit is present in all liquefaction facilities regardless if the contaminant has been identified in the inlet gas. This unit can be placed before the acid gas treatment unit or after the dehydration unit. It typically consists of a bed of sulfur-impregnated activated carbon.

This is a nonregenerative process, so at the end of the life cycle, which could be as long as 10 years depending on mercury content of the gas, the spent carbon must be disposed [7].

11.3.3.6 INERT GAS REMOVAL

Natural gas usually contains inert gases such as N_2 or helium in variable amounts depending on the gas field. Strictly speaking, these gases are not contaminants because they do not produce any undesirable effect for natural gas processing. However, their presence in natural gas is a problem because it increases the size of gas compression facilities, pipelines, and processing plants. Furthermore, inert gas content must very often be adjusted to meet sales gas specifications, such as HHV and inert content. Hence, simple economic/commercial reasons are involved in the

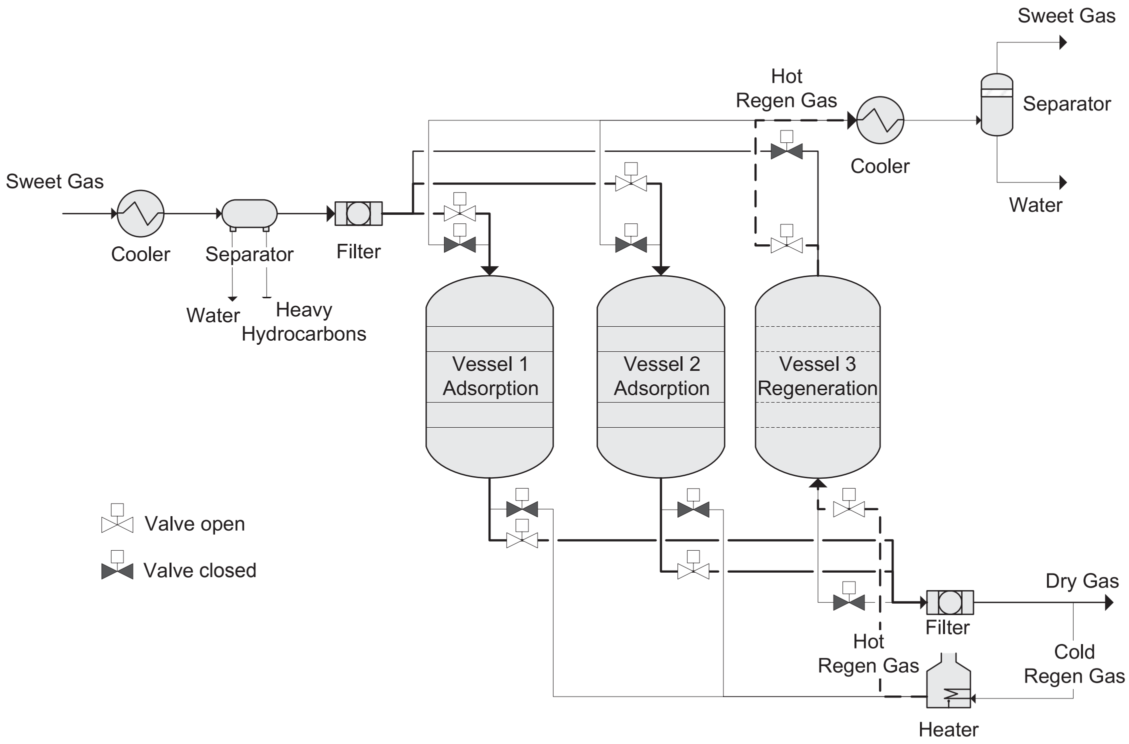


Figure 11.7—Typical three-bed dehydration unit.

decision to remove inerts; on the other hand, natural gas is also the primary market source for helium [8].

These gases are separated from natural gas, when necessary, via N_2 rejection units or helium recovery units. Sometimes, a simple end flash can achieve the specification, but when feed gas composition is rich in N_2, stripping or cryogenic distillation technologies will be necessary. The N_2-rich stream separated from the main stream can then be used as fuel gas, flared, or sent back upstream for injection to maintain field pressure and EOR.

11.4 NGL EXTRACTION AND FRACTIONATION

11.4.1 Introduction

The term NGL applies to liquids recovered from natural gas and as such refers to hydrocarbon components heavier than methane contained in natural gas. The term liquefied petroleum gases (LPG) describes hydrocarbon mixtures in which the main components are propane and iso- and normal butane (see Figure 11.8).

The NGL extraction from natural gas streams can range from ethane and heavier hydrocarbon extraction to pentanes and heavier component removal. The desired degree of liquid recovery has a deep impact on process selection, complexity, and cost of the processing facility.

The NGL extracted from natural gas can be further fractionated to make commercial products such as ethane, propane, butane, and gasoline. The degree of fractionation is dependent on the market and geography.

TABLE 11.6—Typical Conditions of Feed Gas to a Dehydration Unit

Conditions	
Temperature (°C)	30–55
Pressure (bar)	40–75
Molecular weight (kg/kmol)	17.5–19
Water (mol %)	0.1–0.3

11.4.2 NGL Extraction [9–11]

11.4.2.1 DEW POINT CONTROL

Dew point is defined as the temperature at which vapor begins to condense. When gas is transported in pipelines, consideration must be given to the control of the formation of hydrocarbon liquids in the system. Liquid condensation is a problem for gas metering, pressure drop, and safe operation and can cause liquid slugging.

To prevent formation of liquids, it is necessary to control the hydrocarbon dew point below the pipeline operating conditions with the desired safety margin for the operation. Operating conditions are usually fixed by design and environmental considerations, so in practice, single-phase flow can only be assured by removing the heaviest hydrocarbons in the gas. There are different ways to do it.

11.4.2.2 LOW-TEMPERATURE SEPARATION

Low-temperature separation (LTS) can be achieved using Joule-Thompson (J-T) autorefrigeration or mechanical refrigeration.

If sufficient pressure is available, the cooling required for removal of hydrocarbon liquids is achieved through a sudden adiabatic gas expansion (J-T expansion or free expansion) so that heavier hydrocarbons and other condensables condensate. The performance of J-T units are very much dependent on the condition of the incoming raw

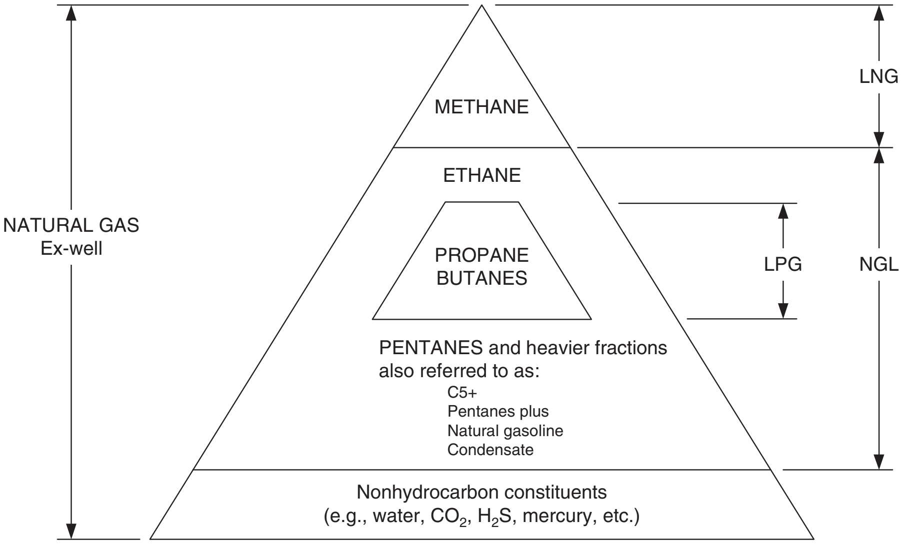


Figure 11.8—Natural gas constituents.

gas streams because they use excess pressure energy of the raw gas stream to autorefrigerate the gas. More particularly, the temperature drop is affected by the gas composition, flow rate, and pressure of the feed gas.

In other cases, inlet pressure is not high enough to allow a LTS system. An alternative option is to utilize a mechanical refrigeration system to remove heavy hydrocarbon components. Mechanical refrigeration consists in cooling the gas stream to the specified temperature by means of an independent refrigeration cycle (e.g., a propane cycle). Liquid is again separated in a cold separator.

If the gas stream contains water, this process requires a previous dehydration unit or glycol injection to avoid hydrate formation.

A new technology called Twister™[5] was recently proposed, which combines expansion, cyclonic liquid/gas separation, and recompression for dew point control and NGL extraction (C_3^+).

Twister™ is a compact tubular device that works as a LTS process with thermodynamics similar to a turboexpander, causing a temperature drop by transforming pressure to supersonic velocity. The condensed hydrocarbons are separated via centrifugal forces caused by the induced swirl of the gas through the device. Afterward, the gas goes through a diffuser where part of the pressure drop is recovered.

11.4.2.3 NONCOOLING PROCESSES

Noncooling processes have not typically been the preferred option since the development of turboexpander processes, but they still are considered because they may provide an optimal solution in certain applications.

The lean oil absorption process is the physical process in which a vapor molecule of a lighter hydrocarbon component dissolves into a heavier hydrocarbon liquid (nonane, decane, and heavier) so that it is separated from the gas stream. The process can be operated at ambient temperatures if only separation of the heavier NGL products is desired. A refrigerated system enhances the recovery of lighter hydrocarbon products such as ethane and propane. These processes have the advantage that the absorber can operate at essentially feed gas pressure with minimal pressure loss, but they require large process equipment and have high energy requirements. Therefore, they are usually less attractive than LTS systems.

The control of water and hydrocarbon dew points of a sales gas can be achieved by the addition of a solvent, such as methanol, glycol, or other proprietary solvents (which improves the solubility of hydrocarbons). This solvent absorption process is often combined with J-T expansion.

The adsorption process, sometimes referred to as "short cycle adsorption process," uses dry desiccant beds (e.g., silica gel) to attract or adsorb hydrocarbons and water. Water is the most strongly attracted compound, whereas heavy hydrocarbons are attracted more strongly than the lighter ones.

11.4.2.4 ETHANE AND PROPANE RECOVERY

Dew point control processes are used for applications in which moderate propane recoveries are desired. To achieve higher propane recoveries, ethane recovery, or both, cryogenic temperatures are required. Generally speaking, the natural gas industry considers cryogenic processes as those that operate below –50°F (approximately –45°C). There are different methods to reach high ethane recovery levels: J-T expansion, turboexpander extraction, and mechanical refrigeration.

11.4.2.4.1 J-T Expansion

The J-T effect consists of cooling down the gas by its expansion across a J-T valve. With large pressure drop across the J-V valve, cryogenic temperatures can be achieved, which results in high extraction efficiencies. To effectively use the J-T effect, inlet gas must be at a high pressure; if not, then compression is required.

When the feed gas pressure is not high enough or the gas is rich in liquefiable hydrocarbons, mechanical refrigeration can be added to the J-T process to improve recovery efficiency. An advantage of the refrigerated J-T process is that lower feed pressures are required.

---

[5] Twister™ Supersonic Separator belongs to Twister BV, Einsteinlaan 10 2289 CC Rijswijk (ZH), The Netherlands.

The J-T process, either refrigerated or nonrefrigerated, offers a simple and flexible option for moderate ethane recovery. It is usually applied to reduced gas flow rates in which some inefficiency can be tolerated, allowing for the reduction of capital and operating costs.

11.4.2.4.2 Turboexpander Extraction

The process that dominates ethane recovery applications is the turboexpander process. A turboexpander, also referred to as an expansion turbine or expander, is a centrifugal or axial flow turbine that extracts work from a high-pressure gas stream. From a thermodynamic point of view, the expansion across a J-T valve follows an isenthalpic path, whereas the ideal expansion through a rotating machine to produce mechanical energy follows an isentropic path (the enthalpy of the fluid decreases). This leads to a larger temperature drop than that achieved through a valve for the same pressure drop. Hence, turboexpander processes allow higher recoveries and efficiencies than J-T valves. The work recovered from the gas stream by the expander is typically used for driving a compressor. Other possible options are expander-pump and expander-generator configurations [12].

The turboexpander process has been applied to a wide range of process conditions for ethane and propane recovery projects. With the conventional turboexpander process configuration, the ethane recovery is limited to approximately 80 %; additional process integration as the residue recycle system is required to recover beyond this level. This system provides more refrigeration to the process, so it can be used for very high ethane recoveries (only limited by the quantity of power provided).

To improve the performance of conventional expander systems, new processes have been developed. Examples are the gas subcooled process (GSP) [13] and the cold residue recycle (CRR) process [14].

11.4.2.5 PARTICULARITIES OF NGL RECOVERY IN LIQUEFACTION PLANTS [15,16]

Although NGL recovery processes are widely used in many gas processing plants, different configurations of the NGL recovery units within the liquefaction plant are reviewed below because of the importance of LNG in the global gas market.

The requirements to remove NGLs in an LNG plant can be based in one or more of the following reasons [17]:

- To adjust the natural gas quality (heating value)
- Commercial interest of NGLs as a separate product
- To prevent freezing up of heavy components in the cryogenic section of the liquefaction process
- To obtain refrigerant makeup for the liquefaction process

The level of NGL extraction from natural gas is somewhat discretionary. Safety issues dictate the minimum extraction level, whereas a balance between technology and the relative market value of the NGLs determines the maximum extraction level.

11.4.2.6 LOCATION OF THE NGL EXTRACTION UNIT IN LNG PLANTS [18,19]

There are various options for locating the NGL extraction unit within a liquefaction plant. The selected position will depend on the level of integration with the LNG unit, the quality and condition of the feed gas, the required level of NGL recovery, and plot plan area considerations.

Hydrocarbon extraction schemes can be divided into two main categories: an NGL extraction unit located in an independent front-end configuration with its own refrigeration system or an NGL unit integrated with the liquefaction unit. Additionally, an intermediate case can be considered in which the NGL extraction unit is integrated with the precooling section, which provides cold for partial condensation and separation. The NGL recovery varies according to its position in the process.

The integrated process is very efficient, but it uses the LNG refrigeration power block to extract the NGL and, consequently, production of LNG is reduced. The nonintegrated NGL extraction process uses an independent refrigeration system and then recompresses the gas stream for efficient liquefaction. It can achieve higher recovery values than the integrated configuration, but it is less efficient.

11.4.3 NGL Fractionation

The bottom liquid stream from the NGL recovery unit may be sold as a mixed product. This is common for small, isolated plants where there exists insufficient local demand. The mixed product is transported by truck, rail, barge, or pipeline to a central location for further processing. Often it is more economical to fractionate the liquid into its various components, which have a market value as pure products.

The process of separating an NGL stream into its components is called fractionation. At the fractionation unit, liquids will be separated into commercial-quality products and then delivered to the market by tankers (exports) or tank trucks (domestic consumption).

NGLs are fractionated by a series of distillation towers. Fractionation takes advantage of the difference in boiling points of the various NGL products. As the temperature of the NGL stream is increased, the lightest (lowest boiling point) NGL product boils off the top of the tower, is condensed into an almost pure liquid, and is then sent to storage. The heavier liquid mixture at the bottom of the first tower is routed to the second tower where the process is repeated and a different NGL product is separated and stored. This process is repeated until the NGLs have been separated into their components.

Fractionators are usually named for the overhead or top product. Therefore, a de-ethanizer implies that the top product is mainly ethane; a depropanizer indicates that the top product is propane, etc. (see Figure 11.9).

11.4.3.1 FRACTIONATION OPERATION

The operation takes place in a vertical column where vapor and liquid mixtures flow countercurrent and are brought into repeated contact. During each contact, part of the liquid vaporizes and part of the vapor condenses. The contact between liquid and vapor takes place in the internals of the column that can be trays or packing.

As the vapor rises through the column, it becomes enriched in the lighter or lower boiling components (rectification section). Conversely, the downward flowing liquid becomes richer in heavier, higher boiling components (stripping section).

The liquid mixture that is to be processed is known as the feed, which is introduced usually somewhere near

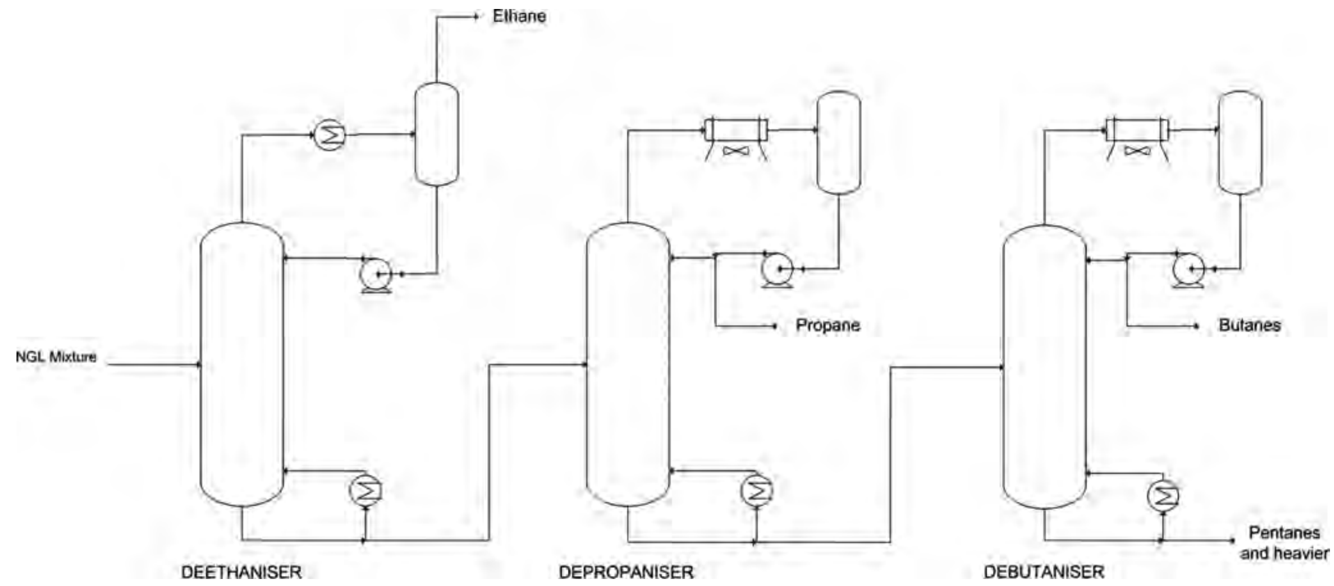


Figure 11.9—NGL fractionation.

the middle of the column. The feed section divides the column into a top (enriching or rectification) section and a bottom (stripping) section. The feed flows down the column where it is collected at the bottom in the reboiler. Heat is supplied to the reboiler to generate vapor. The vapor raised in the reboiler is reintroduced into the unit at the bottom of the column. The liquid removed from the reboiler is known as the bottom product. The vapor moves up in the column, and as it exits the top of the unit, a condenser cools it.

The condensed liquid is stored in a holding vessel known as the reflux drum (accumulator). Some of this liquid is recycled back to the top of the column and is called the reflux. The condensed liquid that is removed from the system is known as the distillate or overhead product (in some cases, the overhead product is a vapor). To avoid reducing the operating pressure of the fractionator (which would require further recompression), the fractionation process should be carried out with minimal loss of pressure.

The only limitation is that high-pressure fractionation must occur at a pressure safely below the critical pressure at every stage of the column to ensure that liquid and vapor phases will be present. The designer must also be concerned about the effect of pressure on the relative volatility of the key components in the fractionating column.

As the operating pressure of the fractionating column increases, the relative volatility decreases, making it more difficult to get a clean separation between the two key components. The operating pressure of a fractionating column is normally set by a desired component separation and the temperature of the reflux condenser cooling medium (i.e. air, water, and refrigerant). This pressure is the minimum pressure at which the column can operate at the chosen condenser temperature. The pressure will correspond to the bubble point or the dew point of the column overhead product. The overhead product will be at its bubble point for a liquid product (total condenser) or at its dew point (partial condenser) for a vapor product.

11.4.3.2 TRANSMISSION PIPELINE (HIGH-PRESSURE PIPELINE)

The transmission pipeline system ensures an uninterrupted supply of gas at the desired flow rate and pressure from the point of production to the delivery point. The delivery point is often a city gate, but it can also be a large-volume user, such as a power plant. The high-pressure pipeline is a very convenient method of transporting gas; however, the pipelines are not flexible because they tie the gas source to a particular destination. If the pipeline has to be shut down, the gas source often has to be shut down as well.

The use of pipelines has been the most important factor in promoting the growth of the natural gas industry throughout the world. More than 90 % of the natural gas consumed in the world is delivered through pipes. Even with LNG, once it is regasified, it can only be delivered through a pipeline system.

In gas pipelines, compression (or formation pressure, or both) drives the flow. Flow resistance is primarily due to pipe friction. The pipeline elevation changes do not influence pressure loss very much because the transport of natural gas is in a single-phase flow and because of the low density of the gas.

The design and analysis of natural gas pipelines involve the use of the gas flow equation:

$$Q_s = k\left(\frac{T_s}{P_s}\right)\left[\frac{\left(P_1^2 - P_2^2\right)}{dZTfL}\right]^{0.5} \tag{11.7}$$

where:
k = gas flow equation constant (=7.574×10^{-4} using SI units),
T_s = temperature at standard conditions,
P_s = pressure at standard conditions,
P_1 = upstream pressure,
P_2 = downstream pressure,
d = relative density of the gas,
Z = gas compressibility factor,
T = flowing temperature,
f = pipe friction factor,
L = length of the pipe.

From equation 11.7 it can be observed that the capacity of the pipe (Q_s) is a function of the upstream pipe pressure, pressure drop, pipeline diameter, and pipeline length. It accounts for variations in compressibility factor, kinetic energy, pressure, and temperature for any typical line section. The equation also involves the friction factor, which fundamentally relates the energy lost due to friction. The friction factor is a function of the flow regime and pipe roughness.

Typically, transmission pressure can be in the range of 4–7 MPa and pipe diameters from 60 to 120 cm. For long-distance pipelines, compressors are essential to boost up the pressure lost by friction. Compression within limits set by the maximum operating pressure of the pipeline is also an alternative to increase additional pipeline capacity.

Once the pipeline diameter is fixed, the quantity of gas that can be delivered is then fixed by the pressures. At times, capacity can be increased by adding compressors along the pipeline, installing an extra pipe in the form of loops, or increasing the average pipeline pressure.

Overland pipelines are extensively used throughout Europe and the United States. Subsea pipelines over 3000 km have been regarded as uneconomic because pipeline installation and maintenance are very expensive and any recompression along the route is difficult.

11.4.3.3 COMPARATIVE COST OF MOVING GAS BY PIPELINE AND AS LNG

As mentioned earlier, natural gas is more complex and generally more expensive to store and transport because of its physical nature, which requires high pressures, very low temperatures, or both. Figure 11.10 shows the comparative cost of moving gas by pipeline (offshore and onshore) and LNG [20].

11.4.3.4 NATURAL GAS LIQUEFACTION AND REGASIFICATION

The LNG chain comprises pretreatment, liquefaction of the gas, its transportation in bulk carriers, regasification at the point of delivery, and the transportation to the final users also through high-pressure pipelines.

11.5 NATURAL GAS LIQUEFACTION

Natural gas liquefaction is the process that converts natural gas into LNG by cooling it to –163°C. Figure 11.11 shows the different stages in a liquefaction plant. The major components of an LNG plant are

- Pretreatment
  - Gas reception facilities
  - Acid gas removal
  - Dehydration
  - Mercury removal
  - Gas precooling and heavy (NGL) hydrocarbon removal
- Liquefaction
- Storage and export
  - N_2 removal
  - LNG and NGL storage
  - BOG handling
  - LNG (and NGL) ship loading facilities

11.5.1 Types of LNG Plants

There are different ways to categorize LNG plants; the most usual are based on the size and mode of operation. Thus, according to the size, an LNG plant can be

- Mini: <0.1 MTA
- Small: 0.1–1 million tons per annum (MTA)
- Medium: 1–3 MTA
- Large: 3–6 MTA
- Mega: >6 MTA

According to the mode of operation, there are two types of LNG plants:

1. *Baseload plants:* Baseload plants are in operation throughout the whole year. This type of plant has been used for more than 40 years as an option to monetize gas reserves (i.e., to allow the transport of gas from the field to the market). It is worth mentioning that one of the main targets of liquefaction technologies for baseload plants is to achieve a high efficiency. The first baseload liquefaction plants had a production capacity of approximately 1 MTA, but this capacity has increased over the years to take advantage of the economies of scale; nowadays, capacity can be up to 10 MTA per liquefaction train. Baseload plants can also be found at a mini or small scale. The plants that produce vehicle fuel

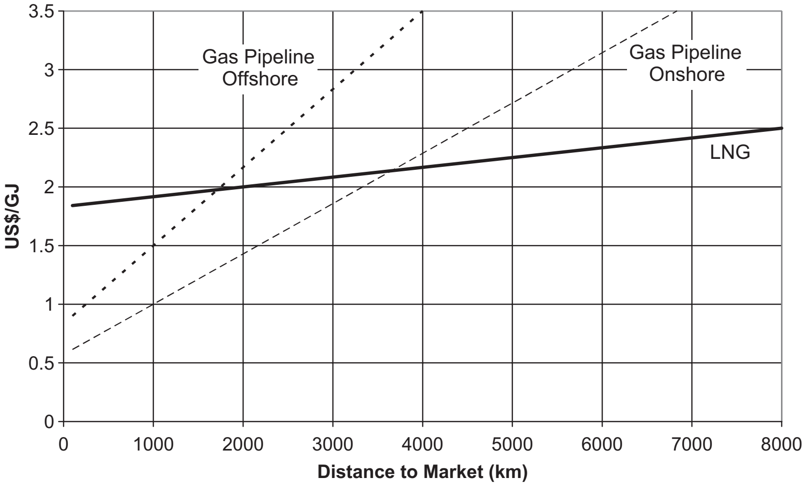


Figure 11.10—Indicative cost of moving gas by pipeline and LNG.

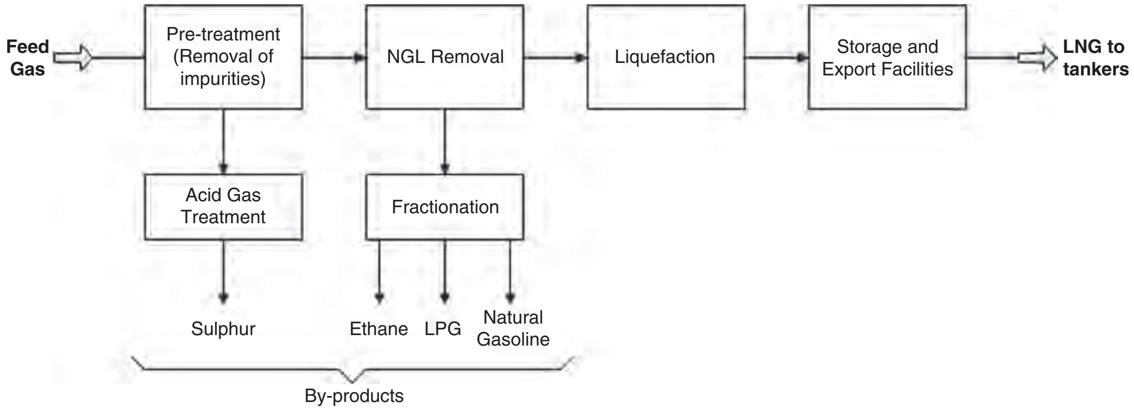


Figure 11.11—Block flow diagram of a typical liquefaction plant.

LNG, with capacities ranging from 10–400 t/day are an example. They have arisen mainly in the United States (e.g., California), where an increasing interest in LNG exists as an alternative fuel for buses, trucks, and taxis. The LNG supplied by small baseload plants can also be used to produce compressed natural gas (CNG) for natural gas vehicles. Other uses of mini or small baseload LNG plants include the natural gas supply to remote areas by truck, rail, or barge LNG transportation.

2. *Peak-shaving plants:* Peak-shaving plants are designed and operated to cover peaks of gas demand. During the summer months, the energy supply companies may buy larger quantities of gas than required for average consumption. This excess is liquefied and stored as LNG. In the winter months, that LNG allows for meeting the requirements of peak consumption. Peak-shaving LNG plants typically have capacities of 10–200 t/day and operate 150–200 days a year. There are more than 240 peak-shaving plants worldwide, particularly in the United States, the Netherlands, Germany, the United Kingdom, and in other highly developed gas supply regions [21].

11.5.2 Major Equipment in an LNG Plant

11.5.2.1 HEAT EXCHANGER

The main cryogenic heat exchanger (MCHE) is the heart of the liquefaction process. There are two main types of MCHE: brazed aluminum plate-fin heat exchangers (BAHX) and spiral wound heat exchangers (SWHE).

BAHX are manufactured by vacuum brazing technology. They can treat many process streams in only one unit, which avoids expensive interconnecting piping. The aluminum alloys used for the fabrication of these heat exchangers provide the best possible heat transfer, allow the application for low-temperature service, and drastically reduce the equipment weight. There are several manufacturers of this type of heat exchanger.

SWHE consist of at least one spiral-wound tube bundle housed within an aluminum or stainless steel pressure shell. For LNG service, these heat exchangers may consist of up to three tube bundles, each one made up of several tube circuits. The spiral-wound heat exchanger is known for its robustness, in particular during startup and shutdown or plant trip conditions. Air Products and Linde are the only companies capable of manufacturing SWHE.

11.5.2.2 COMPRESSORS AND DRIVERS

Refrigerant compressors and their drivers have been a focus of improvement in LNG plant design through the years. Centrifugal compressors are normally utilized in LNG plants, although axial-flow machines can also be used.

Refrigerant compressors are the most energy-demanding part of an LNG plant. In the earliest plants, the steam turbines were the preferred option to drive these compressors; however, the need of a complete steam and water treatment system constitutes an important disadvantage for this solution. Thus, steam turbines gave way to heavy-duty gas turbines, which have been the main compressor drivers selected for the last few years. As the capacity of the LNG plant increased, the size and power output of the gas turbines used as drivers also increased.

Aeroderivative gas turbines are, for some years now, an alternative to heavy-duty gas turbines because of their higher thermal efficiency and lower weight. However, they present some limitations in size and their cost per unit of power is higher. Darwin LNG is the first baseload LNG plant to use this type of turbine as a mechanical driver.

In recent years, the option of using electric motors as compressor drivers has also arisen mainly because of the benefits in availability they can provide. The first application of this solution is the Hammerfest LNG project (Snøhvit, Norway). The installation of a combined cycle power plant (CCGT) to supply the electricity that these motors require can add efficiency and environmental advantages to this alternative, although investment cost increases.

11.5.3 Liquefaction Technologies

11.5.3.1 C3-MR PROCESS

The C3-MR liquefaction process accounts for nearly 90 % of the world's baseload LNG capacity. The typical C3-MR process uses propane in the precooling refrigeration cycle and a mixed refrigerant (MR) composed of N_2, methane, ethane, and propane for the liquefaction cycle [22]. As can be observed in Figure 11.12, a multistage propane cycle precools the feed gas and partially condenses the MR from the MR compressor by using kettle-type heat exchangers. The partially condensed MR feeds the MCHE (a spiral-wound type exchanger), where it is autocooled and expanded so as to achieve matching cooling curves with reasonably small temperature difference. The natural gas is liquefied in the MCHE.

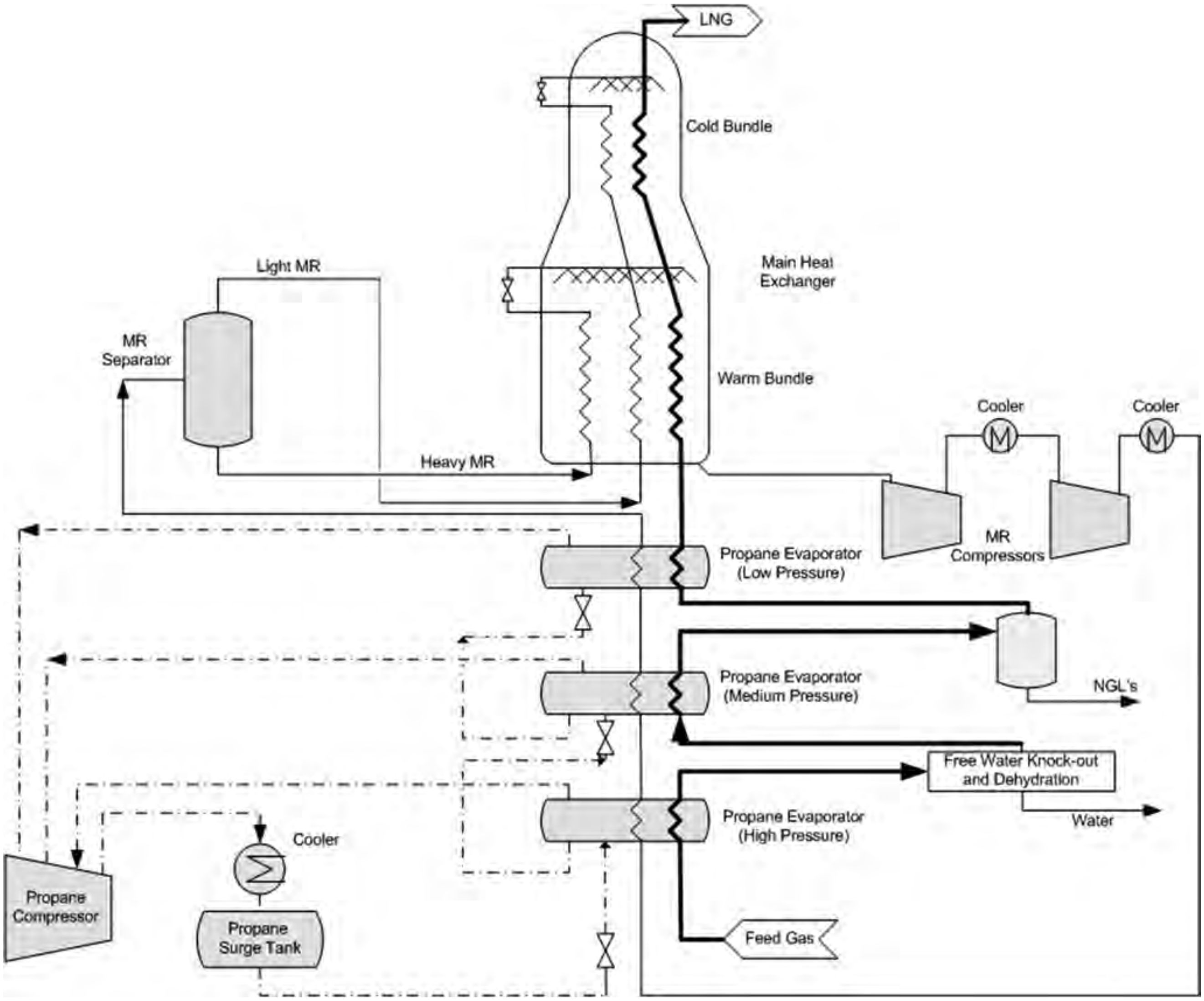


Figure 11.12—C3-MR process. *Source*: Figure courtesy of Air Products and Chemicals, Inc.

There are many possible combinations of gas turbine drivers for the refrigerant compressors. Recent LNG projects have used GE Frame 5, 6, and 7 machines as compressor drivers. The C3-MR process implemented with the Split MR™[6] machinery configuration has the flexibility of efficiently using all available power from the drivers to handle changing ambient conditions. In the Split MR configuration, the low- and medium-pressure MR compressor stages are driven by one gas turbine and the high-pressure MR and the propane compressor are driven by a second gas turbine, allowing for the power split between propane and MR refrigeration to be optimized.

11.5.3.2 CONOCOPHILLIPS OPTIMIZED CASCADE®[7] PROCESS

Far behind C3-MR, the ConocoPhillips Optimized Cascade process has been used in several LNG plants (e.g., Atlantic LNG, Kenai, and Egypt LNG). The Optimized Cascade process (Figure 11.13) was developed from a classical refrigerant cascade system in which the lowest boiling temperature stage of each refrigerant is used in turn to condense the next refrigerant. The process uses pure refrigerants in the consecutive cooling steps, namely propane and ethylene, both in closed cycles, and finally methane in a multistage open cycle. Core-in-kettle-type heat exchangers and plate-fin heat exchangers are used for cooling the natural gas and for cold recovery. Several aluminum exchangers are distributed within the insulated steel cold boxes.

To limit the compression ratio of the methane compressor, the LNG rundown is above atmospheric pressure and runs flashing into the LNG tanks. The BOG from tanks forms part of the methane cycle. To limit the buildup of N_2 in the methane cycle, fuel gas is taken from the methane compressor.

The main characteristics for the Optimized Cascade process are

- Different combinations of compressors and drivers are possible so as to better fit desired LNG train capacity.
- High LPG recoveries (>95–96 %) are achievable with the conventional process design.

---

[6] Split MR™ belongs to Air Products and Chemicals, Inc., Allentown, PA.

[7] ConocoPhillips Optimized Cascade® belongs to ConocoPhillips, Houston, TX.

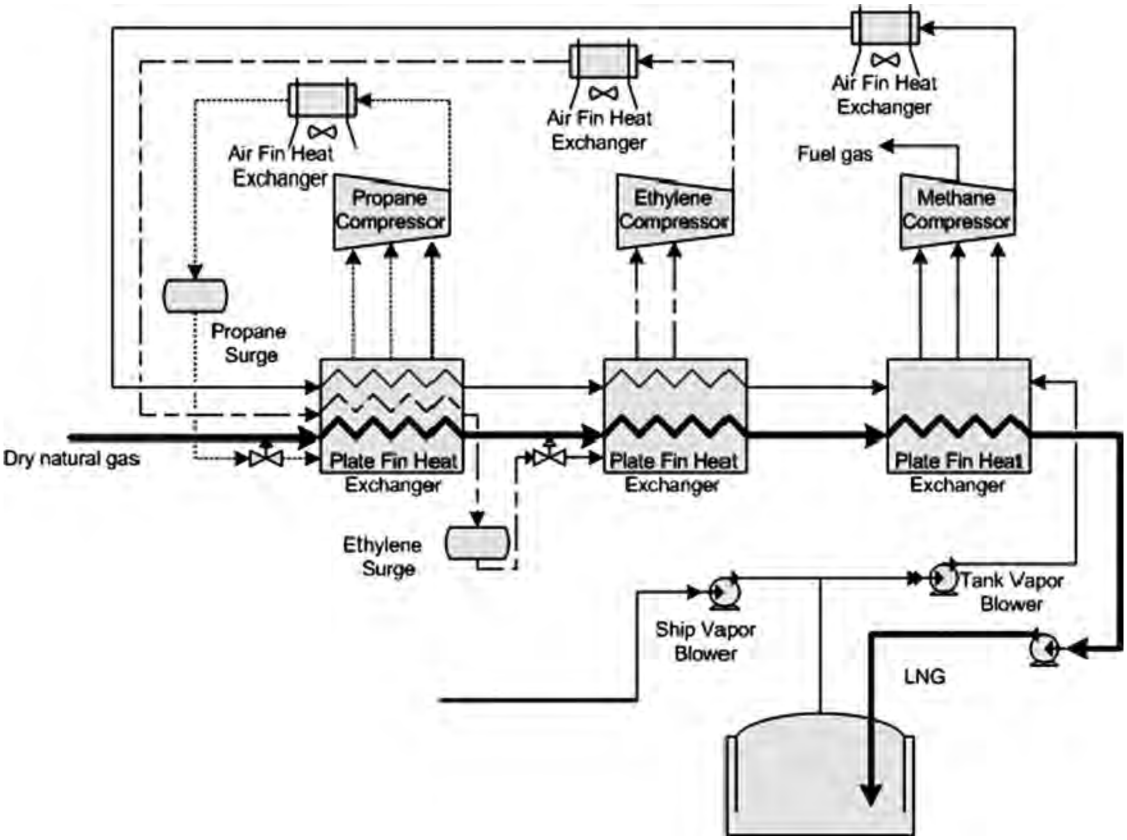


Figure 11.13—ConocoPhillips Optimized Cascade® process. Optimized Cascade is a registered trademark of ConocoPhillips, Co.

- Current maximum train size for the Optimized Cascade process is approximately 5 MTA LNG (train 4 of Atlantic LNG). However, this process could theoretically achieve megatrains of up to approximately 8 MTA.
- Makeup for the propane cycle is obtained from the feed gas, whereas ethylene has to be imported.

11.5.3.3 AP-X®[8] PROCESS

In recent years, interest has grown in ever-larger train capacities so that economies of scale can significantly reduce the unit cost for LNG. To meet this requirement, Air Products has developed and patented the AP-X liquefaction process.

The Air Products AP-X process (Figure 11.14) is an improvement to the C3-MR process in which the LNG is subcooled using a third cycle with a N_2 expander loop. The use of this third stage makes feasible an important capacity increase by reducing the flow of propane and MR necessary in the cycles for the same production. With this process, mega capacities of trains (up to 8–10 MTA per liquefaction line) can be achieved without duplicated or parallel equipment.

One of the advantages of this technology is its flexibility because it is possible to operate at a reduced capacity of 65 % without the N_2 expander loop by adjusting the composition of the MR [23].

The first plant to use this technology is in Qatar. This is also the first plant to use Frame 9 turbines as drivers.

11.5.3.4 LIQUEFIN™[9] PROCESS

The Liquefin process is a new liquefaction process commercialized by Axens and developed by the French Institute of Petroleum [24]. This process has not been industrially implemented yet.

The Liquefin process is a dual MR cycle process that is based on the use of plate-fin heat exchangers (PFHEs) in the exchanger line. When compared with the C3-MR process, the precooling mixed refrigerant (MR1) operates at a much lower temperature, which is adjusted to maximize the use of available power. At this temperature, the cryogenic mixed refrigerant (MR2) is completely condensed, and no phase separation is necessary. Both MRs are used as if they were pure components: the MR is condensed and vaporized at different pressure levels in each section, without any phase separation or fractionation.

All of the heat exchange between the natural gas and the MRs (and between the two MRs) is done in a single exchanger line made of PFHEs inside of a limited number of cold boxes. The exchanger line is modular: each cold box contains several parallel lines of two cores in series. The number of cores and cold boxes depends on the desired capacity. Figure 11.15 presents the typical process scheme for the Liquefin process. The main process features are

- A single exchanger line, made of PFHEs inside of a few cold boxes, is used to cool and liquefy the natural

---

[8] AP-X® belongs to Air Products and Chemicals, Inc., Allentown, PA.

[9] Liquefin™ belongs to Axens-IFP Group Technologies, Rueil-Malmaison, France.

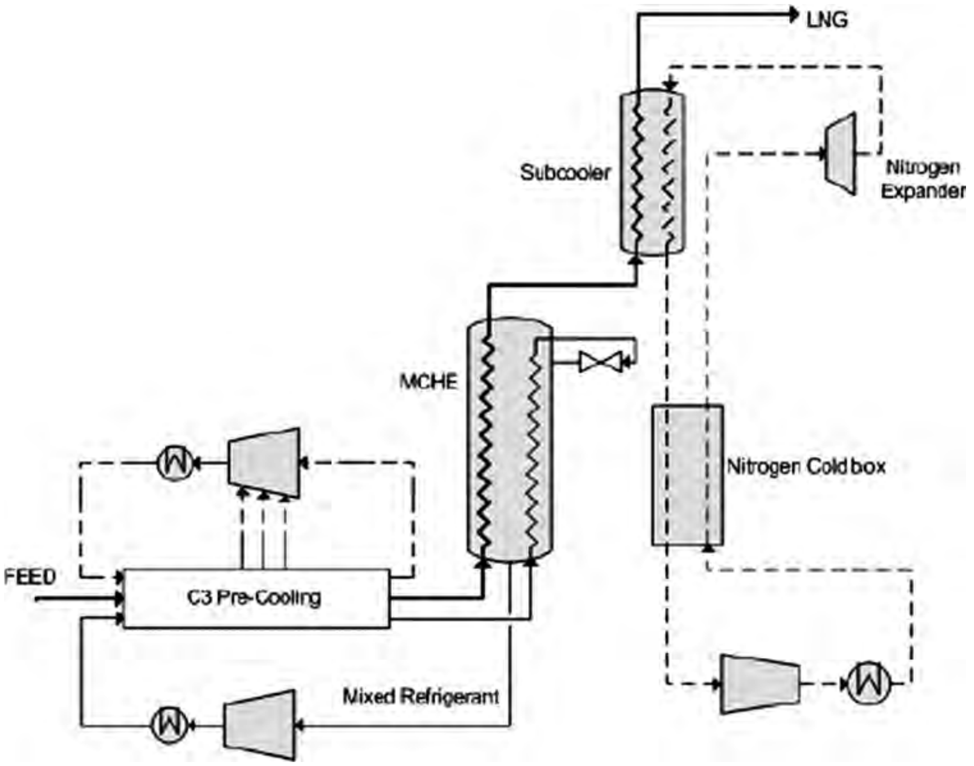


Figure 11.14—AP-X® process. *Source*: Figure courtesy of Air Products and Chemicals, Inc.

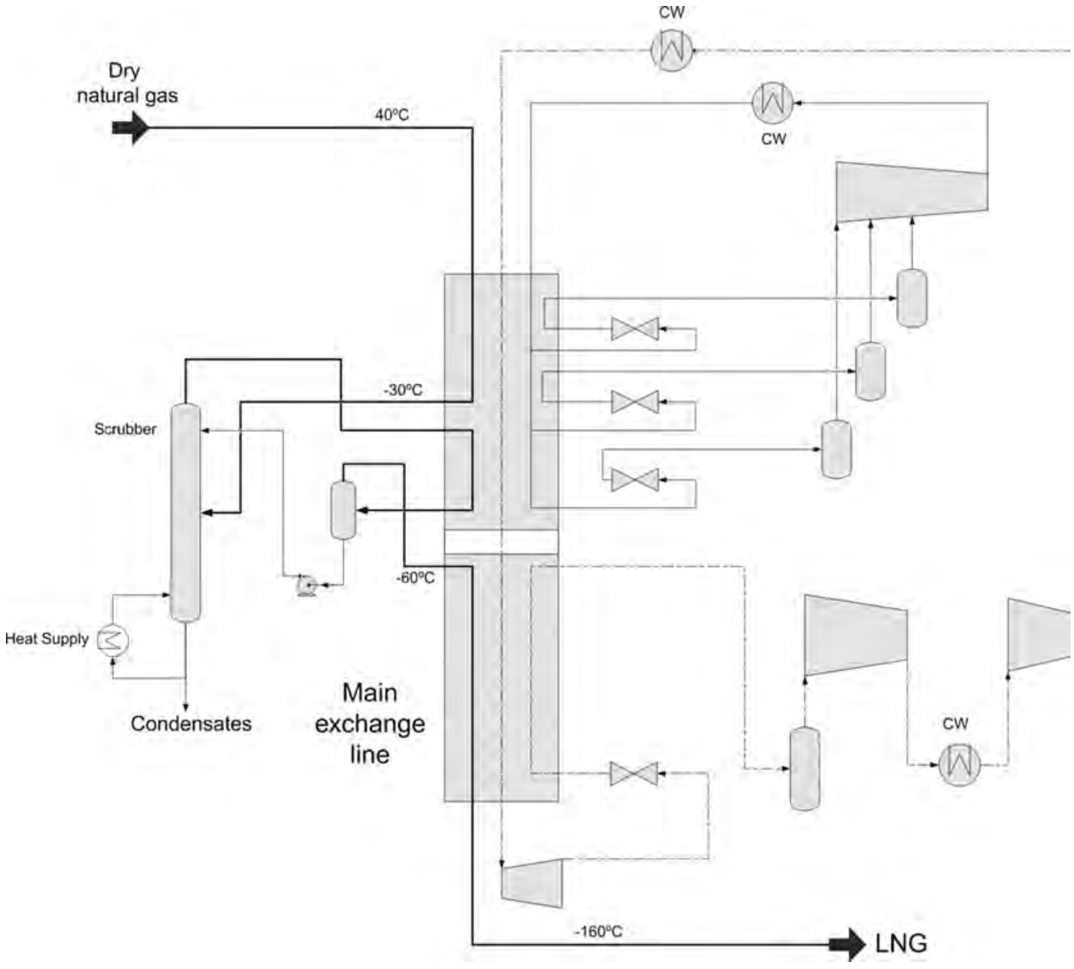


Figure 11.15—Liquefin™ process. *Source*: Figure courtesy of Axens, all rights reserved.

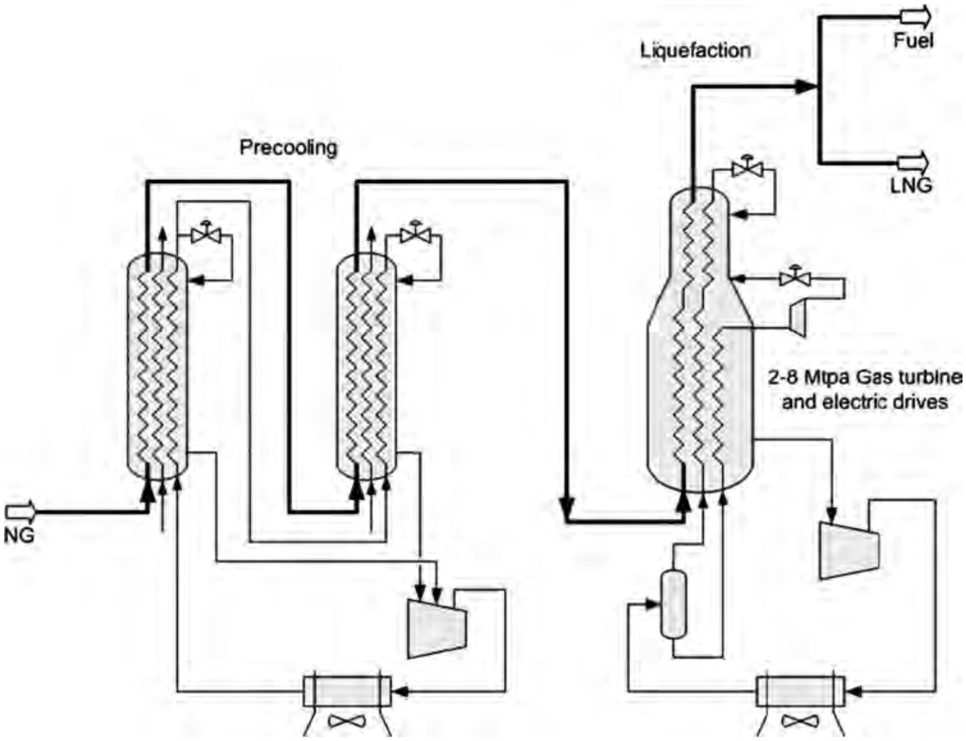


Figure 11.16—The version of the Shell Double Mixed Refrigerant (DMR^{TM}) process as applied in the Sakhalin LNG plant.

gas, achieving very low-temperature approaches and low-pressure drops. Both aspects, together with other process features, lead to achieving a high overall process efficiency, which minimizes the fuel gas consumption and the resulting CO_2 emissions per ton of LNG produced.

- Because the cold boxes are modular, there is no size limitation for the exchanger line. Hence, by implementing parallel compressor lines, this liquefaction technology can be used for megatrains.
- The process can be designed to use any type of mechanical driver (GE Frame 5, 6, 7, 9, aeroderivatives) or electric motors as compressor drivers so as to best fit the desired LNG production.

11.5.3.5 DMR AND PMR SHELL PROCESSES

The configuration of the dual mixed refrigerant (DMR) process (Figure 11.16) is very similar to that of C3-MR; that is, two independent refrigerant cycles—one for precooling and one for liquefaction. However, DMR uses a MR (a mixture of ethane and propane) for precooling instead of pure propane. On the other hand, the MR for liquefaction is a mixture of N_2, methane, ethane, and propane. The use of two MRs facilitates the process optimization to a wide range of ambient temperatures. The use of a MR in the first cycle removes the propane compressor bottleneck existing in the conventional C3-MR process, where the compressor size is limited by the Mach number at the blade tip; using a lower-molecular-weight MR, the Mach number is reduced and the tip speed limit is extended.

In addition, any excess power available from the gas turbine that drives the precooling compressor can be transferred to the second cycle. In this way, the DMR method allows a full utilization of the available power for refrigeration and so increases overall LNG capacity. With this process, an LNG plant can achieve 5–8 MTA of capacity. The Shell DMR liquefaction process uses SWHEs for the precooling and main cooling cycles.

Other benefits of the DMR cycle are the minimization of hydrocarbon inventories compared with the single MR cycle or the C3-MR cycle, which reduces flaring rates in the event of compressor trip and refrigerant blowoff.

The first commercial application of this technology is in Sakhalin LNG, with a capacity of 4.8 MTA per train (two trains).

Another process offered by Shell, especially indicated for large plants (megacapacity trains can be achieved), is parallel mixed refrigerant (PMR), which consists of one precooling cycle (with propane or a MR) and two parallel MR cycles. The parallel lineup of the liquefaction cycles improves the reliability of the train because the LNG production can be designed to continue at 60 % of the train capacity when one of the liquefaction cycles trips [25].

11.5.3.6 MFC[10] LINDE PROCESS

Linde and Statoil have developed a baseload LNG process called Mixed Fluid Cascade (MFC) process. This process can be used for an LNG train capacity from 3 MTA to megacapacity trains. In this process, the pressurized natural gas, once pretreated, is precooled, liquefied, and subcooled by means of three separate MR cycles (Figure 11.17).

The refrigerant used in the precooling cycle is composed of ethane and propane, whereas that used for the liquefaction cycle is a mixture of methane, ethane, and propane, and the subcooling refrigerant is a mixture of N_2,

---

[10] MFC® belongs to Linde, Munich, Germany.

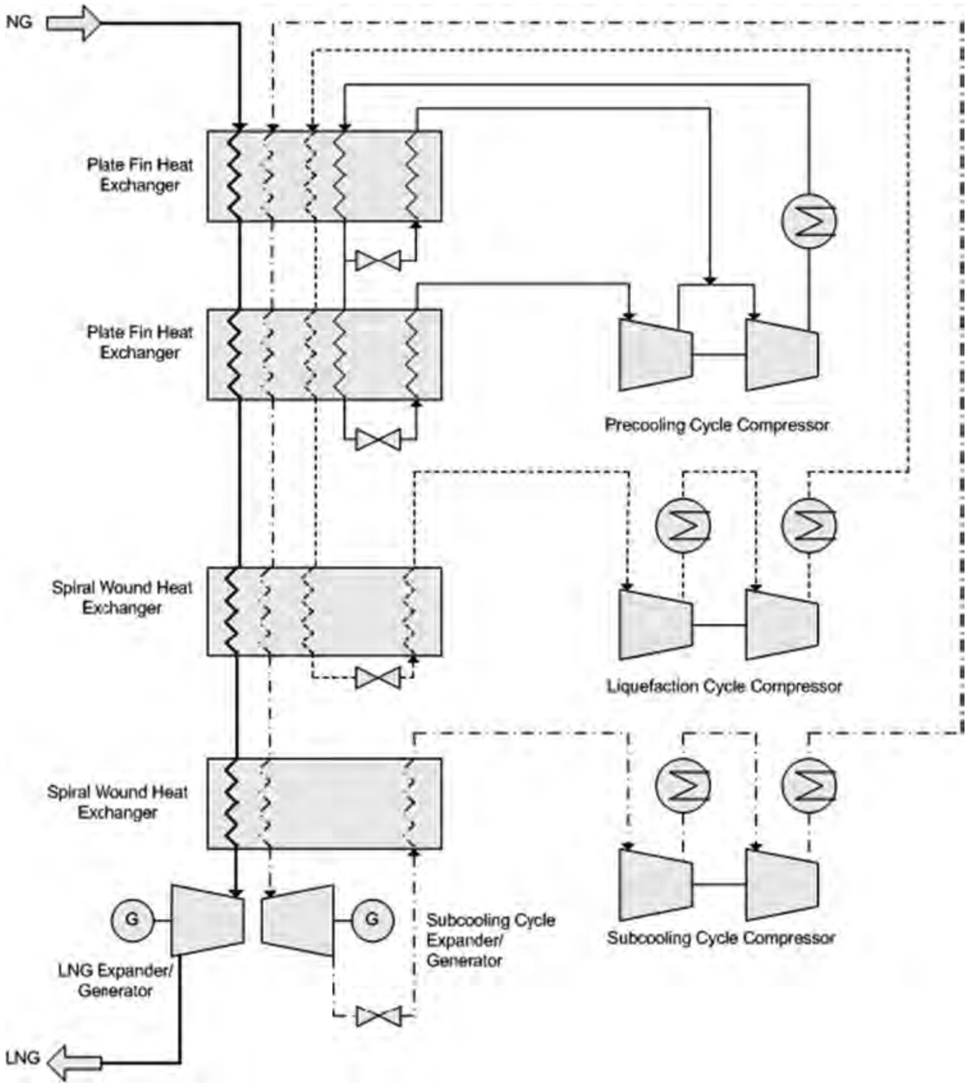


Figure 11.17—MFC® process. *Source:* Figure courtesy of Linde Engineering.

methane, and ethane. The natural gas precooling is performed in PFHEs, reaching a temperature of approximately –50°C in the natural gas side. On the other hand, the liquefaction and the subcooling cycles utilize SWHEs. The temperature of the natural gas after the liquefaction stage is approximately –90°C and approximately –155°C after the subcooling stage. Finally, the LNG is depressurized to atmospheric pressure using a turbine, reaching a temperature of –163°C.

The three-cycle compositions enable optimized match to the three sections of the natural gas cooling curve compared with one- or two-cycle mixtures; this offers higher efficiency or low-energy requirement [26]. The three refrigerant compression systems can have separate drivers or be integrated in two strings of compression.

The main advantage that this technology offers is that liquefaction and subcooling capacity is split into two stages; thus, the suction volumes of the liquefaction and subcooling compressors are smaller and both SWHEs are of similar size, with smaller diameter than the SWHEs of the processes in which the liquefaction and subcooling are accomplished in one stage. This implies that the SWHEs do not constitute the limiting factor for the size of the liquefaction train, and the capacity of a single LNG train can be increased.

Other benefits of the MFC process are [26,27]

- No separator is needed, so large pieces of equipment are avoided.
- Less circulating hydrocarbon is needed, which has beneficial effects with respect to the volume and safety of flammable hydrocarbons.
- The MR circulation rates can be directly adapted for the three mixtures and do not depend on two-phase equilibrium in a separator.
- Lower emissions.

This first commercial application of this technology is in Snøhvit, with the Hammerfest LNG project on Melkøya Island (Norway), with a capacity of 4.3 MTA.

11.5.3.7 OTHER TECHNOLOGIES

The other technologies considered for natural gas liquefaction can be classified into two different categories: MR processes or turboexpander-based processes. Regarding MR processes, the main ones are the following:

- PRICO®[11] (Poly Refrigerant Integrated Cycle Operation) process, licensed by Black & Veatch Pritchard Corporation, is a single MR process. It was used in Skikda (Algeria) in the early 1980s for baseload LNG production.
- APCI single MR process, licensed by Air Products, uses a single multicomponent refrigerant in several refrigeration stages. There is only one LNG plant using this process (Marsa el Brega, Libya), started up in 1970.
- TEAL process, licensed by Technip, is a single MR process. There exists an improved version called TEALARC developed by Technip/Snamprogetti. The first three trains in Skikda (Algeria), started in the early 1970s, use this process.
- Linde's proprietary Multi Stage Mixed Refrigerant process (LiMuM) is a single MR technology that has been used for small-scale LNG plants (<0.5 MTA). It is considered as a good alternative to turboexpander processes for floating medium-scale LNG plants (capacity achievable: 2.5 MTA).

The turboexpander-based processes have been typically selected for small-scale liquefaction plants, particularly the N_2 refrigeration cycle (explained below). Some floating liquefied natural gas (FLNG) designs are also proposing these processes for their application offshore because of their simplicity of operation, shutdown and ease of restart, low equipment count, low deck space requirement, low sensitivity to vessel motion, low weight, and avoidance of hazardous hydrocarbon refrigerants use.

- N_2 refrigeration cycle is the most common turboexpander-based process, in which compressed N_2 is expanded to provide the required cold duty to liquefy the natural gas. The refrigerant is kept in gaseous phase throughout the cycle and the liquefaction is achieved in a less efficient but simpler manner than MR technologies (a gas with uniform flow rate through the cycle cannot closely match the process gas cooling requirements). Efficiency can be increased by using several refrigeration stages. Some of the companies that offer processes based on the N_2 refrigeration cycle are APCI, Hamworthy (Mark I, Mark II, Mark III processes), Mustang Engineering (NDX-1 process), and BHP (Compact LNG process, cLNG™[12]).
- CB&I Lummus has developed a process called Dual Independent Expander Refrigeration Cycle (Niche LNG℠[13]) that includes one methane cycle and one N_2 cycle and improves the efficiency achieved in comparison to other expansion-based processes. This process is applicable for onshore, near shore, or offshore applications [28].
- LNG Smart®[14] liquefaction processes, developed by Mustang, are specifically designed for floating medium-scale LNG plants. The OCX-2 (Open Cycle Expander) process consists of an open refrigeration loop that uses the source gas as refrigerant. Its efficiency can be improved by adding a closed loop of propane for precooling (OCX-R process). The NDX-1 process, mentioned above, is included under the LNG Smart® liquefaction processes.

11.5.3.8 FLNG

Offshore liquefaction appears to be a technically feasible possibility, and it is foreseen as an opportunity to monetize new gas resources (e.g., stranded gas). An offshore LNG plant could be placed on a fixed or gravity-based structure, but the offshore platform selected for most of the developments in the last years is the FPSO. This concept is usually referred to as FLNG or LNG FPSO.

The FLNG concept consists of locating a liquefaction plant above a barge or ship-shape structure and exploiting offshore or near-shore gas fields. This kind of facility is particularly suitable for monetizing stranded gas reserves; that is, reserves that are not economically viable using conventional technology (pipelines or onshore LNG plants). A FLNG plant can also be utilized for monetizing associated gas in offshore fields or for early production in gas fields. One of the advantages is the mobility of the facility; theoretically, the same plant could be used for the exploitation of several fields through its lifetime, although there exist limitations regarding feed gas composition and site Metocean conditions. On the other hand, the floating feature of the facility imposes significant constraints and drawbacks because of the continuous motion of the system, which affects equipment design, operability, and availability. For this reason, the process efficiency in this kind of plant is not typically deemed as important as the safety, simplicity, compactness, ease of operation, quick startup, and availability. Together with these parameters, the main factor that must be faced by a FLNG plant is the berthing and loading of LNG carriers, which constitutes a major technological challenge.

11.6 LNG REGASIFICATION

Regasification terminals, also referred to as "import terminals," take charge of receiving LNG carriers, storing LNG, and vaporizing it according to gas demand. They are intended to provide the necessary infrastructure to link the natural gas producers to the final markets. The main purposes of these receiving facilities are to meet growing natural gas demand and to increase flexibility by reducing the dependency of a single supplier (as for pipelines).

Nowadays, there are more than 50 LNG import terminals in operation around the world. Most of them (64 %) are located in Asia, particularly in Japan and Korea, whereas nearly 75 % of the proposed or under-construction terminals are planned for the European and U.S. markets [29].

11.6.1 General Description of the Regasification Process

Figure 11.18 shows the process flow diagram of a typical LNG receiving terminal. The LNG is offloaded from the LNG carriers and stored in insulated tanks located in the import terminal. Because gas is required to be injected into the grid, the primary pumps pump out a liquid stream from the tanks. It can be directed either to the recondenser, when the terminal has this piece of equipment for vapor handling, or directly to the high-pressure pumps (also known as secondary pumps), when there is no recondenser.

---

[11] PRICO® belongs to Black & Veatch, Kansas City, MO.

[12] cLNG™ belongs to BHP Billiton, Melbourne, Australia.

[13] Niche LNGSM belongs to CB&I Lummus, The Hague, The Netherlands.

[14] LNG Smart® belongs to Mustang, Houston, TX.

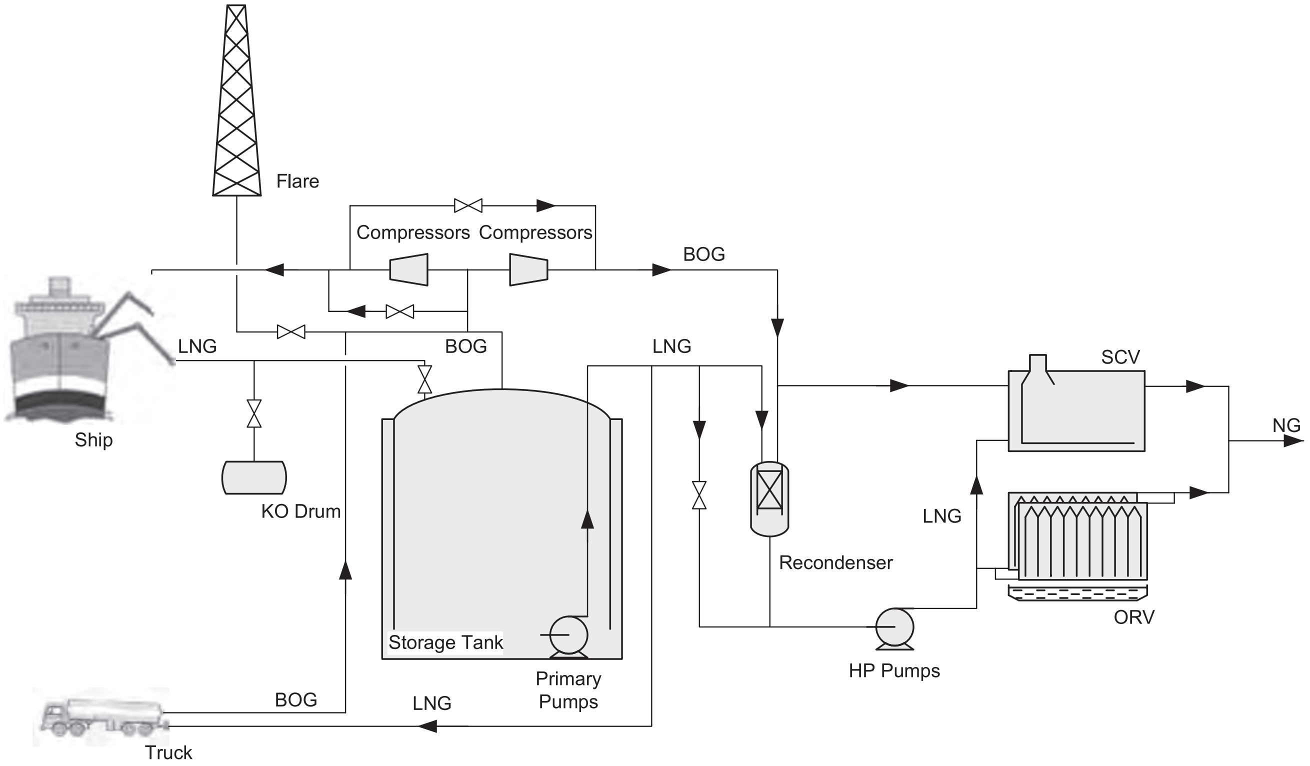


Figure 11.18—Process flow diagram of an LNG import terminal.

The liquid stream from the secondary pumps is vaporized in the vaporizers. The phase change requires the addition of heat, which can be done using different technologies; the amount of energy depends on the composition of the LNG and the final temperature required. Before being delivered to the grid, natural gas must be metered for billing purposes and odorized for safety reasons.

Another important part of the LNG import terminal process is the vapor handling system. BOG is continuously produced inside of the storage tanks because of external heat input. To maintain the internal pressure at a constant level, the generated BOG must be processed. During the offloading of an LNG carrier, larger quantities of vapor are produced mainly because of energy input from the unloading pumps of the LNG ship and also from heat in-leak in the transfer line. There is also a significant amount of vapor due to the displacement produced in the tanks. Part of this vapor is returned to the tanker, but the rest must be also processed. There are two approaches for BOG processing: compression up to the discharge pressure and injection into the pipeline grid, used in terminals without recondenser, or compression up to the primary pump discharge pressure and sending to the recondenser where it is reliquefied by direct contact with subcooled LNG. The main process systems in a regasification facility will be described in more detail in the following sections.

11.6.2 Main Process Systems [30,31]

11.6.2.1 OFFLOADING SYSTEM

The offloading system comprises the equipment and infrastructure required to dock the LNG tanker and transfer its cargo to the onshore piping, as well as the necessary facilities for disconnecting and undocking the ship once the offloading operation is completed. LNG carriers are berthed in the jetty while LNG is pumped out using the pumps located in the vessel itself. The LNG is conducted through the offloading arms and the pipeline routed to shore over the trestle. Part of the vapor displaced from the tanks during the offloading operation is sent to the carrier through a vapor return arm.

11.6.2.2 STORAGE SYSTEM

The storage system consists of one or more specially designed tanks that provide a buffer between the discharge from the ships and the vaporization. Further description of the type of storage tanks is presented under *LNG Storage*.

In regasification plants, special attention is to be paid to LNG stratification and rollover. Terminals receive LNG from different locations, and therefore with different compositions and densities, which can cause stratification. If one of the upper layers has a density higher than the lower ones, a rapid mixing between layers, known as “rollover,” can happen. This would lead to a huge amount of BOG generation, which the plant may not be able to process. To prevent this phenomenon, terminals have lines to circulate LNG between tanks and use different filling procedures (bottom filling and upper filling) to cope with density differences between stored LNG and unloaded LNG.

11.6.2.3 LNG PUMPOUT SYSTEM

To reach the required pressure for the send-out gas, the LNG is pumped before its regasification (liquid pumping is easier and cheaper than gas compression). There are two pressure levels along the LNG flow path. The primary pumps are almost always located inside of the storage tanks, so they pump the LNG from a pressure slightly above atmospheric pressure up to an intermediate pressure

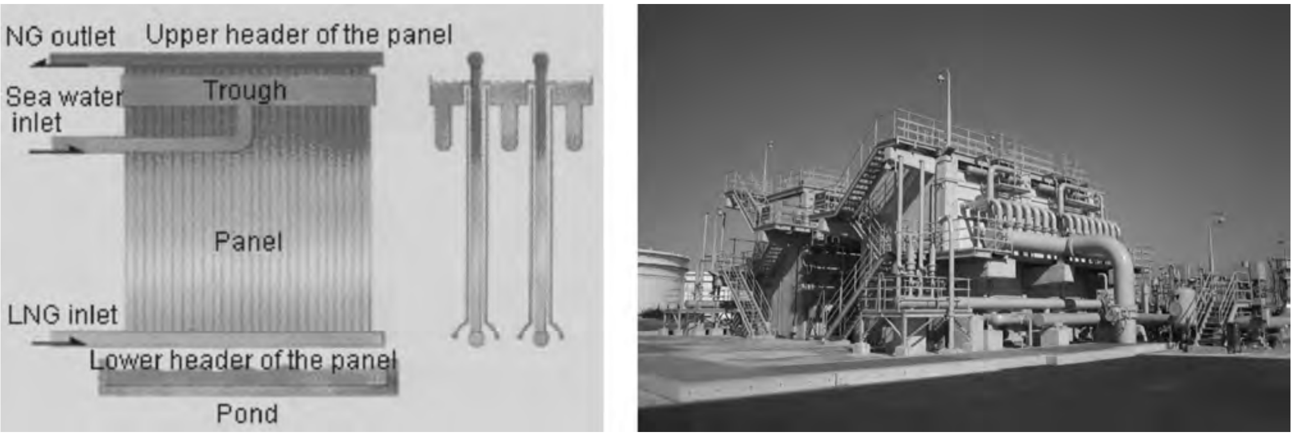


Figure 11.19—ORV at Sumitomo Precision Products, Co., Ltd. (left) and Tokyo Gas, Co., Ltd. (right).

level, typically 7–10 bar (700–1000 kPa). The secondary or high-pressure pumps are located outside of the tanks and discharge at a pressure high enough to satisfy the battery limit pressure at the terminal fence.

11.6.2.4 BOG GENERATION AND HANDLING

BOG is essentially LNG gasified in the storage tanks at atmospheric pressure because of three factors:

1. LNG unloaded from the ship is warmer than the temperature inside of the storage tanks.
2. Heat input due to the LNG pumps.
3. Ambient heat transferred through the cryogenic insulated pipelines, equipment, and tank walls.

The balance of BOG during unloading mode and the BOG generated during holding mode must be processed, used as fuel in the terminal, or, under certain conditions, flared.

The BOG to be processed is compressed by the BOG compressors up to the recondenser pressure level or to the discharge pressure, depending on the vapor handling configuration of the terminal.

New terminals normally have a recondenser because it increases the plant efficiency. The energy for compressing a mass of gas is more than 10 times that required for pumping the same mass of liquid; the best way to process the BOG generated is therefore to condense it again.

The recondenser consists of a vertical vessel that comprises an inner packed bed where BOG condenses as it comes into contact with subcooled LNG and an outer annular space that acts as a liquid buffer volume for the high-pressure pumps located downstream of the recondenser.

11.7 LNG VAPORIZATION

Several vaporization systems exist for which the main difference is the heat source used for the regasification. The most important are

- Gas combustion
- Seawater or ambient air as heating medium
- Integration with other facilities with energy surplus

The two systems most commonly used are open rack vaporizers (ORVs) and submerged combustion vaporizers (SCVs), although the intermediate fluid vaporizer (IFV) is also used in some terminals.

An ORV consists of a group of panels formed by finned tubes with the LNG flowing upward through them (see Figure 11.19). A film of seawater flows downward outside of the tubes, absorbing the cold from the LNG and returning to the sea a few degrees colder. The heat used is essentially free, although capital and operating costs related to pumping and piping seawater should be taken into account. The use of such vaporizers is not advisable when the seawater temperature is lower than 5°C.

The SCV consists of a warm water bath with a bundle of tubes immersed in it. The LNG flows through the tubes, requiring the burning of a certain percentage of the send-out gas for its vaporization. The hot gases from the combustion are bubbled through the water, heating up the bath. Hence, the hot water acts as an intermediate fluid between the hot gases and the LNG (see Figure 11.20).

The IFV consists of three shell and tube heat exchangers, which use an intermediate heating medium for the energy exchange between seawater and LNG. This intermediate fluid prevents ice from forming on the heat transfer

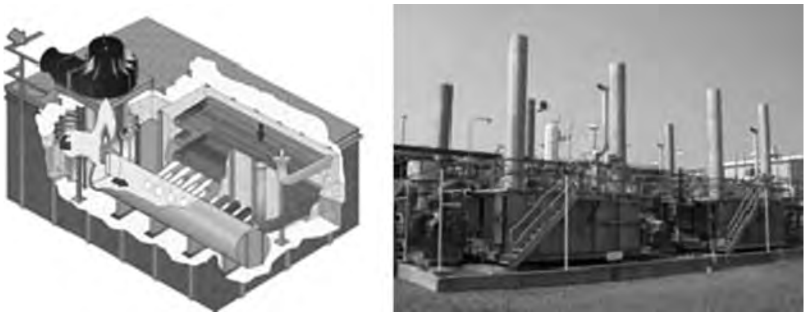


Figure 11.20—SCV. *Source:* Pictures courtesy of Selas-Linde GmbH.

surface. This type of vaporizer has high capital costs and significant environmental impact because of chlorination and low return temperature.

Some new terminals are beginning to use ambient air vaporizers (AAVs) to take advantage of the ambient air heat. The main advantages are low power consumption and zero emissions, although they require a great deal of plot space for their installation.

Other vaporization technologies used for small-scale regasification terminals are heating water tower, intermediate thermosyphon vaporizer, quench water vaporization system, and reverse cooling tower technologies.

The selection of the type of vaporizer to be used in a specific terminal depends on several factors, such as investment cost, operational cost, maintenance, reliability, availability, footprint, air emissions, and environmental impact. A comparison of vaporizer systems is provided in Table 11.7. In any particular case, the environmental conditions of the site to a great extent determine the technology selection. ORVs and AAVs are not advisable in cold weather locations; conversely, SCVs and IFVs are more suitable.

11.7.1 Gas Metering and Send Out

Gas is measured in the receiving terminals for billing purposes before its injection to the grid. Quantity and quality are required. The quantity can be measured by orifice plates and ultrasonic and turbine flow meters, among others. The quality of the natural gas is normally analyzed by chromatography.

Before the send out, natural gas is odorized by adding organosulfur compounds [e.g., tetrahydrothiophene (THT) and tertiary butyl mercaptan (TBM)] to meet health and safety regulations.

11.7.2 Cryogenic Energy Recovery

From a thermodynamic point of view, the conventional regasification process has in fact a lack of utilization of the available cryogenic energy, which decreases the global energy efficiency of the liquefied natural gas (LNG) chain. Cryogenic energy recovery is technically feasible and has already been implemented at many industrial sites. For instance, Japan started using cryogenic energy in air separation units in the 1970s.

Cryogenic energy can be used for several applications, all of which are intended to increase the efficiency of the processes involved and capitalize the benefits related to it: reduction in operating cost and in environmental impact, among others. The benefits of recovering the available cryogenic energy are not limited to the direct economic return generated from the energy recovery itself, but also include those related to the reduction in CO_2 emissions, the positive impact to the community as a green operator, and the probable reduction on the grid power consumption, among others.

It is advisable to consider the cryogenic energy recovery from the beginning in an LNG import terminal project. During the initial project definition stages, important factors can be taken into account to take full advantage of the available energy with a minimal interference into the regasification process. Some of them are

- To use the cryogenic energy at the lowest possible temperature, keeping the process efficiency at a maximum; however, the number of applications of such effective utilization is very limited.
- The natural gas consumption pattern does not necessarily match with the cryogenic energy utilization rate. Therefore, the integration system should be designed to be capable of coping with variations in gas demands. Otherwise, the cryogenic energy exchanged will be limited to the minimum send-out capacity of the import terminal.
- Natural gas must be pressurized before its injection in the pipeline grid. It is more economical to pressurize LNG before gasifying it; however, extracting LNG cryogenic energy at high pressure is less profitable because the amount of available energy is lower than the amount at low pressure.
- The distance between the LNG import terminal and the cryogenic energy receiving facility should be less than approximately 3 km because the installation cost of longer pipelines, heat, inleak, and pressure losses are considerable and may make a project unfeasible.
- Despite having good properties as a coolant, LNG direct use is limited because of its flammability. To avoid any possible explosive mixture, the usual practice is to use an inert intermediate fluid, although system cost and complexity are increased.

The available energy in the vaporization process can have a direct or indirect use. Table 11.8 shows the main applications in which the cryogenic energy can be used. The applications of a greater importance are those related to cryogenic air separation and power generation, by its integration with an existent power generation facility, or

TABLE 11.7—Comparison of Vaporizer Systems [32]

Technology		Capital Cost	Installation Cost	Power	Fuel	Maintenance	Emissions	Space	Simplicity
Open rack	ORV	–	–	0	++	–	0	0	–
Submerged combustion	SCV	++	++	–	–	0	–	0	0
Air–natural draft	AAV	+	+	++	++	++	++	–	++
Air–forced draft	FAV	+	–	+	++	+	+	0	+
Intermediate fluid	IFV	–	0	–	++	–	–	0	–

+, positive feature of the technology; –, negative feature of the technology; 0, neutral feature of the technology.

TABLE 11.8—Potential Uses for Cryogenic Energy

CRYOGENIC ENERGY RECOVERY	Integration with power generation facilities	Cooling of condensate
		Cooling of inlet air to the gas turbine (GT)
		Cooling of exhaust from the GT
	Integration with cryogenic facilities	Cryogenic air separation
		CO_2 liquefaction
		Dry ice production
		Food conservation
	Integration with other facilities	Seawater desalinization
		HHV adjustment
	Direct power generation	Rankine cycle
		Inverted Brayton cycle

in-house power generation by means of a Rankine cycle. When analyzing an integration scheme, it is important to consider the impact on the receiving facility. If no third party is involved, the recovery unit can be started up and shut down whenever is convenient according to the LNG import terminal send-out and other operational parameters.

11.7.2.1 INTEGRATION WITH POWER GENERATION FACILITIES

Integrating the import terminal with a combined-cycle or an open-cycle gas turbine power generation plant offers a considerable positive impact for both facilities. Furthermore, the capital cost is reduced, and there is a lower environmental impact because of the reduction of emissions, thermal pollution, and chlorination of water. When integrated, the power plant becomes the sink of the LNG cryogenic energy available in the import terminal. There are several configurations that allow for the proposed integration depending on the end use of the cryogenic energy:

- Cooling of condensate water (for combined-cycle power plant)
- Inlet air cooling
- Exhaust gas cooling

An example of this way of integration is Bahía de Bizcaia Gas (BBG), a Spanish import terminal, which is integrated with a combined-cycle power plant Bahía de Bizcaia Electricidad, BBE (800 MW). There is an intermediate pool where the power plant pours hot water from the steam condenser; the LNG import terminal takes water from that pool to use it in the ORVs (see Figure 11.21).

11.7.2.2 INTEGRATION WITH CRYOGENIC FACILITIES

Cryogenic facilities require high power consumption to produce the refrigeration required for the process. Cryogenic energy recovered from LNG could significantly decrease the aforementioned power consumption.

Integration schemes that use lower temperatures are preferred because they take full advantage of the available energy from the LNG. Therefore, the most relevant applications of LNG cryogenic energy recovery for integration with cryogenic facilities are those related to cryogenic air separation, CO_2 liquefaction, dry ice production, and food conservation.

For example, the air separation unit at Tokyo Oxygen and Nitrogen Co., Ltd. is placed next to the Sodegaura LNG import terminal, operating in an integrated manner since 1978. Another example is a refrigerated warehouse next to the Negishi import terminal (Tokyo), the Japan Super Freeze Co., Ltd., operating since 1974 [33].

11.7.2.3 INTEGRATION WITH OTHER FACILITIES

LNG cryogenic energy can also be used in many other process facilities that require refrigeration, as for seawater desalinization using crystallization technology, or for natural gas HHV adjustment by means of NGL extraction. Trunkline LNG Company is planning to install an HHV adjustment facility at their Lake Charles terminal (United States) [34].

11.7.2.4 POWER GENERATION

Finally, it is worth highlighting the direct power generation by means of a Rankine cycle or an inverted Brayton cycle, commonly called a mirror gas turbine. The LNG cryogenic energy condenses the working fluid used in the Rankine cycle, or cools down the exhaust gas from a turbine in the inverted Brayton cycle, recovering its energy under the atmospheric pressure level.

Among others, the LNG import terminal of Negishi generates 4 MW using the Rankine cycle. Despite the predicted thermodynamic efficiency improvement using the

Figure 11.21—LNG import terminal integrated with a power generation plant (BBG-BBE). *Source:* Picture courtesy of Bahía de Bizkaia Gas, S.L.

mirror gas turbine, no power system using this principle has been built to date.

11.7.3 Offshore LNG Import Terminals

Traditionally, conventional terminals have been placed onshore; however, several factors are driving the regasification facilities offshore: fast implementation, lower social impact [the "not in my back yard" (NIMBY) effect], and environmental constraints (difficulty in obtaining permits for onshore plants).

There are different approaches for designing and operating offshore facilities depending on the final markets and infrastructure requirements. The main variables to be considered during the design stage are the water depth, the distance from shore, and the storage capacity required. Water depth determines the type of structure to be considered; the minimum depth is constrained by the safe maneuvering of the LNG carriers—typically 14 m of draft. Other parameters that define safe and economic operation are wave action and the relief of the seafloor, among others.

There is a simple classification of offshore terminals depending on the type of structure:

- Fixed structures are appropriate for shallow-water offshore locations and where the seafloor is relatively leveled and the sediments are able to support the foundation and weight of the structure. There are mainly three types: gravity-based structures, offshore platforms, and artificial offshore islands.
- Floating structures are considered when water depth increases beyond permissible limits for fixed structures (although they can be applied in some shallow water applications). There are two types depending on whether storage capacity is included or not: floating, storage, and regasification units (FSRUs) and floating regasification units (FRUs).

The operation of the LNG import facility depends on its storage capacity. Terminals with sufficient storage capacity can supply natural gas on a constant basis, whereas those without associated storage must deliver natural gas in an intermittent way, at the same rate that the LNG carriers offload in the regasification facility.

11.8 LNG STORAGE

11.8.1 Overview

The objective of the LNG tank at the receiving terminal and liquefaction plant is to act as a buffer. Thus, the processing plant is free to operate independently of any variability in the LNG chain from production, shipping, or market demand. The main aspects regarding storage in an LNG plant are total storage capacity, tank size, and containment technology of the tank.

11.8.1.1 STORAGE CAPACITY

The LNG industry is in the process of optimizing the entire LNG chain through economies of scale. Liquefaction throughput and ship size have increased over recent years. To adapt to these increases, the storage capacity of LNG at liquefaction and regasification terminals has also grown. A simplified calculation of the desirable storage capacity for a particular plant would be the higher number between the volume delivered by the largest LNG tanker contracted and the volume of the LNG allocation logistic model. Nevertheless, at the end must be plant owners, who define the storage philosophy on the basis of the business structure, contracts in place, and client demands.

Another way to look at the storage capacity is in terms of days of LNG production or gas send out. In liquefaction plants, the storage capacity usually ranges from 5 to 8 days of liquefaction capacity. The storage capacity in regasification terminals depends more on demand shapes and it is typically approximately 10–20 days of the terminal capacity. Some Japanese terminals supplying power plants tend to have an even larger storage capacity [31]. Tables 11.9 and 11.10 show the storage capacity for some liquefaction plants and regasification terminals.

11.8.1.2 LNG TANKS: TYPES AND SIZES

LNG is stored in tanks at temperatures of approximately –160°C and pressures slightly above atmosphere at its bubble point. Storage tanks can be classified into three categories: underground, in ground, and above ground (Figure 11.22). Underground and in-ground storage tanks have a higher level of safety but also have a higher investment cost; they are mainly applied in earthquake-prone regions such as Korea and Japan. There are three main aboveground tank containment types: single containment, double containment, and full containment (Figure 11.23). Technical features and main advantages of above-ground tank containment technologies are described in Table 11.11.

The trend over the years, as Figure 11.24 shows, has been to evolve from single containment, through double containment, to full containment because of the increase

TABLE 11.9—Example of Liquefaction Plant Storage Capacity [35]

Name	Country	Plant Capacity (MTA)	Storage Capacity		Number of Tanks	Tank Capacity (1000 m³ LNG)
			1000 m³ LNG	Days		
Malaysia LNG (F1–F3)	Malaysia	23.3	445	3	6	65–120
Nigeria LNG (T1–T5)	Nigeria	18.2	337	3	4	36–84
Bethioua (GL1Z–GL2Z)	Algeria	16.5	600	5	6	100
Atlantic LNG (T1–T4)	Trinidad	15.3	560	5	4	120–160
Tangguh	Indonesia	7.6	340	6	2	170
Peru LNG	Peru	4.5	260	8	2	130
Snøhvit	Norway	4.1	250	9	2	125

TABLE 11.10—Example of Regasification Terminal Storage Capacity [35]

Name	Country	Plant Capacity (MTA)	Storage Capacity		Number of Tanks	Individual Tank Capacity (10^3 m^3 LNG)
			Installed Capacity (10^3 m^3 LNG)	Days of LNG Storage		
Sodegaura	Japan	39.9	2660	13	35	60–140
Incheon	South Korea	35.2	2080	12	16	100–200
Barcelona	Spain	18.2	680	7	8	40–150
Senboku II	Japan	17.5	1585	18	22	75-180
Huelva	Spain	12.5	610	10	4	60–150
Canaport	Canada	10.4	320	6	2	160
Dapeng LNG	China	4.9	480	19	3	160

in safety and reduced plot space. Full containment type is extensively used in LNG import terminals. However, in liquefaction plants the containment technology is more project specific.

Because LNG tanks have very high reliability, larger tanks are preferred over multiple smaller tanks. Since the first LNG tank constructed in Canvey Island, United Kingdom, in 1957, the size has significantly increased over the years, as can be seen in Figure 11.24. Currently, the largest above-ground tank has a storage volume of 190,000 m^3, whereas the largest in-ground tank has a storage capacity of 200,000 m^3 [36]. Most of the new developments favor above-ground tanks and aim for even larger capacities, up to 300,000 m^3. The main advantages for larger tanks are the economy of scale and footprint. Moreover, the construction schedule, which is commonly in the critical path of LNG project execution, is not increased as the tank becomes larger [37].

11.9 OTHER NATURAL GAS TECHNOLOGIES

11.9.1 Gas-to-Liquids

11.9.1.1 INTRODUCTION TO GAS-TO-LIQUIDS

Gas-to-liquids (GTL) is the chemical conversion of natural gas into long-chain hydrocarbon liquids, such as naphtha, diesel fuel, or lubes. The term GTL is also used for the products of the previous process.

From a business perspective, GTL is mainly envisaged as an option for natural gas monetization—an alternative to the gas transportation options. The high

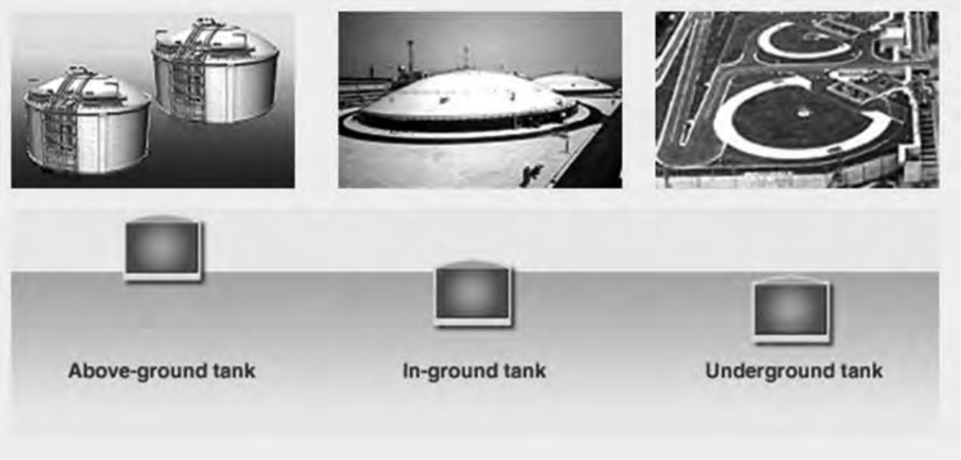


Figure 11.22—Storage tanks categories [38].

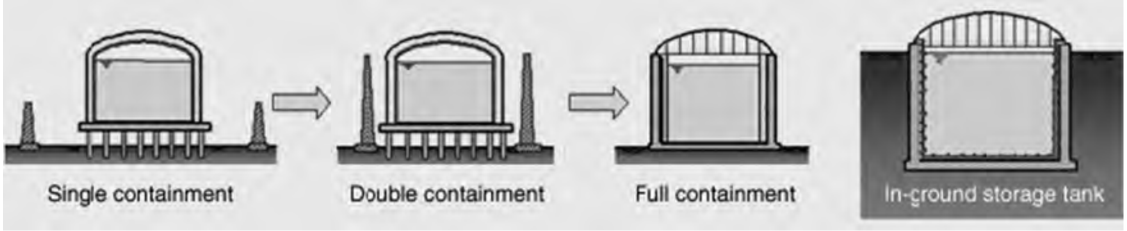


Figure 11.23—Storage tanks containment technologies [38].

TABLE 11.11—Above-Ground Tank Containment Features and Main Advantages [31]

	Single Containment	Double Containment	Full Containment
Primary container	LNG storage	LNG storage	LNG storage
Outer shell	For retention and protection of the insulation and for containing the gas phase	For retention and protection of the insulation and for containing the gas phase	Not applicable
Secondary container	A bund wall or dike surrounding the tank capable of containing any LNG leakage but not the BOG	An outer wall capable of containing any LNG leakage in a reduced area but not the BOG	Secondary container capable of LNG and BOG storage in case of primary container failure
Main advantage	Lower capex	Tradeoff between single and full containment	Higher safety and lower layout requirement

quality of the products, with virtually no sulfur and very few aromatics, also makes this process very attractive from the product marketing point of view. From a technology standpoint, Fischer–Tropsch (FT) synthesis is the core of the GTL process, to the point that both terms have become practically synonyms. Strictly speaking, other processes exist that are also GTL processes, such as methanol synthesis. However, the markets for non-FT GTL products are much smaller than the markets for FT products, so FT synthesis is the only GTL option economically viable for large-scale gas monetization projects. The main advantages of GTL are

- The ability to bring large gas reserves to market.
- *Market diversification:* GTL products are addressed to the oil derivative market instead of the natural gas market.
- *Spot, unconstraint market:* GTL products can be easily transported and stored, which increases commercial flexibility.
- Different product slates can be obtained in a GTL plant.
- GTL products have higher added value than natural gas, and the quality is also higher than that of the equivalent products from crude oil.

On the other hand, GTL presents several drawbacks with respect to competitive products and processes:

- Very scarce industrial experience
- Complex technology, so relatively high operational risk
- Low thermal efficiency of GTL processes compared with gas transportation
- Very high capital costs

11.9.1.2 FUNDAMENTALS OF THE GTL PROCESS

The GTL process consists of three main stages (Figure 11.25):

1. Natural gas reforming to produce synthesis gas, a mixture of CO and hydrogen (H_2). This is achieved by a partial oxidation of natural gas using steam, oxygen (O_2), or a mixture of them. This step is common to all of the GTL alternatives—FT, methanol, dimethyl ether, etc.
2. FT synthesis, which is the technology core of the GTL process because the chemical structure of the final products, and therefore most of their properties, is achieved at this step. Synthesis gas is converted to linear hydrocarbons with variable chain lengths, according to the reaction $CO + 2H_2 \rightarrow -CH^{-}_{2} + H_2O$.

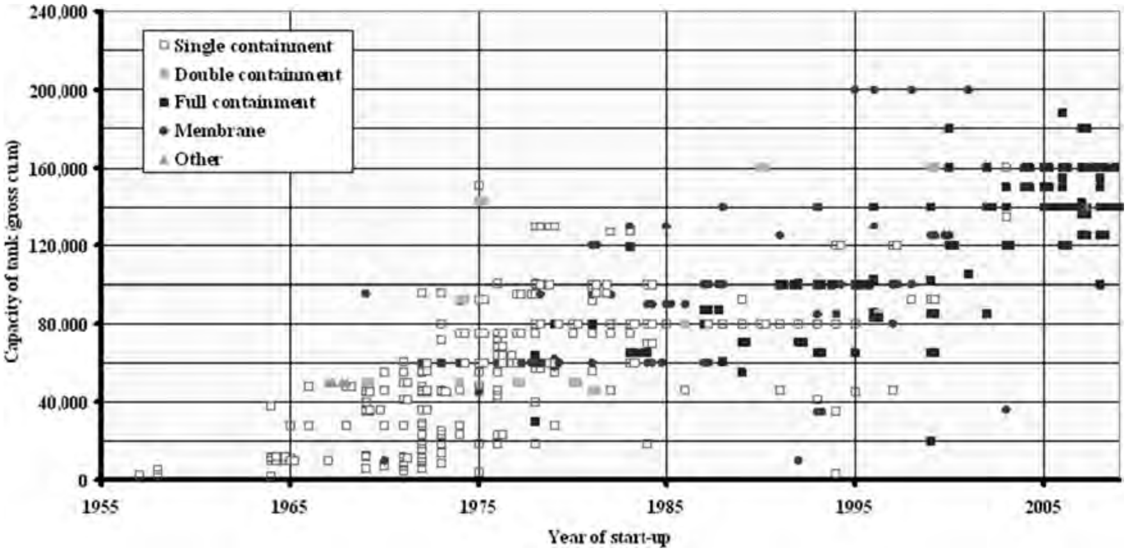


Figure 11.24—LNG tank sizes and types with time [37]. *Source*: Reprinted with permission from the BP Exploration Operating Company Limited.

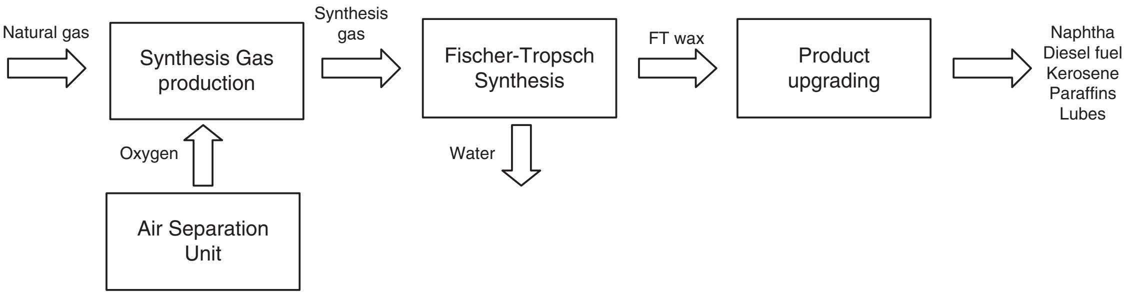


Figure 11.25—Block flow diagram of GTL processes.

This reaction can be understood as a polymerization-hydrogenation reaction of CO. Product molecular weight distribution depends on reaction conditions, particularly on temperature. In low-temperature FT processes (200–250°C), high-molecular-weight wax (the FT wax) is produced; in high-temperature processes (300–350°C), the products are lighter and remain in the gas phase at reaction conditions. Nowadays, low-temperature processes are preferred because of their improved economics. Water is always produced in large quantities as a byproduct (1 mole of water per mole of CO reacted).

3. *Product upgrading:* The FT wax obtained in low-temperature processes needs to be further processed to obtain the final GTL products within the required specifications. This is typically achieved by hydrotreatment/hydrocracking processes, together with product fractionation. Depending on the process configuration and operating conditions in this section, different product distributions are obtained. Hence, there exists some flexibility to decide the final process products, which may include naphtha, diesel fuel, kerosene, paraffin, or lubes, among others.

A more detailed diagram of a typical GTL-FT process is presented in Figure 11.26.

11.9.1.3 EXISTING GTL TECHNOLOGIES

A summary of the most developed GTL concepts is presented in Table 11.12. A general configuration of existing plants using each technology has been included, as well as the demonstration level achieved by 2009. FT technology is the distinctive aspect of any GTL concept. In most cases, the synthesis gas and the upgrading sections, although being an integral part of the facility, are not considered part of the GTL technology concept and are instead provided by specialized technologists. The following describes in more detail the main options available for the three process stages.

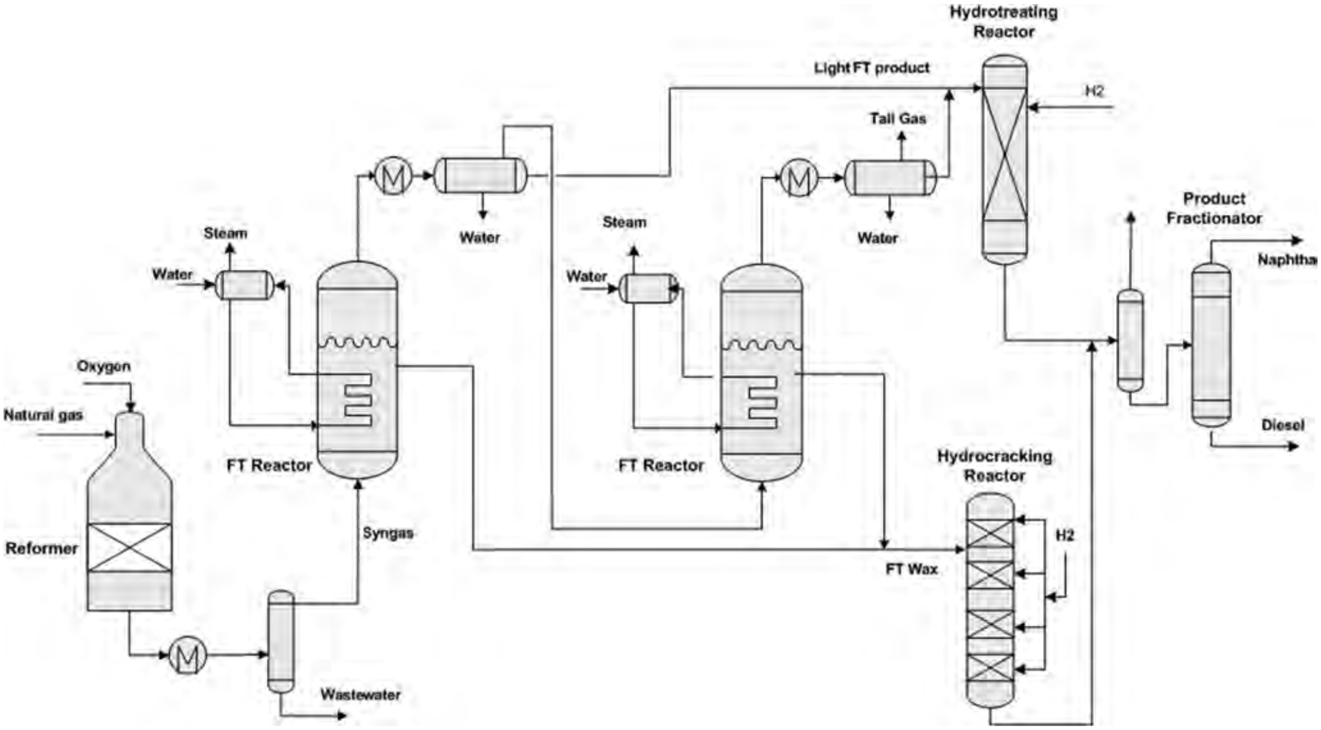


Figure 11.26—Typical GTL process diagram (slurry FT technology).

TABLE 11.12—Main Features of Existing GTL Plants for Different Technologies

Company	Synthesis Gas	FT	Scale
Shell	Noncatalytic POX	Fixed bed, cobalt	Industrial (14,500 bbl/day)
Sasol	ATR (Haldor Topsøe)	Slurry, cobalt	Industrial (34,000 bbl/day)
GTL.F1 (StatoilHydro–PetroSA, Lurgi)	Combined reformer (Lurgi)	Slurry, cobalt	FT demo (1000 bbl/day)
ConocoPhillips	Catalytic POX	Slurry, cobalt	Demo (400 bbl/day)
BP Davy Process Technology	Compact SMR	Fixed bed, cobalt	Demo (300 bbl/day)
ExxonMobil	ATR	Slurry, cobalt	Demo (200 bbl/day)
Syntroleum	ATR with air	Slurry, cobalt	Demo (70 bbl/day)
IFP-ENI	–	Slurry, cobalt	FT demo (20 bbl/day)

11.9.1.3.1 Synthesis Gas Technologies

Three basic process options can be used for synthesis gas production from natural gas:

1. *Steam methane reforming (SMR):* This process takes place in multitubular reactors. The reaction is highly endothermic, so the tubes are located inside of a fire-heated furnace (Figure 11.27). Two main reactions are involved in the SMR process:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{11.8}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{11.9}$$

   The first reaction is actually the steam reforming reaction, whereas the second is known as the water gas shift (WGS) reaction. At process conditions, both reactions are close to chemical equilibrium. The catalyst, in pellets, is typically based on nickel on an alumina support. To avoid coke formation on the catalyst surface, a high steam-to-carbon ratio must be used. Therefore, the resulting H_2/CO ratio in the product gas is much higher than the optimum value for FT synthesis, so some type of H_2 removal system is required to obtain the desired synthesis gas composition. This inconvenience, the need for external heating, and a high capital cost are the reasons that the SMR process is not recommended in conventional, large-scale GTL plants. However, some SMR options have been proposed for niche GTL applications, such as the compact reformer (BP-Davy Process Technology), which could be an interesting option, for instance, for small or medium-scale offshore facilities. On the other hand, SMR is the usual process for H_2 production, so from a technical standpoint, it is a simple and mature technology. In addition, most GTL plants include an SMR unit to produce the required H_2 for the third stage of the process (product upgrading). Many technology and engineering companies exist that can provide SMR units, including Lurgi, Johnson Matthey, Davy Process Technology, and Haldor Topsøe, among others.
2. *Partial oxidation (POX; catalytic or noncatalytic):* This process is highly exothermic (Figure 11.28). The main chemical reaction that takes place in the system is $CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2$. Some CO_2 and H_2O are also produced in the POX reactor, so the WGS reaction also takes place in the system. Hence, the final H_2/CO ratio is always less than 1.9, which requires gas composition adjustment before the FT reactor, as for the SMR process. The noncatalytic process, used by Shell in their GTL process [Shell middle distillate synthesis (SMDS)], takes place at very high temperatures (~1300–1400°C). Catalytic POX, as the process used by ConocoPhillips, operates at lower temperatures, but it is not proven for industrial-scale GTL plants.
3. *Autothermal reforming (ATR):* ATR is the combination of SMR and POX processes in the same reaction vessel (Figure 11.29). This process allows the fine-tuning

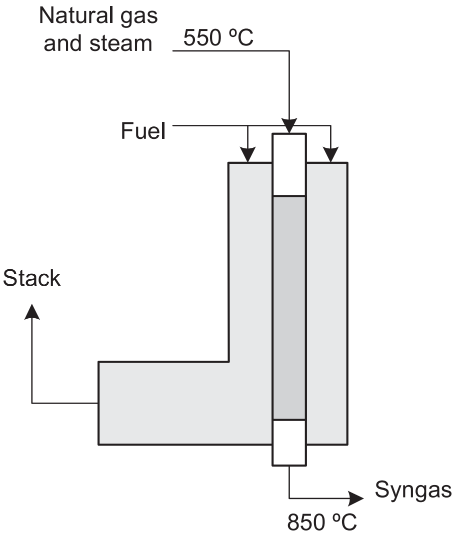


Figure 11.27—Steam methane reformer.

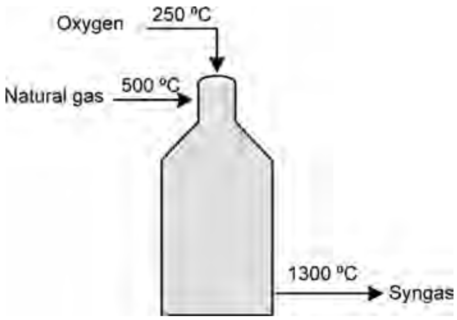


Figure 11.28—Noncatalytic POX.

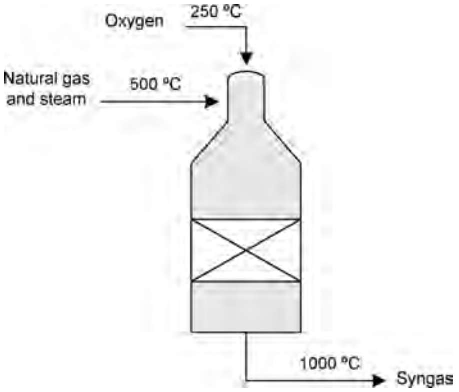


Figure 11.29—Autothermal reformer.

of the H_2/CO product ratio to the required value for FT synthesis and eliminates the need of an external heat source. It is a catalytic process. An industrial ATR example is the technology provided by Haldor Topsøe for the Oryx GTL plant (Sasol + Qatar Petroleum) in Qatar. Lurgi and Johnson Matthey also offer ATR units.

Other synthesis gas production processes exist that consist of different arrangements of the previous three basic options. An example is combined reforming, which includes a SMR reactor and an ATR reactor (Figure 11.30). Lurgi's combined reforming is the option used by PetroSA in their high-temperature FT plants in Mossel Bay (South Africa) and by Methanex and BP at the Atlas methanol plant in Trinidad and Tobago.

11.9.1.3.2 FT Technologies

FT technologies can be classified in low-temperature (LTFT) and high-temperature (HTFT) processes. Nowadays, the low-temperature option is the preferred one because of its improved economics and the high-quality products that are obtained.

Two different high-temperature processes, developed by Sasol in the 1990s, can be mentioned. Both are based on fluidized bed reactors, either a circulating bed (Synthol process) or a bubbled fluid bed (advanced Synthol process), and use iron catalysts.

As far as LTFT processes are concerned, technologies can be classified into two main groups, depending on the type of reactor used.

1. *Fixed-bed reactors (FBRs):* FBRs are operated with gas recycle at moderate conversion per pass. FBRs are easily scalable and operated, but investment costs tend to be higher. Heat removal and catalyst replacement are other issues to be solved in a fixed-bed FT technology. This reactor type is the option used by Shell (SMDS process) and BP and by Sasol in the past (Arge technology).
2. *Slurry bubble column reactors (SBCRs):* Fine-powdered catalyst is suspended in the liquid product wax, in which synthesis gas is bubbled. Reaction heat is removed internally by cooling pipes immersed in the slurry. This kind of reactor presents several advantages: the slurry hydrodynamic regime allows for achieving an excellent isothermal operation; the small solid particle size results in good productivity, good interface contacting, and low pressure drop; and spent catalyst can be easily replaced with fresh catalyst during normal operation. All of these features allow higher efficiencies than FBRs. However, there exists little industrial experience with slurry reactors, so several issues need to be solved. Slurry reactors are difficult to scale-up because their fluid dynamic behavior is very complex. Catalyst attrition is another common issue; attrition causes loss of catalytic material, makes solid-liquid separation difficult, and produces equipment erosion. Despite the technical issues, this type of reactor has been selected by most of the existing FT technologies: Sasol slurry-phase distillate (SPD technology), ExxonMobil (AG-21 technology), ConocoPhillips, GTL.F1 (StatoilHydro-PetroSA-Lurgi), Syntroleum, IFP-ENI, (joint development between the French Institute of Petroleum and ENI), Rentech, and the Japan Oil, Gas, and Metals National Corporation, to mention those who have reached at least a demonstration scale. Other three-phase FT reactors have been proposed, such as the ebullating bed reactor (Petroleós de Venezuela, S.A.), or the advanced slurry reactor (BP),

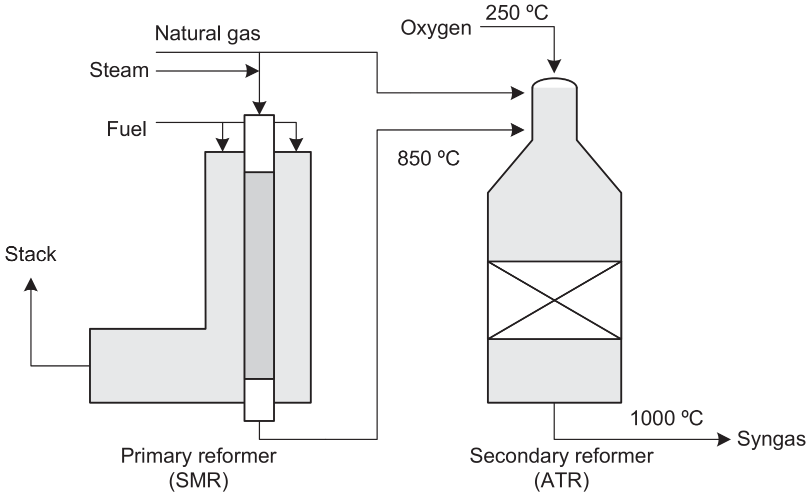


Figure 11.30—Combined reformer.

but they are still at a pilot scale. All of them use cobalt-based catalysts, except the Rentech process, which uses iron-based catalyst.

11.9.1.4 PRODUCT UPGRADING

The raw product from FT reactors is a wax, solid at ambient temperature, with a significant amount of olefins and some oxygenates. Hence, hydrotreatment and hydrocracking processes are required to obtain the desired final products, mainly middle distillates. Available options are very similar to those normally used in refineries, with some particularities due to the different nature of the feedstock. The higher molecular weight fraction of the FT wax is processed as in hydrocrackers and mild hydrocrackers. The lower molecular weight fraction is hydrotreated. Isomerization is also desirable to improve cold properties because FT products are highly paraffinic. If lubricants are to be obtained, isomerization and dewaxing processes are required; Chevron's Isodewaxing® is an example of such a process. Other companies such as Shell, ExxonMobil, Axens, and Syntroleum also have specific processes for FT product workup.

11.10 COMPRESSED NATURAL GAS

11.10.1 What Is CNG?

In the gas processing industry, CNG is understood as natural gas that has been compressed and is transported in pressure vessels instead of traditional pipelines. CNG is a feasible transportation method to monetize associated gas or stranded gas reserves and is a way to deliver gas to remote markets. The term CNG is also used for the fuel of natural gas vehicles, but this product is out of the scope of this chapter. Hence, the CNG process described here exclusively refers to that applied for marine transportation of CNG.

11.10.2 CNG Chain

The CNG chain can be divided into three main stages: compression, refrigeration, (depending on technology) and transportation; loading, journey, and unloading are included in the transportation stage.

- *Compression:* After a suitable gas treatment (mainly dehydration to prevent freezing or hydrate formation) to achieve the quality requirements demanded by the destination market, natural gas is compressed onshore. The final pressure is set between 100 and 250 bar (10,000 to 25,000 kPa), depending on the technology.
- *Refrigeration:* In some cases, the gas is cooled down to –30°C after the compression to improve storage efficiency.
- *Transportation:* This stage is the most capital-intensive, requiring 85–90 % of the total capital of the chain [39]. It starts with the loading of the vessel (barge or ship) typically from a single point mooring (SPM) system, a jetty, or a submerged turret loading system (other configurations are possible; the final system selected will depend on the sea states, availability of docking facilities, and other local conditions). Once the loading is complete, the vessel moves to the destination terminal, where the unloading step takes place. Usually, the gas is to be delivered into a pipeline at a pressure ranging from 25 to 70 bar (2500 to 7000 kPa). The high-pressure gas in the vessels at the start of unloading is let down across a valve to delivery pressure, which causes a temperature drop and requires the gas to be heated. A scavenging compressor may be needed to empty the vessel below the pressure of the pipeline. If previous refrigeration is used, unloading of the gas may be done using a fluid displacement mechanism.

Apart from ships, CNG transportation can also be made at a smaller scale by trains or trucks.

The arrival frequency of ships can be balanced with storage at the delivery point. This storage can be onshore or with an extra ship. CNG does not require large investments in liquefaction or regasification capacity, although the ships themselves are not cheap. It is generally accepted that CNG provides a cost-effective way for a different distance/volume niche in comparison to LNG and pipeline gas transportation. Typical cases in which CNG is supposed to be economically competitive consist of transportation distances from 800 km up to approximately 3000 km and natural gas volumes of 200–600 MMscfd ($5.7–17 \times 10^6$ m^3).

11.10.3 Advantages and Drawbacks

Advantages:

- Ecofriendly technology:
    - The energy consumed is approximately one-half that of the LNG chain, or one-eighth that of a GTL/methanol project.
    - No "boil-off" losses
- Not a cryogenic liquid
- Flexibility:
    - Loading and unloading from offshore terminals is possible. Use of buoy system
    - Once the project reserves are depleted, the facilities can be reused in a new project.
    - Easily scalable due to its modularity
- CNG technology is relatively simple and most of the system components can be designed using first principles.

Disadvantages:

- Unfeasibility of transporting either large gas volumes or to long distances
- Ship CNG concept not commercialized to date (non proven technology)

11.10.4 CNG Technologies

11.10.4.1 GAS TRANSPORT MODULES (GTM™[15])

TransCanada uses GTM™ for CNG transportation, in which the gas is stored at 250 bar and ambient temperature. In these modules, a high-strength composite material is applied to the external surface of a steel pressure vessel, with a ratio of composite to steel that can vary depending on the application. GTM are approximately 35 % lighter than conventional all-steel CNG transportation alternatives. GTM transportation can be performed on ships or barges. The maximum capacity envisaged for a GTM-based ship is 1000 MMscf (28×10^6 m^3 measured at standard conditions). With this concept, the facilities required for the loading and unloading systems are simple and incorporate proven technology, very similar to that in use for 20 years on bulk CNG trucking. Because ships operate at ambient temperature, they require no complicated loading schemes or refrigerated hull. TransCanada has received the "Class Approval in Principle" (AIP) by Lloyds Register for the use of GTM pressure vessels in ships (Figure 11.31) [40].

---

[15] GTM™: Manufactured under license from NCF Industries, Inc., to TransCanada, Calgary, Alberta, Canada.

Figure 11.31—Conceptual ship and barge design using GTMs. Figure courtesy of TransCanada, all rights reserved.

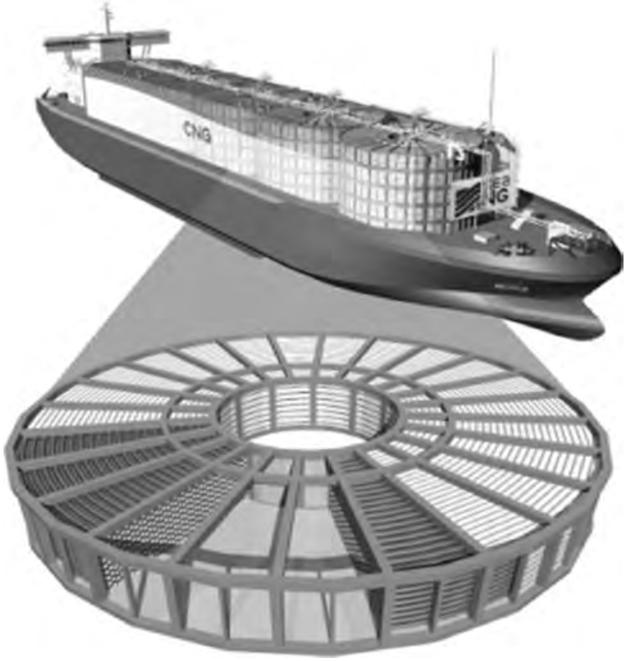


Figure 11.32—Sea NG ship with Coselle. *Source*: Image courtesy of Sea NG Corporation.

11.10.4.2 COSELLE™[16]

Sea NG uses the Coselle concept, which consists of high-strength steel pipe coiled on a carousel permanently installed in the ship [41]. Each Coselle has approximately 10 mi (16 km) of pipe, with a diameter of 6/8 in. (152/203 mm), and can store up to 3.6 MMscf (0.1 × 10^6 m^3 measured at standard conditions) of gas at 250 bar and ambient temperature. Coselles are carried in stacks within the ship's hold, which is 520 MMscf (14.7 × 10^6 m^3), the maximum capacity of a Coselle-based ship (see Figure 11.32). Because the Coselles have a large storage capacity, only a relatively simple manifold with few valves and controlling systems are required. Some of the advantages of Coselle over bottles are lower cost, safer (lower probability of failure and lower consequence of failure), faster to manufacture, and more reliable gas handling. The 50-MMscf (1.42 × 10^6 m^3) ship from Sea NG has full approval for construction from the American Bureau of Shipping (ABS) [42].

11.10.4.3 VOLUME OPTIMIZED TRANSPORT AND STORAGE (VOTRANS™[17])

EnerSea developed the VOTRANS™ concept, in which the natural gas is compressed, cooled, and then stored in a series of API carbon-steel pipes that can be stacked horizontally or vertically. The innovations introduced by VOTRANS include a 60–100 % increase in the gas that can be stored per unit of containment steel, along with a 10–20 % increase in the quantity of gas cargo that can be cost-effectively evacuated from the CNG storage system, compared with conventional CNG concepts (nonrefrigerated). It is claimed that this performance is made possible by optimizing the storage conditions (temperatures of –17 to 4ºC and pressures of ~100 bar) and using their proprietary gas-loading and discharging processes [43]. The VOTRANS vessel design has achieved AIP from ABS (Figure 11.33) [44].

EnerSea offers ship or barge-based systems. The relevant variables to specify for a specific project are gas flow rate, distance from supply to market, and terminal availability. Ranges for rates and distances are:

- *Ship:* 70 to ≥500 MMscf/day (2 to ≥14 × 10^6 m^3/day) of gas and 135 to ≥2700 nautical miles (250 to ≥5000 km)
- *Barge:* 10–75 MMscf/day (0.3–2.1 × 10^6 m^3/day) and 50 to ≥500 nautical miles (92 to ≥926 km).

EnerSea has also a specific concept for onshore CNG storage called VOLANDS™[18] (Volume Optimized Land Storage), which improves the reliability of supply and is intended to be used as a buffer to manage market demand fluctuations.

11.10.4.4 FIBRE REINFORCED PLASTIC (FRP™[19]) VESSELS

Trans Ocean Gas proposes the use of FRP pressure vessels supported vertically in a lightweight steel frame called a cassette. It is a system with references in critical applications such as aerospace, national defense, and public transport industries. By using a combination of pressure and low temperature, natural gas is efficiently stored in FRP pressure vessels. These vessels get stronger at low temperature (they resist up to –100°C), so they are ideal for chilled CNG storage. Some of the advantages of this system are light weight (one third that of steel), corrosion resistance, safety, and reliability [45]. FRP vessels can be outfitted on ships or barges, and the storage capacity of the carriers can reach 1000 MMscf (28 × 10^6 m^3) (see Figure 11.34).

---

[16] Coselle™ belongs to Sea NG Corporation, Calgary, Alberta, Canada.

[17] VOTRANS™ belongs to EnerSea, Houston, Texas, USA.

[18] VOTRANS™ belongs to EnerSea, Houston, TX.

[19] FRP™ belongs to Trans Ocean Gas, St. John's, Newfoundland and Labrador, Canada.

Figure 11.33—EnerSea's CNG barge and ship (VOTRANS). CNG can be delivered using EnerSea's VOTRANS CNG marine service with ships (right) or barges (left) as shown in the illustration.

Figure 11.34—Trans Ocean Gas CNG ship (FRP). *Source*: Picture courtesy of Trans Ocean Gas, Inc.

11.10.4.5 PRESSURIZED NATURAL GAS (PNG®[20])

Knutsen is a shipping company that proposes the use of a technology called PNG (Figure 11.35). It consists of steel cargo containment cylinders, with a diameter of 42 in. (1.07 m) each, packed vertically in a composite shelter. This shelter has the following advantages: light weight, resistance to fire, and resistance to heat variations. The gas is stored at 250 bar (25,000 kPa) and ambient temperature, so no insulation is required to prevent heating during the voyage [46]. This containment system can be used in vessels ranging from 60 to 1000 MMscf ($1.7–28 \times 10^6$ m^3). Regarding certification, the PNG containment tank has received an approval by Det Norske Veritas (DNV).

11.10.4.6 CNG COMMERCIALIZATION

The marine CNG business has the potential to be a multibillion dollar business, although there are no large-scale commercial CNG projects yet (2011). Technology developers have spent several years to fully engineer the designs into a commercial product, get classification approval, and build physical prototype models of the containment systems and functional process systems for the testing [47]. As a consequence, advances in marine CNG transport systems have been truly remarkable; there are arguably three to four competing systems developers ready to make a commercial commitment.

By definition, the initial marine CNG applications will not be commissioned in areas where "conventional" gas transport options can be economically applied. Project developers must be prepared to share risk to obtain first mover advantage. Introduction of natural gas supply through marine CNG involves risk for the consuming nation—security of supply, technology uncertainty, and reliability. Hence, work with governments/consumers is needed to address real and perceived risks [48].

11.11 NATURAL GAS HYDRATES

11.11.1 Overview

Water can combine with low-molecular-weight natural gases to form a solid hydrate, even if the temperature is above the water freezing point. Hydrates have the property to concentrate hydrocarbons; in other words, the volume of a given gas hydrate is much less than the normal volume of the gas from which the hydrate is formed.

The natural gas hydrate (NGH) chain is a technology option for transportation and storage of natural gas [20]. The gas volume content of hydrates is approximately 180 times that of natural gas at standard conditions. They require moderate cooling to be produced, and once produced, they are stable at atmospheric pressure and relatively mild temperatures, in the range of –5 to –15°C. The disadvantage is that for each mole of gas, there are approximately six moles of water being transported.

The following section provides a general overview about what a gas hydrate is and describes the NGH chain as an opportunity for transportation and storage of natural gas.

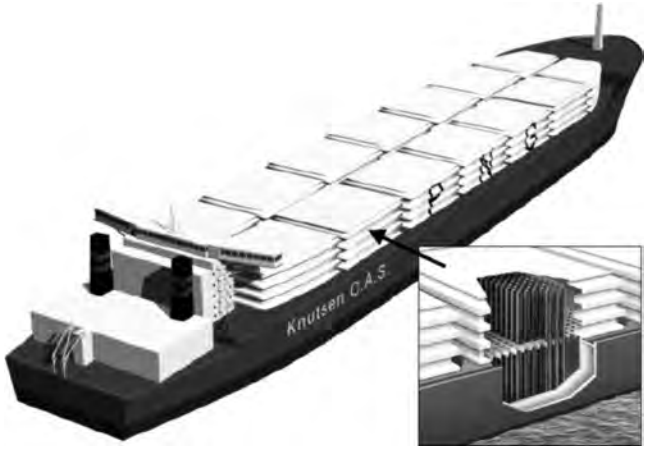


Figure 11.35—Knutsen CNG ship (PNG). *Source*: Picture courtesy of Knutsen.

---

[20] PNG® belongs to Knutsen, Haugesund, Norway.

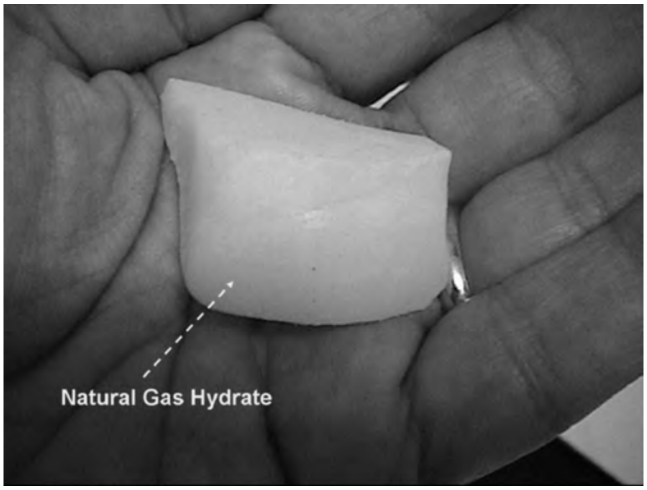


Figure 11.36—**NGH (laboratory manufactured) [20].** *Source*: Picture courtesy of Calogero Migliore.

11.11.2 What Is a Gas Hydrate?

Gas hydrates are crystalline "ice-like" solids (see Figure 11.36), one form of the chemical inclusion compounds known as clathrates. Clathrates are nonstoichiometric compounds in which guest molecules are entrapped in a cage structure composed of host molecules. There is no chemical bond between the guest and host molecules. The crystal lattice is made of hydrogen-bonded molecules. NGHs exist because of the ability of water molecules to form a lattice structure through hydrogen bonding. The water molecules are oriented such that they build a sharing-faces polyhedron. The cages are stabilized by the van der Waals forces between the water and the enclathered gas molecule [49]. Figure 11.37 shows a schematic representation of a cage with methane as a guest molecule.

11.11.3 NGH Chain

The use of gas hydrate technology for the transportation and storage of natural gas is seen as an opportunity for the gas industry to develop the NGH chain. The interest is based on the energy content of the hydrates because their volume is much smaller than the normal volume of the gas from which the hydrate is formed. NGHs might contain a theoretical maximum of approximately 180 m^3 standard of gas per cubic metre of hydrate; in other words, 180 m^3 of natural gas at standard conditions are released when melting 1 m^3 of NGHs.

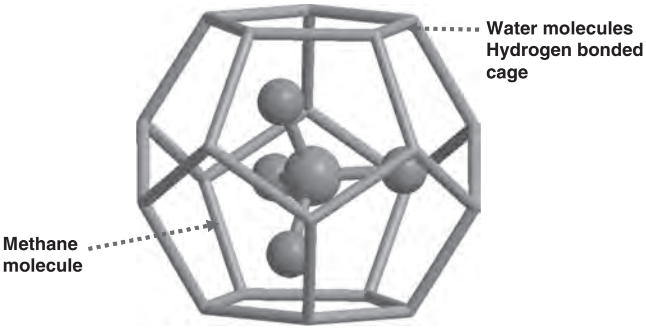


Figure 11.37—Representation of the 5^{12} cage with methane as a guest molecule.

The major stages involved in this chain (Figure 11.38) are the manufacture of NGHs from natural gas and water, transportation of hydrates by ship, and regasification (or dissociation to natural gas and water) at the point of use. Two different concept technologies are under development: dry hydrate and slurry hydrate. The slurry hydrate concept includes two different particular processes: the slurry water-based hydrate and the slurry oil-based hydrate processes. The application of each process is foreseen as follows:

- The dry hydrate process, where natural gas is converted to solid hydrates and transported at atmospheric pressure in bulk carriers.
- The slurry water-based hydrate process, where natural gas is converted to solid hydrates and transported as a concentrated water hydrate slurry in a shuttle tanker at low pressure.
- The slurry oil-based hydrate process, where natural gas is converted to solid hydrates and transported together with crude oil/condensate as a slurry in a shuttle tanker at low pressure.

11.11.3.1 THE DRY HYDRATE PROCESS

The dry hydrate process is an option to store and transport significant volumes of natural gas in the form of solid hydrate at atmospheric pressure in competition with CNG technology. Natural gas could be converted into solid hydrate and then conveyed to bulk carriers. The bulk carriers take the solid hydrate to distant gas markets where the hydrate is melted and the gas is recovered and transferred to the final user.

The dry hydrate process basically consists in three main stages: dry hydrate production, dry hydrate shipping, and dry hydrate regasification (dissociation) [50]. Figure 11.39 shows a simplified diagram of the dry hydrate production process.

For dry hydrate production, gas from a gas processing facility passes through a set of continuous stirred tank reactors, operating in the range of 50–90 bar (5000 to 9000 kPa) and 10–15°C, where it reacts with water and is converted to hydrates. Because the reaction is exothermic, energy is released (~410 kJ/kg). This heat is removed from the system to keep the reactor at constant temperature [51].

Hydrate shipping is carried out using standard ships. Experimental studies have shown that NGHs remain stable at atmospheric pressure when kept frozen in the range of –5 to –15°C at adiabatic conditions; therefore, shipping is at atmospheric pressure and –15°C. These storage conditions are possible because of the metastability property of hydrates [52].

Regasification takes place by melting hydrates with warm water in direct contact. Natural gas and water are then separated. Gas is compressed and dehydrated before being sent to the final user or to a distribution system (see Figure 11.40). The separated water is a combination of the water carried by the hydrates and the water used for melting. The same amount of water carried by hydrates is loaded back to the ship and shipped back to the production plant for its use in the manufacturing of the hydrates. This water contains seeds of hydrate crystals that facilitate reaction rates in the hydrate production process [52].

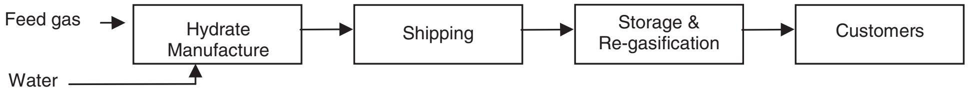


Figure 11.38—Block diagram of the major stages of the NGH chain.

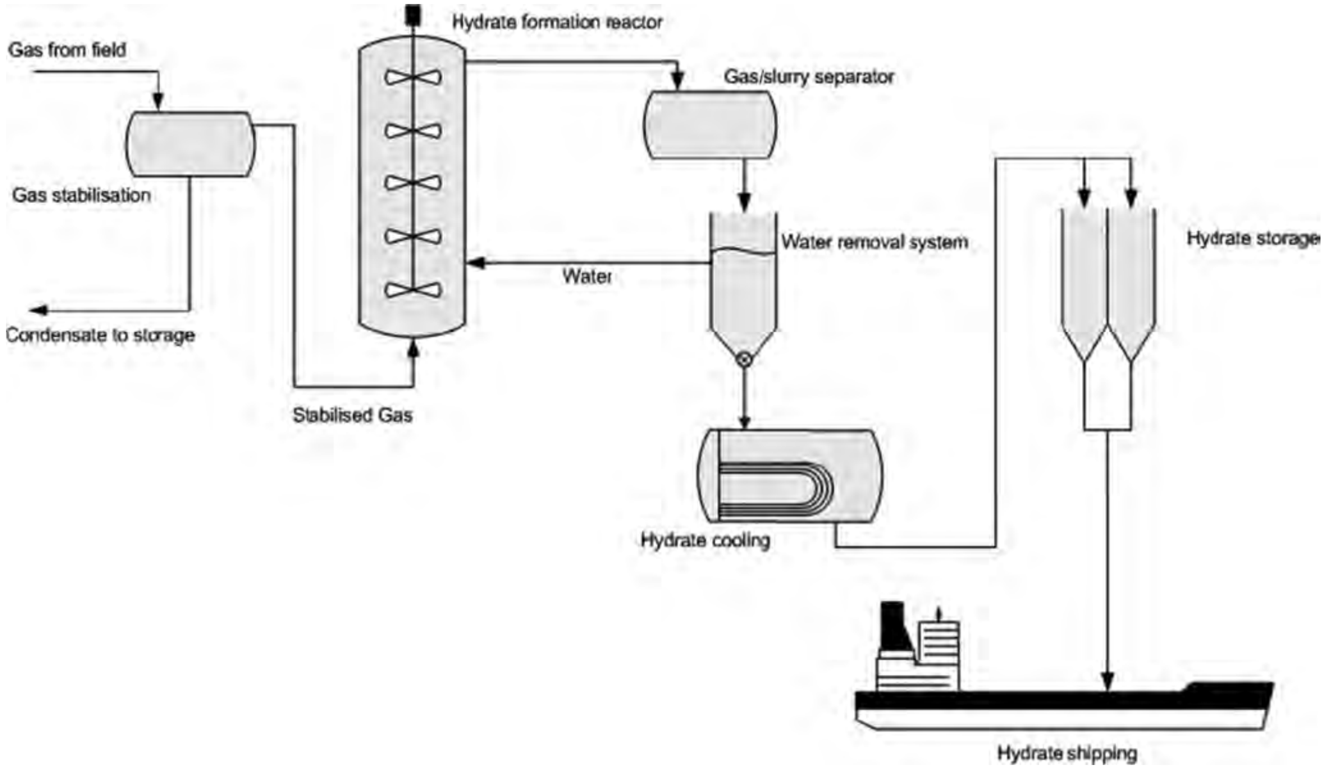


Figure 11.39—Simplified diagram of the dry hydrate production process. *Source*: Figure courtesy of GL Industrial Services, UK, Ltd. (formerly Advantica, Ltd.).

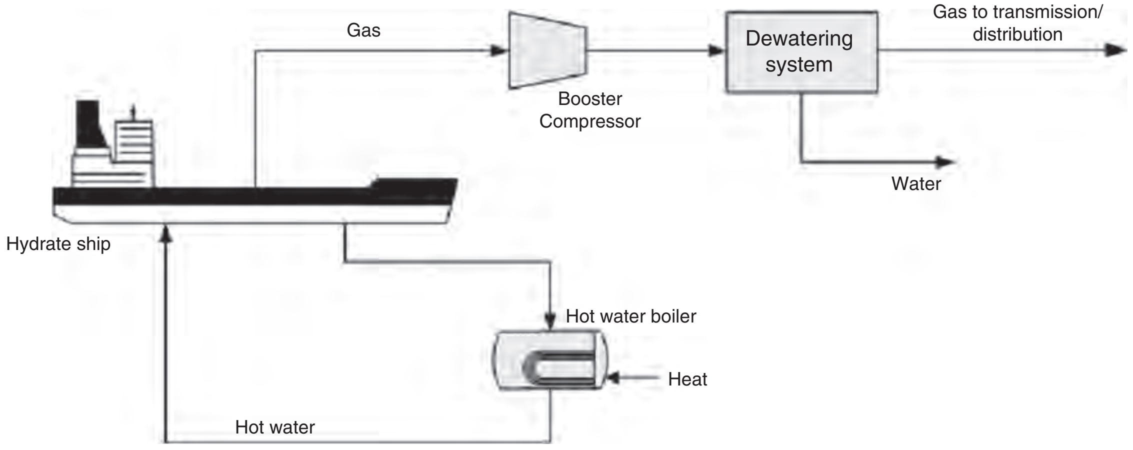


Figure 11.40—Simplified diagram of the hydrate regasification (dissociation) process. *Source*: Figure courtesy of GL Industrial Services UK, Ltd. (formerly Advantica, Ltd.).

11.11.3.2 THE SLURRY WATER-BASED HYDRATE PROCESS

The slurry water-based hydrate process could provide a technology solution to monetize offshore associated gas, where reserves are too small to justify a gas pipeline. Flaring is no longer an option and the conventional practice of reinjecting the gas to enhance oil recovery is increasingly being questioned because the potential revenues of the gas are not achieved.

The slurry water-based hydrate production process is a simplification of the dry process in which the water removal stage consists of just the bulk separation stage.

The partial dewatering produces concentrated but pumpable hydrate slurry containing at least 75 volumes of gas per volume of hydrate. The hydrate is then transferred to a shipping vessel, at approximately 10 bar (1000 kPa) and 2–3°C to be transported to the customers [51]. At the receiving terminal, the hydrate slurry is heated to dissociation and then follows the same path as in the dry hydrate regasification process.

11.11.3.3 THE SLURRY OIL-BASED HYDRATE PROCESS

The niche of application of the slurry oil-based hydrate technology would be the same as the slurry hydrate water-based technology—to capture and handle offshore associated gas where the reserves are too small to justify a gas pipeline. In the slurry oil-based hydrate process, the hydrate reactor consists of a cooling unit, where gas reacts with water to produce hydrates. The resulting NGHs are then mixed with refrigerated crude oil or condensate to make oil-based slurry. The oil-hydrate slurry is stored at –10°C and at pressure close to atmospheric [53]. The transportation of the slurry to shore can be in an isolated low-pressure shuttle tank or under pressure using a pipeline. At the receiving terminal the slurry is sent to the recovery process, where it is heated to dissociation and separated in a three-phase separation unit. The recovery process produces water-saturated natural gas, oil, and liquid water [53].

ACKNOWLEDGMENTS

The coordinating author acknowledges the following colleagues from the LNG Technology Group at Repsol's Technology Center who contributed to the writing of this chapter: Eduardo Carbón, Roberto Coll, Eduardo Machado, Julieta Maresca, Silvia Pérez, José Luis Rivas, and Cristina Tubilleja. Each of them in their area of expertise contributed their full knowledge of the gas industry and researched to include the updated situation of each element of the natural gas value chain. Special thanks to Mar González, from Repsol's corporate head office, who kindly helped to organize and manage the permissions for reprint required to complete the writing of this chapter. Furthermore, we thank the many companies that have kindly allowed us to use their graphic material to illustrate this chapter.

REFERENCES

[1] *Gas Making and Natural Gas*, 1st ed., The British Petroleum Company Limited, London, 1972.

[2] Everett, G.J., van Waters, K.L., and Saar, R., "An Operational Comparison of DEA versus Formulated High Performance Selective Amine Technology," presented at the Third Quarterly Meeting of Union Carbide Canada Inc., Canadian Gas Processors Association/Canadian Gas Processors Suppliers Association, Calgary, Alberta, 1998.

[3] Maddox, R.N., and Morgan, D.J., *Gas Conditioning and Processing, Volume 4: Gas Treating and Sulfur Recovery*, 4th ed., John M. Campbell and Company, Norman, OK, 1998.

[4] Campbell, J.M., *Gas Conditioning and Processing, Volume 2: The Equipment Modules*, 8th ed., John M. Campbell and Company, Norman, OK, 2000.

[5] Pyburn, C.M., Cahil, F.F., and Lennox R.K., "The Effect of Sulfur Compound Interactions on the Copper Corrosion Test in Propane," in Proceedings 57th Annual Convention, Gas Processors Association, 1978 as reported in Section 2 of the *Gas Processors Suppliers Association Engineering Data Book*, 10th ed., Gas Processors Suppliers Association, Tulsa, OK, 1987.

[6] Eckersley, N., and Kane, J.A., "Designing Customized Desulfurization System for the Treatments of NGL Streams," paper presented at the Laurance Reid Gas Conference, Norman, OK, 2004.

[7] Leeper, J.E., "Mercury—LNG's Problem. Under Some Conditions Mercury Can Be a Major Source for Concern in LNG Processing," http://www.calgoncarbon.com/documents/Mercury-LNGsproblem.pdf.

[8] "Nitrogen Rejection/Helium Recovery Units," Chicago Bridge & Iron Company, http://www.cbi.com/services/nitrogen-rejection-helium-recovery.aspx.

[9] *Gas Processors Suppliers Association Engineering Data Book*, 12th ed., Gas Processors Suppliers Association, Tulsa, OK, 2004.

[10] Mokhatab, S., Poe, W.A., and Speight, J.G., *Handbook of Natural Gas Transmission and Processing*, Gulf Professional Publishing, London, 2006.

[11] "Twister Supersonic Separator," http://twisterbv.com/products-services/twister-supersonic-separator/.

[12] Bloch, H., and Soares, C., *Turboexpanders and Process Applications*, Butterworth-Heinemann, Woburn, MA, 2001.

[13] Jibril, K., Al-Humaizi, A., Idriss, A., and Ibrahim, A., "Simulation Study Determines Optimum Turboexpander Process for NGL Recovery," *Oil Gas J.*, Vol. 104, 2006, pp. 58–62.

[14] "NGL Extraction Technologies," PERP Report, NEXANT Chem Systems, San Francisco, CA, 2007.

[15] Hagyard P., Paradowski H., and Gadelle D., "Simultaneous Production of LNG and NGL," 2004, http://www.ivt.ntnu.no/ept/fag/tep4215/innhold/LNG%20Conferences/2004/Data/Papers-PDF/PS2-2-Hagyard.pdf.

[16] Coyle, D., de la Vega, F.F., and Durr, C., "Natural Gas Specification Challenges in the LNG Industry," 2004, http://www.kbr.com/Newsroom/Publications/technical-papers/Natural-Gas-Specification-Challenges-in-the-LNG-Industry.pdf.

[17] Chiu, C.H., "LPG Recovery in Baseload LNG Plant Examined," *Oil Gas J.*, Vol. 95, 1997, pp. 59–63.

[18] Elliot, D., Qualls, W.R., Huang, S., Chen, J.J., Lee, R.J., Yao, J., and Zhang, Y., "Benefits of Integrating NGL Extraction and LNG Liquefaction Technology," paper presented at the American Institute of Chemical Engineers, Spring Meeting, Cincinnati, OH, 2005.

[19] Attaway, D.A., Huang, S., Kotzot, H., and Durr, C.A., "Optimal Process Location for NGL Recovery in LNG Plant," paper presented at the AIChE Spring Meeting, Atlanta, GA, 2005.

[20] Migliore, C., "Design and Economic Analysis of the Hydrate Technologies for Transportation and Storage of Natural Gas," M.Sc. Dissertation, University of Salford, United Kingdom, 2003.

[21] "Fuel Switching with NGLs/Small Scale LNG," PERP 04/05S1, Nexant Chem Systems, San Francisco, CA, 2005.

[22] "Advances in LNG Technologies," PERP 03/04S10, Nexant Chem Systems, San Francisco, CA, 2004.

[23] Roberts, M.J., Petrowski, J.M., Liu, Y.-N., and Bronfenbrenner, J.C., "Large Capacity Single Train AP-X Hybrid LNG Process," Air Products and Chemicals, Inc., GasTech, Doha, Qatar, 2002.

[24] Martin, P.-Y., Pigourier, J., and Boutelant, P., "Liquefin: An Innovative Process to Reduce LNG Costs," paper presented at the Axens 22nd World Gas Conference, Tokyo, Japan, 2003.

[25] van de Graaf, J.M., and Pek, B., "The Shell PMR Process for Large Capacity LNG Trains," paper presented at the AIChE Spring Meeting, 5th Topical Conference on Natural Gas Utilization, Atlanta, GA, April 2005.

[26] Berger, E., Förg, W., Heiersted, R.S., and Paurola, P., "The Snøhvit Project," Linde Technology, Reports on Science and Technology, 2003, www.linde.de.

[27] "Snøhvit Process and Plant," Statoil Research & Technology, Memoir No. 6, 2004, Norway.

[28] Huebel, R., "Niche LNG—An Economic Solution for Stranded Gas," in *Fundamentals of the World Gas Industry*, Petroleum Economist, London, 2006.

[29] "LNG Receiving Terminals," PERP Report 05/06S12, Nexant Chem Systems, San Francisco, CA, 2007.

[30] "Advances in LNG Technologies," PERP Report 03/04S10, Nexant Chem Systems, San Francisco, CA, 2004.

[31] Tarakad, R.R., "LNG Receiving and Regasification Terminals," Zeus Development Corporation, Houston, TX, 2000.

[32] Himmelberger, L., and Billman, P., "LNG Vaporization Technology: The Environment vs. Energy Sourcing," paper presented at the 2005 AIChE Spring National Meeting LNG Sessions, Atlanta, GA, 2005.

[33] Hirakawa, S., and Kosugi, K., "Utilization of LNG Cold," Rev. Int. Froid, Vol. 4, 1981, pp. 17–21.

[34] "Trunkline LNG Expansion," Panhandle Energy, http://www.panhandleenergy.com/expansion_lng.asp.

[35] Wood Mackenzie, LNG Service, http://www.woodmacresearch.com/home/index.html.

[36] Tsuiji, H., and Kashima, H., "Construction of the World's Largest LNG In-Ground Storage Tank," Toho Gas, Co., Mitsubishi Heavy Industries, Nagoya, Japan, 2001.

[37] Scarr, D., "Achieving Economies of Scale with Very Large LNG Storage Tanks," BP Exploration and Production Technology Group and Gordon Jackson, Arup Energy, PO-15, LNG 15, Barcelona, Spain, 2007.

[38] "In-Ground LNG Storage Tanks," Tokyo Gas Co., Ltd., http://www.tokyo-gas.co.jp/lngtech/ug-tank/index.html.

[39] Deshpande, A., and Economides, M.J., "CNG: An Alternative Transport for Natural Gas Instead of LNG," University of Houston, SPE Gulf Coast Section, http://www.spegcs.org/attachments/studygroups/6/CNG-An_Alternative_Transport_for_Natural_Gas.pdf.

[40] http://www.transcng.com/home.

[41] http://www.coselle-system.com/overview.

[42] "Sea NG Ships, Key Features," http://www.coselle-system.com/coselle-ship.

[43] Dunlop, J., "EnerSea CNG System Offers Valuable Gas Delivery Solution," Energy Tribune, 2007, USA, http://www.energytribune.com.

[44] Enersea VOTRANS™ CNG Technology, http://www.enersea.com/cng-technology.html.

[45] "Business Plan Overview," Trans Ocean Gas, Inc., St. John's, Newfoundland, Canada, 2007.

[46] Valsgård, S., Mørk, K.J., Lothe, P., and Kristian Strøm, N., "Compressed Natural Gas Carrier Development—The Knutsen PNG Concept," 2004 Society of Naval Architects and Marine Engineers Annual Meeting, Washington, DC, 2004.

[47] Interview of John Dunlop, VP Business Development EnerSea Transport, Business News Americas Report, February 6, 2008, Chile, http://www.bnamericas.com.

[48] Reinsch, A.E., "Advancements in CNG-Marine Transport Conference: The Final Approach to Commercialization," Artumas Group, Inc., Houston, TX, 2007.

[49] Mork, M., "Formation Rate of Natural Gas Hydrate," Ph.D. Thesis, Norwegian University of Science and Technology, Trondheim, Norway, 2002.

[50] Taylor, M., "The BG Hydrate Project Technology Development Presentation," paper presented at the 2nd International Workshop on Methane Hydrates R&D, Washington, DC, 2002.

[51] Fitzgerald, A., and Taylor, M., "Offshore Gas-to-Solids Technology," SPE 71805, paper presented at the Offshore Europe Conference, Aberdeen, Scotland, 2001.

[52] Gudmundsson, J.S., Hveding, F., and Børrehaug, A., "Transport of Natural Gas as Frozen Hydrate," paper presented at the 5th International Offshore and Polar Engineering Conference, The Hague, The Netherlands, 1995.

[53] Gudmundsson, J.S., Andersson, V., Levik, O.I., and Parlaktuna, M., "Hydrate Concept for Capturing Associated Gas," SPE 50598, paper presented at the SPE European Petroleum Conference, The Hague, The Netherlands, 1998.

12

Hydrogen Management

N. Zhang[1] and F. Liu[2]

12.1 INTRODUCTION

The concern of hydrogen balance has increased over the last 15 years. Haun et al. [1] recollected the history of the hydrogen issue in refining. During the early age of oil refining, refiners paid little attention to hydrogen production, consumption, or distribution among the products. By the mid-1950s, after the prevalent use of catalytic reforming, refiners had a cheap hydrogen resource that could be used as a reagent in their refining schemes. The hydrogen supply generally exceeded the demand. Although hydrogen became more and more important in improving process performance, hydrogen management was of little importance in refineries.

Hydrogen availability becomes a focal point because refiners are facing challenges of stringent environmental regulations and increasing demand of transport fuel. Along with the legislation of environmental protection, tougher gasoline and diesel quality specifications in the European Union and the United States have been implemented to reduce smog-forming and other pollutants in automotive exhaust. Such a trend can be clearly foreseen in the near future. For example, the gasoline fuel specifications in the European Union decreased the maximum sulfur from 150 ppm to 10 ppm before 2009, and the maximum aromatics from 42 % vol to 35 %, while the maximum sulfur in diesel fuel specifications decreased from 350 ppm to 10 ppm. To stay in business, one of the options for refiners is to switch their feedstock to light sweet crude if they believe such supply is ample and under a decent price in the future. At the same time, they must look at a significant investment in desulfurization. Lower-sulfur fuel means more hydrogen is necessary for deeper hydrodesulfurization. In the meantime, lower aromatic gasoline specifications will decrease the operation severity in catalyst reformers, leading to reduction of the byproduct hydrogen (Table 12.1). Another future environmental effect is that the legislation of greenhouse gas abatement may urge refineries to reduce hydrogen production.

Other big effects on the refinery hydrogen balance are caused by bottom-of-barrel upgrade. According to more and more strict limitation of pollutant emissions, the market share of fuel oil has declined for a long period. On the other hand, the market trends indicate a very large increase in the share of middle distillates, reflecting spectacular growth in diesel oil and jet fuel production (Figure 12.1) [2].

Although crude is expected to become heavier and contain more sulfur (Table 12.2), the refiners are pressured to add more conversion capacity to be competitive.

There are two different kinds of processes to increase the hydrogen-to-carbon ratio in the refinery product slate: one rejects carbon from petroleum streams (e.g., fluid catalyst cracking and delay coking) and the other adds hydrogen (e.g., residue hydrotreating and hydrocracking). Although the latter is much more expensive in capital and operating cost than the former [3], it is still predictable that hydrocracking processes will play the main role in the heavy-end conversion because of their considerable flexibility of the feedstock, processability of the yields, and quality of the products. Especially when a refinery processes sour feedstock, the poor product quality after "carbon-reject" processes causes further problems in product blending and requires extra hydroprocessing. Available processes for heavy crude upgrading are compatible and can be integrated to achieve the optimal economic results [4]. Generally, the additional "on-purpose" hydrogen capacity is required if the hydrocracking process is implemented.

Many efforts have been contributed to analyze how these impacts affect hydrogen balance in refineries. Haun et al. [1] looked at the amount of hydrogen presented in the feedstock versus the amount in the desired product slate as the ultimate determinant of the hydrogen balance problem. The impact of the refinery evolution from hydroskimming to complex conversion is illustrated by comparing the hydrogen content in feeds and products. Two upgraded hypothetical refineries—gasoline refinery and diesel refinery—were investigated. The case studies show that modern refineries can not only achieve anticipated product specifications but also dramatically improve their profitability. However, the hydrogen requirement is also largely increased. For the gasoline refinery, the hydrogen from catalytic reforming cannot supply sufficient hydrogen, and hydrogen has to be recovered from other refinery off-gases to settle the hydrogen balance. For the diesel refinery, hydrogen has to be produced through a hydrogen plant. Hydrogen management becomes essential for profitable operations in upgraded refineries. Lamber et al. [5] analyzed how the environmental impacts on product qualities and changes in product slates shifted the hydrogen balance in refineries. It can be seen from Table 12.3 that vacuum distillate and residue hydroprocessing provide the main incentive for hydrogen demand. Heavy-end gasification is suggested as an attractive option complying with the hydrogen demand, residue disposal, and clean energy requirement of refineries.

Philips [6] discussed the approach to find the optimal hydrogen scenarios from the engineering point of view. An example project shows that through hydrogen management, hydrogen production capacity is decreased, resulting not only in a reduction in capital and operating expense but also in a significant decrease in carbon dioxide (CO_2) emissions. However, it has been pointed out that any hydrogen

---

[1] The University of Manchester, Manchester, UK
[2] British Petroleum Plc., Beijing, China

TABLE 12.1—EU Gasoline and Diesel Regulations

EU - MOTOR GASOLINE REGULATIONS				
	2003	**2005**	**2009**	**2012**
Sulfur, ppm (max)	**150**	**50/10**	**10**	**10**
Benzene, % vol (max)	**1**	**1**	**1**	**1**
Aromatics, % vol (max)	**42**	**35**	**35**	**35**
Olefins, % vol (max)	**18**	**18**	**18**	**18**
EU - ON-ROAD DIESEL REGULATIONS				
	2003	**2005**	**2009**	**2012**
Sulfur, ppm (max)	350	50/10	10	10
Density (max)	0.845	0.845	0.845	0.845
Distillation T95, degC (max)	360	360	360	360
Cetane index (min)	46	46	46	46
Cetane number (min)	51	51	51	51

solution must be tested not just for economic viability, but the technical robustness, refinery integration, and constructability should also be taken into account.

12.2 HYDROGEN PRODUCTION PROCESSES

When hydrogen consumers with large hydrogen requirement (e.g., hydrocrackers) are operating in a refinery, the supplemental hydrogen often needs to be provided by hydrogen generation processes other than catalytic reforming units. To produce hydrogen by a steam reforming process, the available feedstock in a refinery can be methane (CH_4), saturated liquefied petroleum gas (LPG), straight-run naphtha, and some refinery off-gases. The management of hydrogen generation and hydrogen recovery depends on the refinery hydrogen balance, raw material prices, fuel prices of hydrogen generation, total operating cost, and investment incurred.

TABLE 12.2—U.S. Crude Characteristics

Year	API Gravity	Sulfur (wt %)
1990	31.86	1.10
1992	31.32	1.16
1994	31.39	1.14
1996	31.14	1.15
1998	30.98	1.31
2000	30.99	1.34
2002	30.42	1.41
2004	30.18	1.43
2006	30.44	1.41
2008	30.21	1.47

Hydrogen generation processes in a refinery are steam reforming and partial oxidation. Gardner [7] addressed the distinguishable factors of hydrogen generation processes. For gaseous feedstock, the capital costs inside battery limits for steam reforming and partial oxidation are similar. However, the high-pressure oxygen requirement adds extra expense to partial oxidation. For heavy feedstock, the capital cost for partial oxidation is significantly higher than for gas-based steam reforming because of the requirement for sulfur removal and feedstock handling facilities. Except for the facts that gaseous feedstock is extremely expensive and

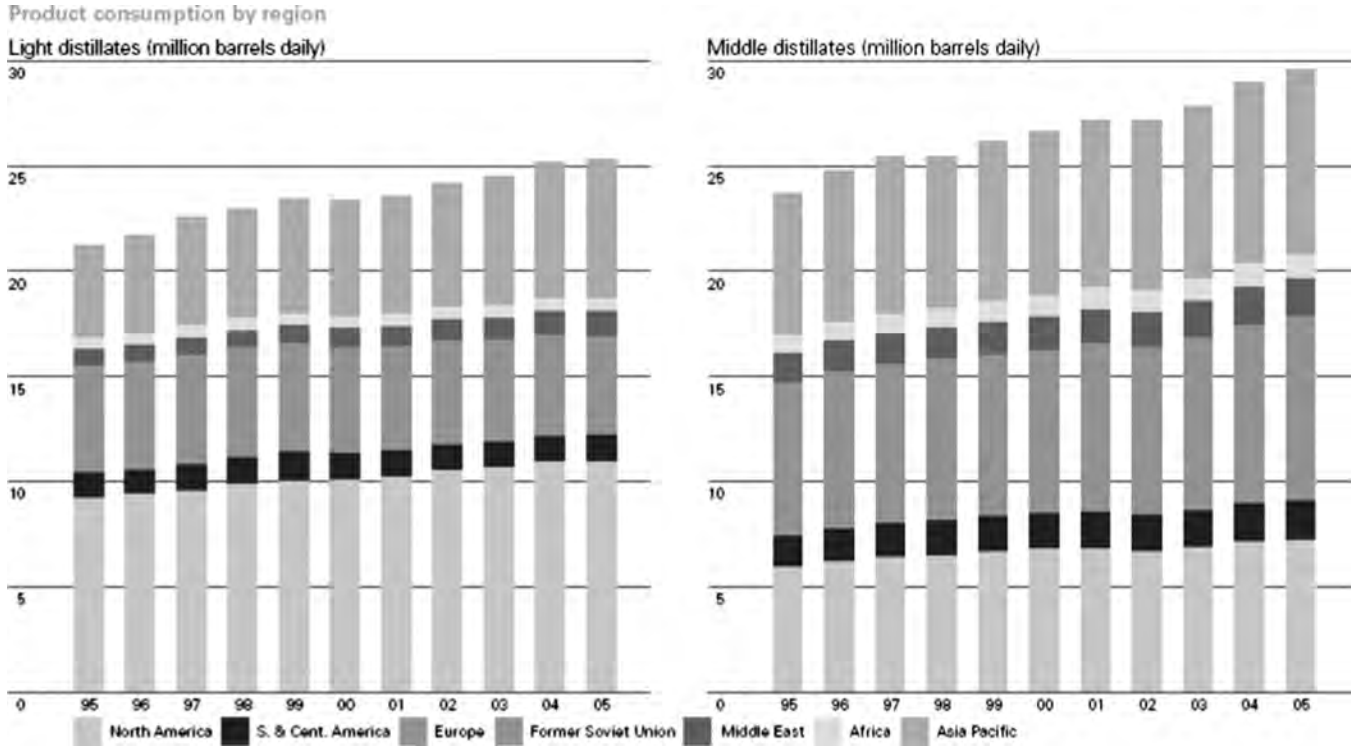


Figure 12.1—The growing consumption of light and middle distillates [2].

TABLE 12.3—Typical Hydrogen Consumption; Data Chemical Consumption Only

Process	Percent Weight on Feed	Percent Weight on Crude
HT Straight run naphtha	0.05	0.01
HT FCC/TC naphtha	1	0.05–1
HT kerosene	0.1	0.01–0.02
HDS LS gasoline to 0.2 % S	0.1	0.03
HDS HS gasoline to 0.2 % S	0.3	0.04
HDS LS gasoline to 0.05 % S	0.15	0.04
HDS HS gasoline to 0.05 % S	0.35	0.05
HDS FCC/TC gasoline	1	0.1
Cycle oils hydrogenation	3	0.3
Hydrocracking VGO	2-3	0.5–0.8
Deep residue conversion	2-3.5	1–2

Data from Lamber et al. [5]. HT, hydrotreating; FCC, fluid catalytic cracking; HDS, hydrodesulfurization; VGO, vacuum gas oil.

heavy feedstock is very cheap, high capital cost for partial oxidation processes plus oxygen supply requirements make the hydrogen cost substantially higher than that from steam reforming processes. Because of the capability to handle heavy feedstock, a partial oxidation process is an opportunity to overcome bottom-of-barrel problems in refineries, whereas the amount of available heavy feedstock in a refinery typically far exceeds the required amount to satisfy the hydrogen balance. Therefore, alternative consumers of hydrogen or synthesis gas must be found to make this option viable. Steam reforming currently dominates the hydrogen generation processes in refineries.

12.2.1 Steam Reforming

There are two typical processes in steam reforming with different purification processes. In conventional processes, the low-temperature shift reactor is necessary to reduce residual carbon monoxide (CO) in synthesis gas further after the high-temperature shift conversion. The product is then cooled and scrubbed with circulating amine or hot potassium carbonate solution to remove CO_2 by absorption. The remaining small quantities of CO and CO_2 are converted to CH_4 by methanation. The hydrogen purity in the conventional processes is typically 95–97 %. The impurities are mainly CH_4 and carbon oxidant at parts per million levels.

Pressure swing adsorption (PSA) was introduced as a replacement of the conventional purification process in the 1970s. The high-temperature shift gas is cooled and purified by PSA. The hydrogen purity by PSA purification can reach more than 99.9 %. The residue of PSA is recycled to the reformer as fuel. Because a part of generated hydrogen is discharged as residue in PSA, the hydrogen yield of unit feedstock with PSA is lower than with conventional processes but needs less external fuel. The investment of hydrogen plants with PSA is higher than the conventional plants with regards to the same hydrogen production. The economics of hydrogen generation depend on the price of feedstock and fuel. Whereas feedstock is expensive and fuel is relatively cheap, the conventional process shows lower hydrogen cost, or vice versa. However, hydrogen plants with PSA become a preferred choice for hydrogen generation in refineries nowadays for the following reasons:

- Hydrogen purity has significant effects on the design and operation of hydroprocessors. High purity is favorable to hydroprocessor design [8].
- The state-of-art PSA technology provides high hydrogen recovery up to 90 % [9], which enormously reduces hydrogen cost.
- A PSA process is easier to design and operate for a large-scale hydrogen plant than an adsorption process that normally uses packing columns.

A hydrogen plant with PSA has low turndown ratio, high operation flexibility, modest control, short startup and turndown periods, long-term operation, and relative ease of expansion.

The process description for a hydrogen plant with PSA (process flow diagram Figure 12.2 shows a top-fired reformer) is as follows:

- The feedstock combined with recycled hydrogen is preheated in the convection section of the reformer. The preheated hydrocarbon feed is routed to the sulfur absorber, where unsaturated hydrocarbons are hydrogenated and organic sulfur (mercaptans) is converted to hydrogen sulfide (H_2S) in the first catalyst bed of cobalt molybdenum oxide. H_2S is removed from the feed gas in the second bed of zinc oxide.
- The desulfurized feed is then mixed with superheated high-pressure steam and preheated in the convection section of the reformer. The mixed feed enters the radiant section of the reformer and flows down through catalyst-filled tubes, where it reacts to produce hydrogen gas (H_2), CO, CO_2, and CH_4.
- Combustion air and convection-section flue gases are moved through the reformer by the flue gas fan.
- The reformer effluent is routed through the waste heat boiler, where the recovered heat is used to generate high-pressure saturated steam and feed to the high-temperature shift converter, where excess steam converts most of the CO to CO_2 and H_2 over a bed of catalyst. The shifted gas is cooled in a heat exchanger train, which generates high-pressure steam and preheats boiler feed water (BFW). Condensed water from the gas cooling is removed in a knockout drum.

The raw hydrogen stream is purified to produce high-purity hydrogen by a PSA unit, where impurities are removed by a cyclic adsorption process. The tail gas stream from the PSA unit, containing the removed impurities and some residual hydrogen, is returned to the reformer as fuel gas. A hydrogen product purity of more than 99.9 vol % can be achieved through PSA.

Process description for a conventional hydrogen plant (process flow diagram Figure 12.3 shows a side-fired reformer) is as follows:

- The feedstock combined with recycled hydrogen is preheated in the convection section of the reformer. The preheated hydrocarbon feed is routed to the sulfur absorber, where unsaturated hydrocarbons are hydrogenated and organic sulfur (mercaptans) is converted to H_2S in the first catalyst bed of cobalt molybdenum oxide. H_2S is removed from the feed gas in the second bed of zinc oxide.

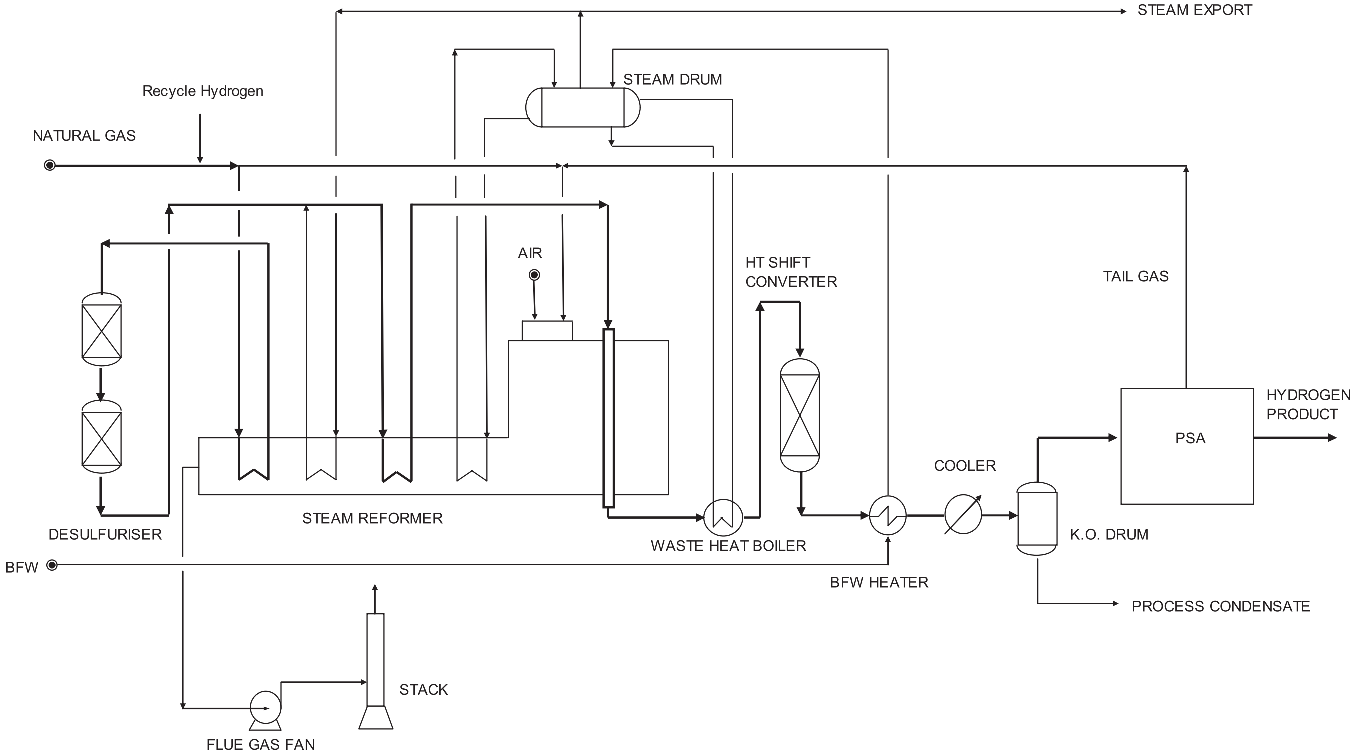


Figure 12.2—Process flow diagram of a hydrogen plant with PSA.

- The desulfurized feed is then mixed with superheated high-pressure steam and preheated in the convection section of the reformer. The mixed feed enters the radiant section of the reformer and flows down through catalyst-filled tubes, where it reacts to produce H_2, CO, CO_2, and CH_4.
- Combustion air and convection-section flue gases are moved through the reformer by the flue gas fan.
- The reformer effluent is routed through the waste heat boiler, where the recovered heat is used to generate high-pressure saturated steam and feed to the high-temperature shift converter, where excess steam converts most of the CO to CO_2 and H_2 over a bed of catalyst. After recovering the heat from this stream, the effluent is routed to the low-temperature shift converter to further reduce the level of CO. The shifted gas is cooled in a heat exchanger train, which generates high-pressure steam, preheats BFW, and provides heating duty to the reboiler for the regenerator within the CO_2 scrubbing package.
- The product is then cooled and scrubbed with circulating hot potassium carbonate solution to remove CO_2 by absorption. The raw hydrogen stream is purified by converting the remaining CO and CO_2 to CH_4 through the methanator. The hydrogen product purity is approximately 95–97 vol %.
- Condensed water from the gas cooling is removed in the knockout drums.
- BFW is preheated by shifted gas before feeding to the steam drum. High-pressure steam is generated by the waste heat boiler reformer convection section and by exchanging heat with shifted gas.
- Saturated steam is drawn from the steam drum and superheated in the reformer convection section before being used for the process. The remaining steam is exported after superheating.

The pretreated feedstock is mixed with superheated steam and preheated to 500°C (932°F) before passing to the radiant section of the reformer. The steam reforming reaction takes place in the furnace tube packed with nickel-based catalyst. The steam reforming reaction is not just one reaction but can be described briefly by the following equations:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 - \Delta H \tag{12.1}$$

$$C_nH_m + nH_2O \Leftrightarrow nCO + (n + \frac{m}{2})H_2 - \Delta H \tag{12.2}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 + \Delta H \tag{12.3}$$

Although the reactions in equations 12.1 and 12.2 are endothermic and the reaction in equation 12.3 is exothermic, the overall reaction is highly endothermic. The burners in the furnace radiant section provide heat to maintain the operating temperature of steam reforming at approximately 850°C (1562°F). Addition of excess steam not only shifts the reaction equilibrium to produce more hydrogen but also avoids carbon formation in catalyst. However, high steam import increases the duty of a steam reformer.

Low operating pressure promotes hydrogen generation, but most hydrogen plants with PSA operate above 20 atm (294 psi) on the basis of the consideration of the optimum PSA operating pressure, compression cost, and equipment size.

12.2.2 Reformed Gas Shifting

The temperature of the gases exiting from a reformer is reduced to 340–360°C (644–680°F) by generating steam.

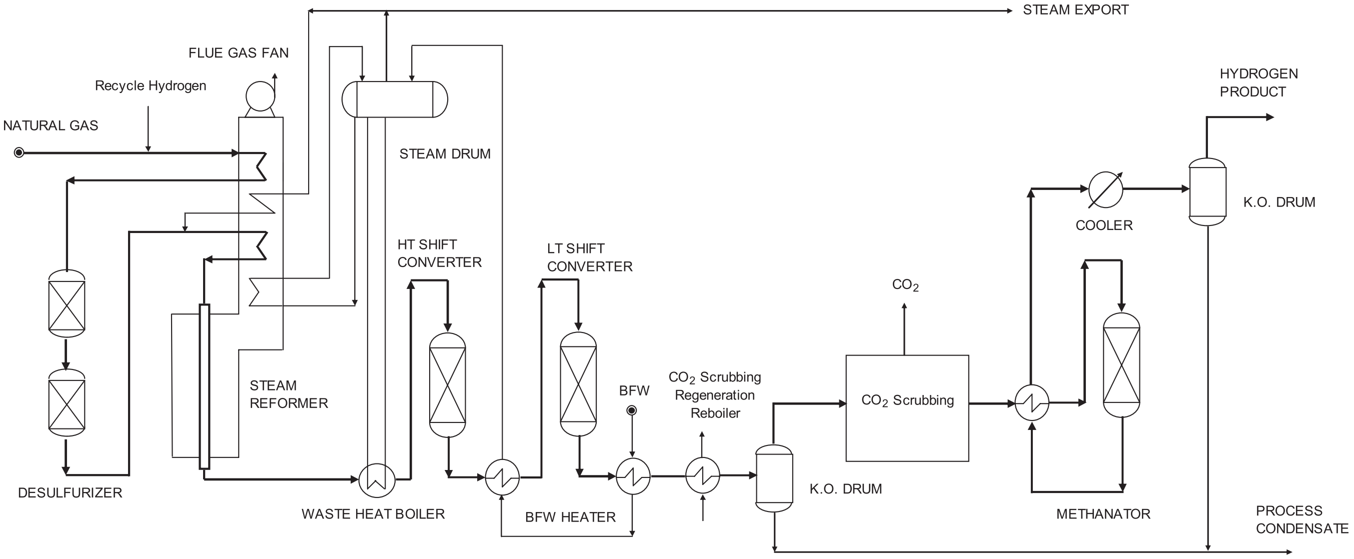


Figure 12.3—Process flow diagram of a conventional hydrogen plant.

CO is converted further to hydrogen in a high-temperature shifting reactor on magnetite iron oxide-based catalyst. Equation 12.3 shows the reaction procedure. Normally, a low-temperature shifting reactor is only used in the conventional processes.

The gases exiting from the shifting reactor are cooled in stages to generate steam and preheat BFW. They are finally cooled by air and water to normal temperature (40°C, or 104°F). The gases are then purified by PSA. The condensed sour water is recycled to the boiler after stripping.

12.2.3 PSA and Fuel System

The process characteristics of PSA are discussed in Section 12.2.1. The adsorption forces for the components in the shift gas are water >> CO_2 > CO > CH_4 > hydrogen on the molecule sieve adsorbent. The product of PSA is hydrogen at more than 99.9 %. The impurities in the product are mainly CH_4 with carbon oxides at part-per-million levels. The rest of the components appear in the residue. Because the discharge pressure of PSA is very low (approximately 1.5 atm or 22 psi) to achieve high hydrogen recovery, the residue from PSA is directly sent back to the steam reformer with specific low operating pressure burners as fuel instead of compressing to a fuel system.

The additional fuel is supplied by a refinery fuel system. The mixture of fuel gas is mixed with air preheated in the convective section of the reformer furnace and sent to burners in the radiant section. The high-temperature flue gas enters the convention section, heats the reformer feed, superheats the exporting steam, generates steam, and separately heats combustion air.

12.2.4 Steam Generation System

Hydrogen plants with steam reforming generate steam to supply the reaction and recover energy. BFW is pumped and preheated by the shift gas before entering the boiler. The steam generation is completed by exchanging heat with the reformed gas, the shift gas, and the flue gas. The steam generated in a hydrogen plant is always more than the reaction requirement. The extra is exported to a refinery steam system after superheating.

12.2.5 Gasification

Partial oxidation plants are capable of processing a wide variety of feedstocks, including

- Gas (natural gas, refinery off-gas)
- Heavy residue (vacuum residual, fuel oil, asphalt)
- Petroleum coke

The partial oxidation reaction proceeds as follows:

$$C_nH_m + (n/2)O_2 \rightarrow nCO + (m/2)H_2 - \Delta H \qquad (12.4)$$

The term of "partial oxidation" may be replaced by "gasification." The reaction involves the combustion of a hydrocarbon in a flame with less than stoichiometric quantities of oxygen to form CO_2 and steam, which, in turn, react with the unreacted hydrocarbon to produce CO and hydrogen. The overall reaction remains exothermal.

Various secondary reactions including hydrocracking, the steam carbon reaction, hydrocarbon reforming, and the water-gas shift reaction also take place.

12.2.6 Hydrogen Production from Nonhydrocarbon Sources

Steam reforming and partial oxidation/gasification produce hydrogen mainly from fossil fuels, which is one of the major CO_2 emission sources in oil refineries. Because of growing concerns over greenhouse gas emissions in industry, there is a strong interest to exploit nonhydrocarbon hydrogen sources. Some potential hydrogen sources can be summarized as follows:

- *Electrolysis of water*: Production of hydrogen from water using electrolysis can be done on an industrial scale. However, it requires a large amount of energy. Usually the electricity consumed is more valuable than the hydrogen produced. Therefore, it is uncompetitive with the hydrogen production from coal or natural gas. Nevertheless, this option may become attractive if hydrogen is used as a media to store renewable electricity in the future.
- *Thermolysis of water*: Water is spontaneously discomposed at approximately 2500°C. However, such a temperature is simply too high for usual process piping

and equipment, which makes any potential industrial-scale applications too expensive.

- *Urea electrolysis*: Hydrogen can be made from urine via urea electrolysis [10], which is 332 % more energy efficient than using water. However, this technology is still in the research stage.
- *Biohydrogen routes*: Biomass and organic waste streams can be converted into biohydrogen, either with biomass gasification or steam reforming as discussed above, or with biological conversion processes such as fermentative hydrogen production [11] and biocatalyzed electrolysis [12]. Although these routes are theoretically feasible, the challenge here is to make such technologies commercially viable.

12.3 HYDROGEN PURIFICATION PROCESSES

Alternatives available to satisfy the hydrogen requirement in refineries are limited. Hydrogen can be generated by steam reforming or partial oxidation, or it can be recovered from refinery off-gases. In some cases, the refiners can buy hydrogen from a third party. Among these options, recovering hydrogen from refinery off-gases can be considerably cheaper in operating cost and capital investment. It is worth prioritizing the recovery of hydrogen from refinery off-gases with reasonable amounts.

The off-gases containing hydrogen are from catalytic reformers, hydroprocessors, fluid catalytic cracking (FCC) units, and other refining or petrochemical units. The typical content of some off-gases is listed in Table 12.4.

The purification processes include PSA, membrane separation, cryogenic processes, and gas-liquid absorption. Each of these processes is based on different separation principles and therefore have specific process characteristics. The selection of these purification processes depends on the economic aspects as well as process flexibility, reliability, and ease of future expansion. Tremendous effort has been made to find the guidelines for the proper selection. Although most methods give the physical insights, they are only instructive for the purification process design.

The appropriate purification system can decrease the hydrogen plant capacity in a new design or provide cheaper hydrogen in a retrofit project.

TABLE 12.4—Typical Content of Some Refinery Off-Gases

Off-Gas Sources	Hydrogen Concentration (vol %)	Pressure (psig)
Catalytic reformer	70–90+	250–400
Hydroprocessor		
High pressure	75–90	800–2500
Low pressure	50–75	100–250
FCC unit	15–20	100–250
Delay coker (DCU)		
Toluene hydrodealkylation (TDA)	55	400–500

Data from Miller and Stoecker [13].

12.3.1 *Pressure Swing Adsorption*

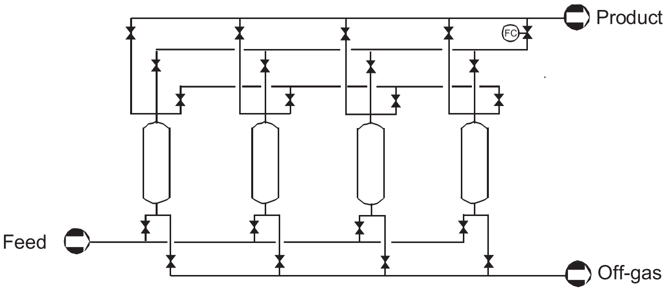
A PSA process is based on the principle that the specific adsorbents are capable of adsorbing different gas molecules with different affinity on the basis of partial pressure, size, and polarity. Two basic stages are involved: adsorption and regeneration or desorption. The operating pressure in the adsorption stage is higher than in the desorption stage. Because the adsorbent capability for impurities is much higher than for hydrogen at certain partial pressures, most of the impurities are adsorbed together with only a small amount of hydrogen. The impurities can then be removed from the adsorbent by reducing the pressure.

The process operates on a cyclic basis. Multiple adsorbers are used to continuously purify a feedstock and provide a constant product and a tail gas. A typical sequence chart is shown in Figure 12.4 for a system with four adsorbers. A hydrogen stream is separated from the feedstock in the adsorption phase. The adsorber then goes through co-current depressurization to repressure other adsorbers and remove impurities from the adsorbent while producing a tail gas. The purge from other adsorbers and finally the product hydrogen are used to repressure the adsorber until it is ready for the next adsorption.

The product hydrogen is available at roughly the same pressure as the feed. The pressure drop between feed and product is nominal at 10 psi. The product hydrogen is always in very high purity (up to ≥99.9 %) and the impurities will appear in product in the sequence of adsorption strength to adsorbent. The relative adsorptivity of typical feed impurities is given in Table 12.5.

The performance of a PSA unit can be evaluated by the hydrogen recovery, which is defined as the ratio of the amount of hydrogen contained in the product by the amount of hydrogen contained in the feedstock. The hydrogen recovery is influenced by tail gas pressure, feed pressure, feed and product purity, unit configuration, numbers of equalization phases, etc. Low tail gas pressure can significantly improve the hydrogen recovery (Figure 12.5). However, compressing tail gas may be necessary in order to match the fuel system pressure in a refinery or for other usage, which perils the economics of PSA units. Therefore, the selection of the appropriate tail gas pressure is extremely important. The effect of feed gas pressure on hydrogen recovery is less than that of the tail gas pressure. Figure 12.6 shows there is an optimal feed pressure. Miller and Stoecker suggested that the minimum pressure ratio between the feed and the tail gas is approximate 4:1, and the optimal range of feed pressure is 200–400 psig. A low feed purity is not recommended because of poor hydrogen recovery. The low product hydrogen purity can increase the hydrogen recovery, but the effect is relatively small (Figure 12.7). Most PSA units are designed to achieve high hydrogen purities.

The advantage of using PSA processes to separate hydrogen from refinery off-gas is that the product purity can be very high and the impurities can be controlled in part-per-million levels. However, the tail gas is difficult to reuse because of its low pressure. A computer aid control gives PSA a wide operation range, and its reliability has been proven by long-term operations.



ADSORBER	411 CYCLE											
1	Adsorption			E1	PP		BD	P		E2	R	
2	E2	R		Adsorption			E1	PP		EB	P	
3	BD	P		E2	R		Adsorption			E1	PP	
4	E1	PP		BD	P		E2	R		Adsorption		

E1= Equalization (co-current depressurization)

E2 = Equalization (countercurrent repressurization)

PP = Provide purge (co-current depressurization)

P = Purge

BD = Blowdown (countercurrent depressurization)

R = Final repressurization

Figure 12.4—PSA cycle sequence chart.

12.3.2 Membrane Separation

A membrane separation is achieved by different permeations between hydrogen and impurities. Table 12.6 gives relative permeabilities of some typical components. The most popular membrane used in hydrogen recovery is composite hollow-fiber membrane, which is composed by an active layer and a support layer. Gases pass through a membrane in two sequential steps: solution and diffusion. A simplified process is shown in Figure 12.8. The permeate is the fast gas, which has higher permeability and enriches the low-pressure side of the membrane. The pressure difference between the permeate and the residue provides the driving force for the diffusion of gas across the membrane. The membrane performance is much more dependent on the feed to permeate the pressure ratio rather than the operating pressure [13,14]. The strength of a membrane limits the design of pressure difference. Because hydrogen is always recovered as a permeate, there is a tradeoff between the hydrogen recovery and the product pressure drop. Figure 12.9 illustrates that when the same recovery is maintained, increasing the permeate pressure decreases hydrogen purity and increases the membrane area—the cost of compression is not taken into account.

Unlike PSA, a membrane process cannot remove impurities to a very low level; thus, it is not suitable when a process requires fine impurity removal. The hydrogen purity in the permeate can be low. The hydrogen recovery increases whereas the product purity drops, as shown in Figure 12.10. A typical membrane design with condensate protection is shown in Figure 12.11.

The performance of a membrane system can be improved by a multistage design. Spillman [14] reviewed the performance principles of gas membrane separation and demonstrated some commercial applications of membrane separation processes, including hydrogen recovery. Through the introduction of designs for single-stage and multistage membranes, it is indicated that the membrane designs are very much case dependent. The advantages of membrane gas separation are low capital cost even at

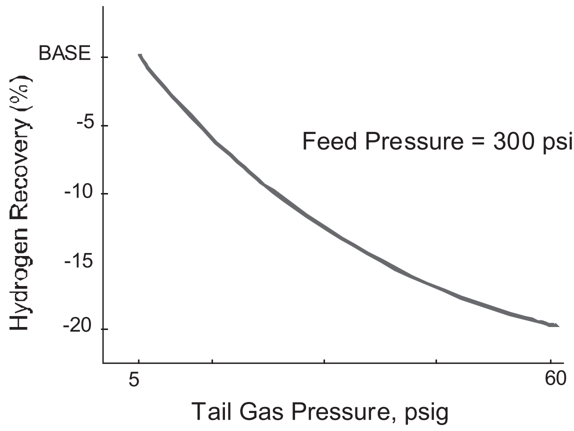


Figure 12.5—Effect of tail gas pressure on PSA recovery. Data from Miller and Stoecker [13].

TABLE 12.5—Relative Adsorptivity of Typical Components

Nonadsorbed	**Light**	**Intermediate**	**Heavy**
H_2	O_2	CO	C_3H_6
He	N_2	CH_4	C_4H_{10}
	Ar	C_2H_6	C_5+
		CO_2	H_2S
		C_3H_8	NH_3
		C_2H_4	BTX
			H_2O

Data from Miller and Stoecker [13].

TABLE 12.6—Relative Permeability of Typical Components

High	Medium	Low
H_2	C_1	C_2+
H_2O	O_2	N_2
H_2S		
CO_2		

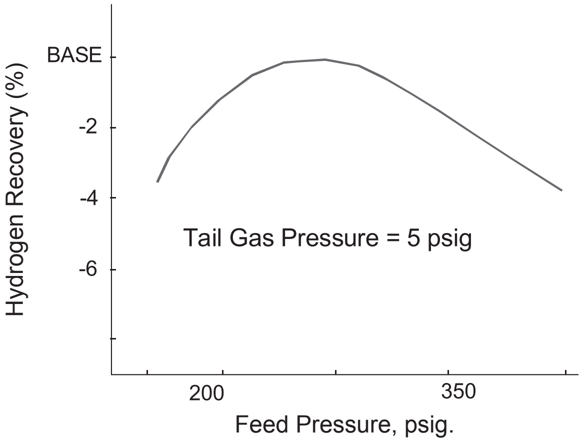


Figure 12.6—Effect of feed pressure levels on PSA system recovery. Data from Miller and Stoecker [13].

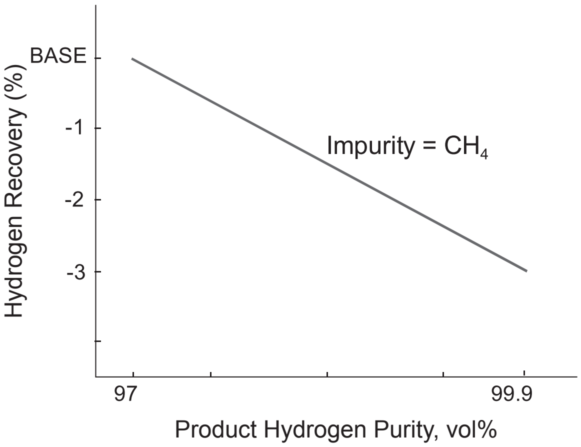


Figure 12.7—Effect of product purity on PSA system hydrogen recovery. Data from Miller and Stoecker [13].

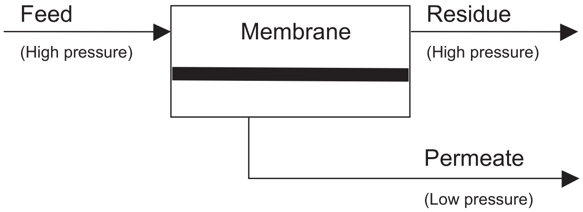


Figure 12.8—Single-stage membrane process.

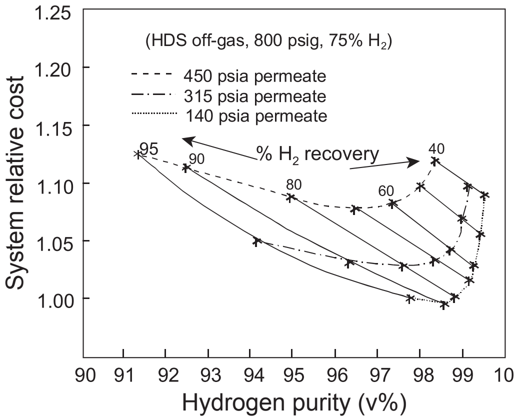


Figure 12.9—Hydrogen vs. purity for membrane system. Data from Spillman [14]

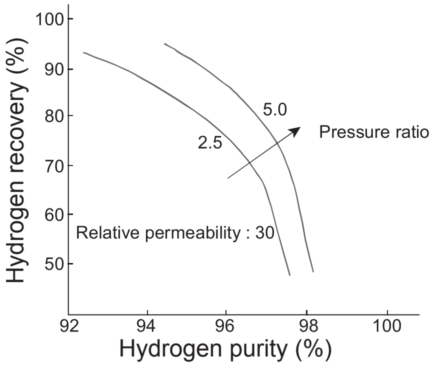


Figure 12.10—Hydrogen recovery vs. purity for membrane system. Data from Miller and Stoecker [13].

low gas volumes, ease of operation, low energy consumption, and good space efficiency. Compared with other gas separation processes, the many research efforts made for new membrane technologies have brought membrane gas separation into an increasingly important process for gas separation and production.

12.3.3 Cryogenic Separation

Cryogenic separation is a low temperature process that exploits the high relative volatility of hydrogen, compared with other gas components, to separate hydrogen. Figure 12.12 shows the flow diagram for a typical partial condensation process. The feed is cooled in exchanger X-1 to a temperature at which most C_2+ hydrocarbons condense. The two-phase stream is then separated in separator S-1. The hydrogen-CH_4 vapor from S-1 is sent to exchanger X-2, where it is cooled to a temperature low enough to provide the required hydrogen product purity. The cooled stream enters separator S-2 and the vapor from S-2 becomes the hydrogen product after it is warmed in X-1 and X-2. The hydrocarbon liquids from S-1 are throttled to a vaporization pressure when exchanged against the incoming feed stream in exchanger X-1. This stream can be withdrawn separately at its highest pressure as a byproduct or mixed with the CH_4 reject stream at a lower pressure. The CH_4-rich liquid from S-2 is throttled to a pressure at which it

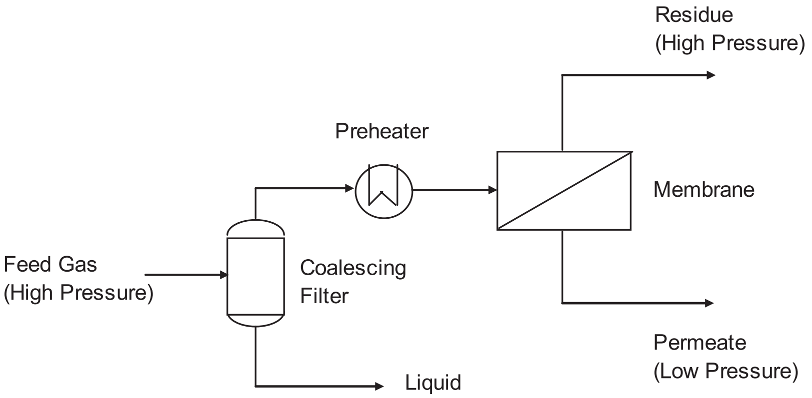


Figure 12.11—Membrane process with filtration for condensate protection.

will boil and provide the necessary temperature difference to the feed to S-2. The S-2 temperature sets the hydrogen product purity by controlling the amount of CH_4 remaining in the vapor phase. The separators S-3 and S-4 are used to provide the proper distribution of liquid and vapor into the multiple passes of the heat exchangers. As shown in the diagram, the refrigeration required by the process is obtained by Joule–Thomson expansion of the hydrocarbon. If the process itself cannot provide sufficient coolant, external refrigeration is required. Therefore, high hydrogen purity in feed can dramatically increase operation cost.

Thermodynamically, a cryogenic process has higher hydrogen recovery than other purification processes (92–97 %). The hydrogen purity in the product is controlled by equilibrium and has less impact on recovery than that in membrane separation. High product purity leads to large investment.

The advantage of using cryogenic separation is that the process can deal with low feed purity and give high hydrogen recovery. However, pretreatment is sometimes necessary to remove low boiling impurities such as N_2 and CO before cryogenic separation as well as the components such as CO_2, H_2O, H_2S, and C_5+ to an appropriate level to avoid freezing. The application is only economically attractive in large-scale units because of high capital cost. The hydrogen recovery cost can be largely reduced if the value of hydrocarbon byproducts is considered.

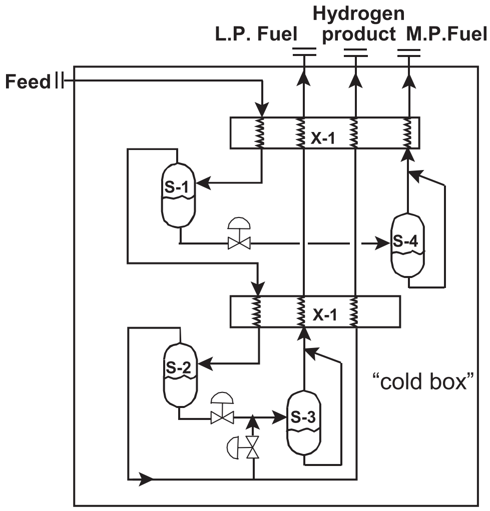


Figure 12.12—Partial condensation cryogenic process. Data from Miller and Stoecker [13].

12.3.4 *Hybrid Systems*

Because different hydrogen purification processes use different separation principles, the characteristics of one process are distinctive from others. Efficient integration of those processes can combine the merits and achieve competitive purification results. The process characteristics that can be taken into account in the hybrid system design are

- *PSA*: Produces high purity product and completely removes low boiling point impurities.
- *Membrane separation*: High hydrogen recovery with high residue pressure.
- *Cryogenic process*: High hydrogen recovery with easy recovery of hydrocarbon byproducts.

Ratan [15] proposed hybrid system designs by the integration of membrane-PSA, cryogenic-membrane, and PSA-cryogenic processes and their possible applications (Figures 12.13–12.15). Pacalowska et al. [16] analyzed the economics and flexibility of a combination of PSA-cryogenic processes by case studies and concluded that this combination has a lower hydrogen production cost after accounting for the byproduct value when compared with a PSA process alone and a hydrogen plant.

12.4 HYDROGEN TRANSPORTATION AND DISTRIBUTION

For the refining industry, pipelines have been used to transport and distribute hydrogen for more than 50 years, which is also the case for gas utility companies (e.g., Air Liquide, Air Products and Chemical, Inc., and Praxair) to supply hydrogen gas to their customers. The operating pressure for hydrogen transportation in pipelines is typically between 1 and 2 MPa, but pressure up to 10 MPa is also used in some cases. Hydrogen pipelines need to be made of nonporous materials such as stainless steel to avoid hydrogen leakage and brittle material. Therefore, the investment cost for hydrogen pipelines of a given diameter is approximately twice that of natural gas pipelines [17]. The energy required to move hydrogen through a pipeline is on average approximately 4.6 times higher per unit of energy than for natural gas. Therefore, compared with natural gas, hydrogen distribution facilities are more expensive to build and operate.

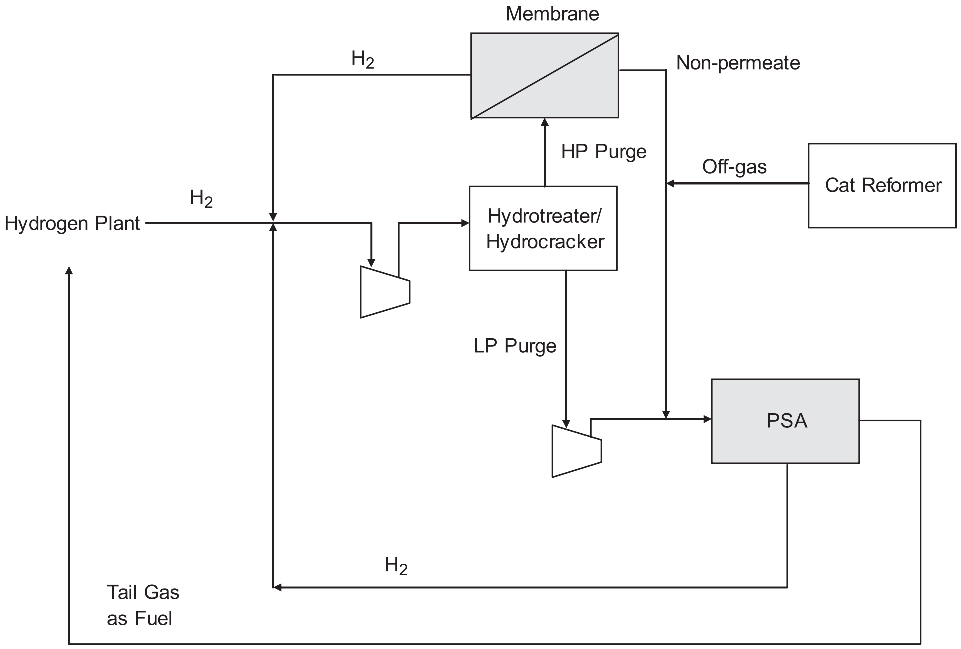


Figure 12.13—A hybrid system: Membrane and PSA system.

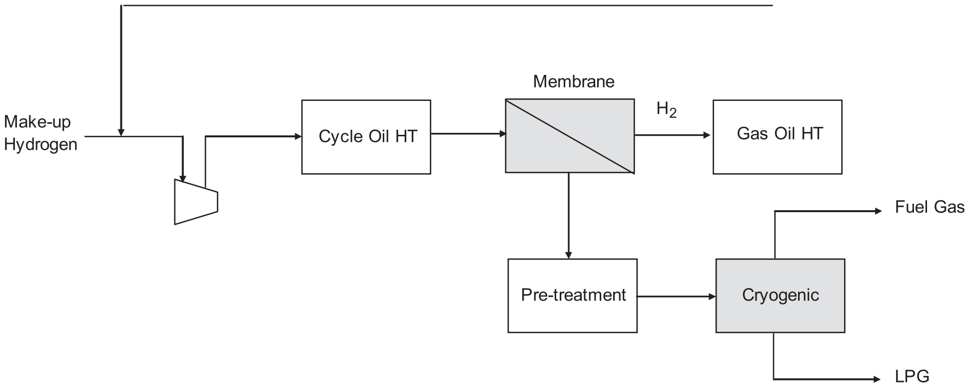


Figure 12.14—A hybrid system: Membrane and cryogenic separation.

In theory, hydrogen could also be transported and distributed in liquid form. However, the liquefaction of hydrogen is hugely expensive because approximately 42 % of the energy content of the liquid hydrogen would be needed to liquefy hydrogen at –253°C [18]. Therefore, oil refineries do not commercially practice liquefaction of hydrogen in their internal hydrogen distribution.

Because of its extremely low boiling point and low molecular weight, storage of hydrogen in whatever form (gaseous, liquid, or solid) is expensive. Therefore, refinery hydrogen systems are designed on the basis of supply on demand. However, for gas utility companies and the future hydrogen economy, hydrogen storage is an important subject. Various technologies for hydrogen storage are available, such as large-scale underground gas storage, on-board gaseous composite tanks or glass microspheres, on-board liquid storage (pure or with solutions), and on-board solid storage with carbon and other high surface area materials or various hydrides, etc. Interested readers can refer to reference 19 for more information on this subject.

12.5 NETWORK TARGETING—THE HYDROGEN PINCH CONCEPT

A refinery hydrogen network contains three main elements: (1) hydrogen producers such as steam and catalytic reformers, (2) hydrogen consumers such as various hydrotreators and hydrocrackers, and (3) hydrogen purification units such as PSA and membrane and cryogenic separation. They are then linked together through necessary piping and compression. An example of a refinery hydrogen network is shown in Figure 12.16. To systematically analyze such a network, Alves [20] proposed a pinch approach for targeting the minimum hydrogen utility. This work is based on pinch technology and exploits an analogy with heat exchanger network synthesis. The method identifies sources and sinks of hydrogen, which are analogous to hot and cold streams in heat exchanger networks.

12.5.1 Sink and Source Location

A typical hydrogen consumer including a hydrotreating reactor and a separator can be simplified as shown in Figure 12.17. Hydrogen is used to react with liquid hydrocar-

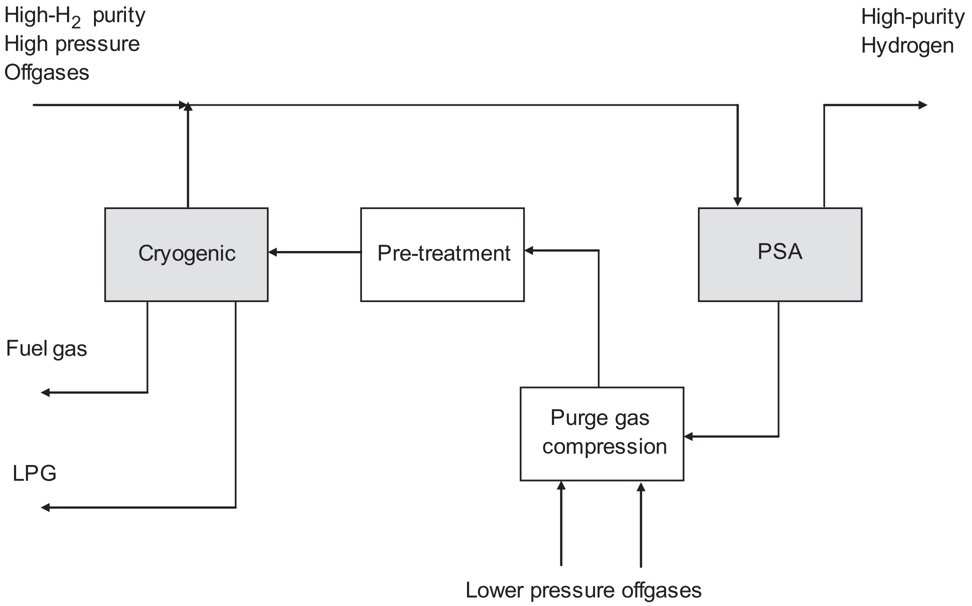


Figure 12.15—A hybrid system: Cryogenic and PSA processes.

bons. The partial pressure in the reactor is a very important parameter in the reaction. In this part of the work, the partial pressure of hydrogen is assumed to be constant, as well as other parameters such as operating temperature, reactor feedstock, products, etc. Under these assumptions, constant flow rate and hydrogen purity is imposed on the reactor gas inlet stream. Therefore, if the operating condition does not change, the inlet of the reactor and the outlet of the separator will be fixed. Thus, the mixture of the make-up hydrogen and the recycle is defined as the sink, and the mixture of the purge and the recycle is defined as the source (Figure 12.17).

12.5.2 Hydrogen Composite Curve and Hydrogen Surplus Curve

The mass balance of each sink and source in a hydrogen distribution network can be conveniently represented in a two-dimensional plot with the flow rate of total gas on the horizontal axis and the purity on the vertical axis. Plotting the hydrogen demand profile and the hydrogen supply profile gives the hydrogen composite curves (Figure 12.18). This purity profile contains the hydrogen sinks and sources ordered by decreasing purity. Separately the sink and the source curves start at zero flow rate and continue until the lowest purity is represented. Where the hydrogen supply curve is above the hydrogen demand curve, the area between the two profiles is marked as surplus (+), which means the sources provide more hydrogen than required by the sinks. If the hydrogen supply is below the hydrogen demand curve, the area between the two profiles is marked as deficit (–), which means sources do not provide enough hydrogen to the sinks [21].

The hydrogen composite curves can be divided into different regions with alternating surplus and deficit of hydrogen. Calculating these surpluses and deficits (area) of hydrogen and plotting them against the purity level constructs the hydrogen surplus diagram, as illustrated in Figure 12.19 [21].

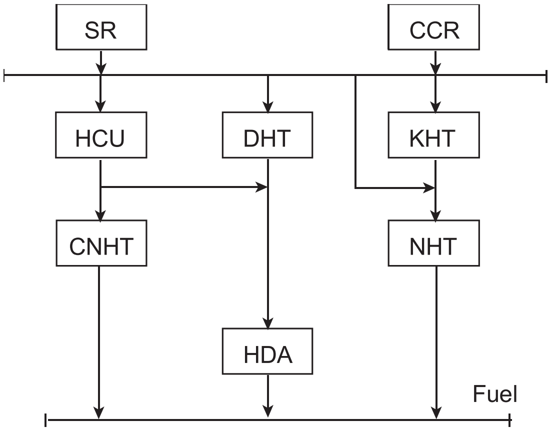


Figure 12.16—A refinery hydrogen network flow diagram.

One of the necessary conditions for a feasible network is that there is no negative hydrogen surplus anywhere in the hydrogen surplus diagram, because if this is the case, the sources cannot provide enough hydrogen to the sinks. For an existing network, parts of the surplus curve are always positive. The hydrogen utility can be reduced through moving the curve toward the vertical axis until a vertical segment between the purity of the sink and the source touches the zero axes (Figure 12.20). The purity at which this occurs is defined as the “hydrogen pinch” and is the theoretical bottleneck on how much hydrogen can be used from the sources to the sinks. The hydrogen utility flow rate that results in a pinch is the minimum target and is determined before any network design [21].

12.5.3 Purity Tradeoff and Purification Analysis

Hydrogen pinch analysis is useful not only to determine the target of minimum hydrogen consumption but also to carry out the analysis of purity tradeoff and placement of purification units [21]. One of the aspects is to reduce hydrogen utility flow rate by increasing the purity of one

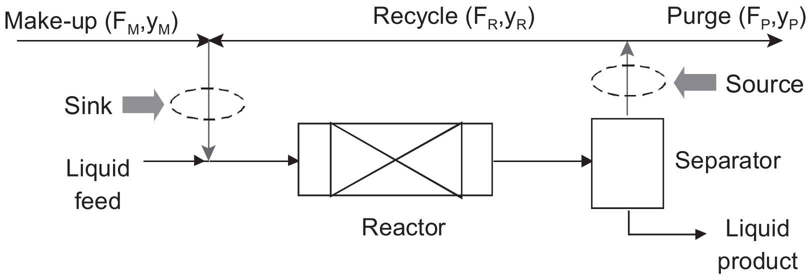


Figure 12.17—Simplified diagram of a hydrogen consumer showing source and sink locations.

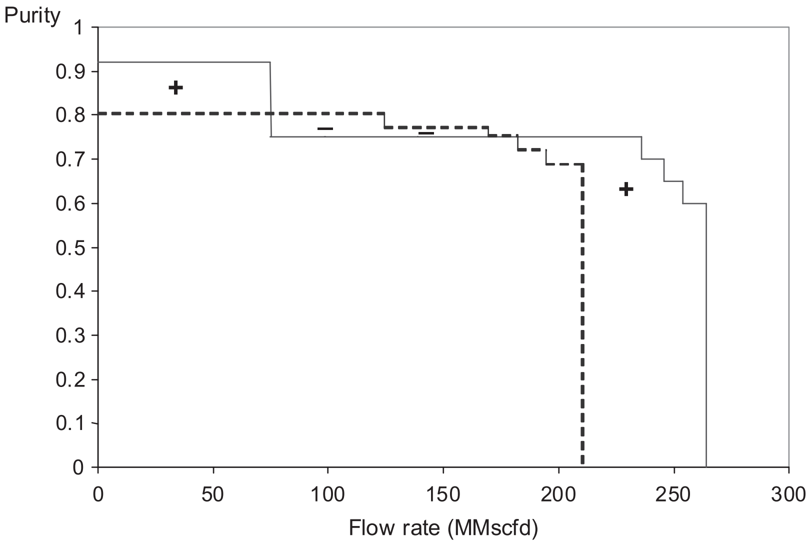


Figure 12.18—Hydrogen composite curve.

or more sources. It takes advantage of the fact that if two streams have the same flow rate of hydrogen, the one with higher purity will provide the hydrogen system with more hydrogen surplus. The resulting effect on the hydrogen surplus curve is shown in Figure 12.21. The initially pinched system (dotted line) becomes unconstrained (solid line) with an increase in the utility purity. The additional hydrogen surplus thus created can be used to reduce the hydrogen utility, resulting in a lower target. This gives an option for debottlenecking the hydrogen distribution system.

The purification of hydrogen sources can also be analyzed. The installation of a hydrogen purification unit adds one more sink and two sources to the hydrogen distribution system. The sink is the feedstock to purification. The sources are the purified product stream and the residue stream. The introduction of a new purification unit usually affects the entire hydrogen system even if the unit is captive to an individual consumer process. The savings generated by the purification unit are assessed in the steps of placing the purification unit inside of the network, applying the pinch method to find a new target. The multiple purification options can be evaluated one by one.

There are three possible placements for a purification unit in the hydrogen surplus curve: (1) above the pinch, (2) across the pinch, or (3) below the pinch. The general conclusions are then made to quantify different purification scenarios. It is found that purification across the pinch can reduce the requirement of the utility; at the same time, because the hydrogen loss happens below the pinch, the utility flow rate will not be affected. The consequences of different placements are shown in Figure 12.22 [21].

12.5.4 Summary of Hydrogen Pinch Analysis

Hydrogen pinch is a graphical approach to find the minimum hydrogen utility in distribution networks. It can provide insights to hydrogen distribution and is easy to develop. It is particularly useful to identify the scope of a potential improvement in an existing hydrogen network before spending a significant amount of time and capital for detailed engineering design. However, it also has some drawbacks.

One of the major limitations with the method is that the targets are set based only on the flow rate and purity requirements. The targeting method assumes that any streams containing hydrogen can be sent to any consumer, regardless of the stream pressure. In reality, a source can only feed a sink if it is in a sufficient pressure level. Significant investment in compression equipment might be required to achieve the target. Thus, the targets generated may be too optimistic in a real design.

In addition, the analysis of the placement of purification units is processed on the basis of arbitrary selection through hydrogen pinch analysis and can give a theoretical

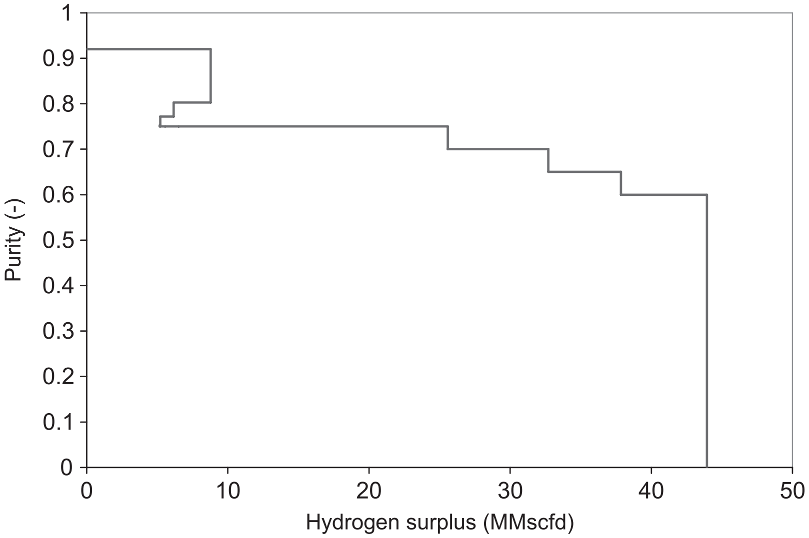


Figure 12.19—Hydrogen surplus diagram.

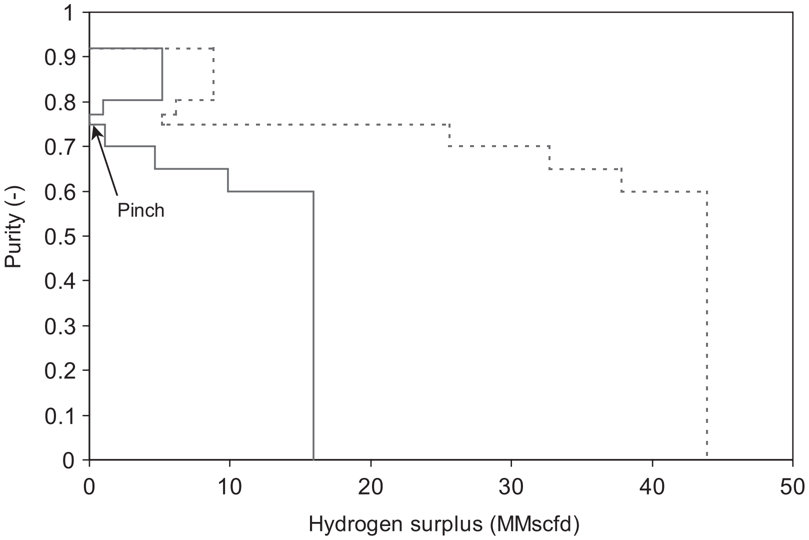


Figure 12.20—Targeting the minimum utility by varying the hydrogen utility flow rate until a pinch is formed.

target before design. However, because the purification is also an important design option subject to practical constraints, this target is not sufficient to be the guide for the overall optimal design or debottlenecking. Therefore, a more comprehensive and detailed approach is necessary for the hydrogen distribution network design, which can also deal with the objective function of the minimum total cost of the network instead of the minimum hydrogen utility.

12.5.5 Detailed Hydrogen Network Optimization and Design

There are four major issues for advanced hydrogen network management:

1. Systematically taking into account practical constraints, such as pressure matching, compression, piping, capital and operating cost, etc.
2. Trading off various purification options.
3. Properly integrating a hydrogen plant with a hydrogen network.
4. Accuracy and feasibility of hydrogen network design.

Methods have been developed to address all four issues above, mainly based on advanced mathematical programming algorithms.

12.5.6 Hydrogen Network Optimization with Pressure Consideration

Hallale and Liu [22] developed an automated design approach for hydrogen network management to account for practical constraints. The method is based on the optimization of a reducible superstructure (Figure 12.23). In this approach, the pressure constraints are included in the design. Multiple constraints can be incorporated to achieve optimal realistic designs. To find the realistic design solution, the objective function is to minimize the total cost instead of only minimizing the hydrogen utility. Capital and operating costs are taken into account by modelling existing and new compressors, purifiers, and piping changes. Hydrogen cost is weighed by the price of hydrogen utility

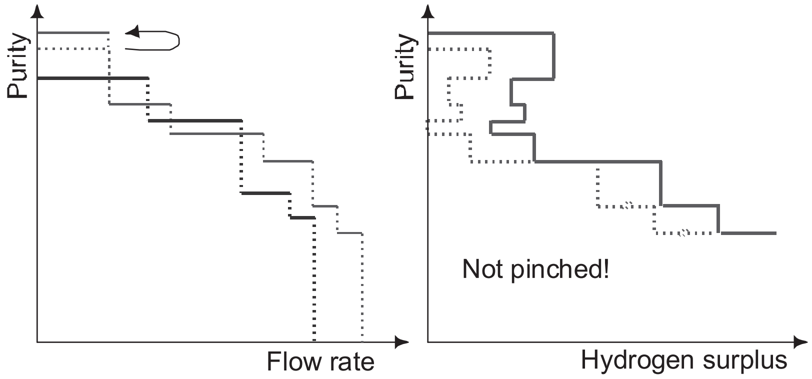


Figure 12.21—Effect of utility purity increment on a hydrogen surplus curve.

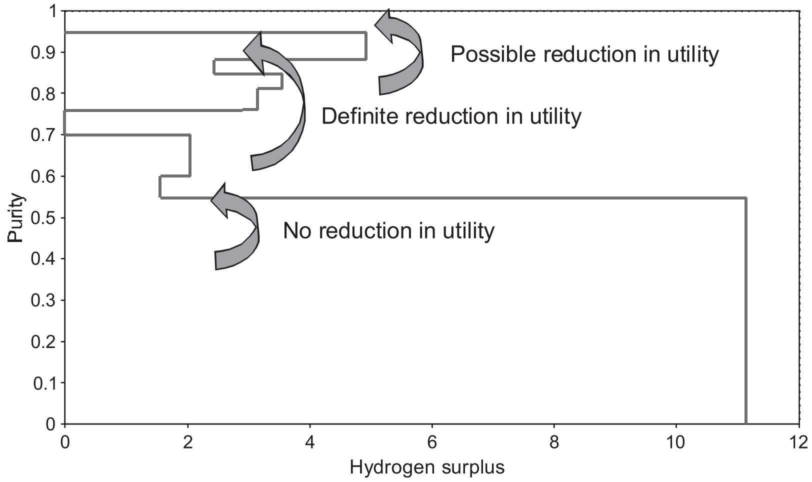


Figure 12.22—Evaluate purification scenario using a hydrogen surplus curve.

in the design. Retrofit options (e.g., additional purification, compression, and piping changes) are decided automatically through optimization.

12.5.7 Purifier Selection and Integration Strategy

Liu and Zhang [23] further extended the automated design approach to integrate hydrogen purification processes in hydrogen networks. A methodology was proposed to select the appropriate purifiers from PSA processes and membrane or hybrid systems for recovering hydrogen from refinery off-gases. Through the understanding of the tradeoffs among hydrogen savings, compression costs, and capital investment, a superstructure similar to the one in Figure 12.23 was built to include possible purification scenarios. The shortcut models for different purification units were developed. The recovery rate of purifiers was also modelled to optimize process parameters. This method achieved the optimal design for overall hydrogen networks at a conceptual level.

12.6 INTEGRATION OF HYDROGEN PLANT

A hydrogen plant not only supplies hydrogen to hydrogen consumers through a hydrogen network, but it also can take off-gas from hydroprocessors and purification units as a feed. Therefore, such interactions need to be properly exploited. Liu [24] developed a method to integrate hydrogen generation into hydrogen networks. The hydrogen plant is modelled by correlating process data from comprehensive process simulation. The hydrogen plant model covers a wide feed range from natural gas and refinery off-gas hydrocarbons to light naphtha. A superstructure (Figure 12.24) is then developed to account for the integration of hydrogen plants and purifier operations. The refinery off-gases are evaluated as the possible feed to hydrogen plants and purification units. The tail gas streams from purification units are considered as candidate feedstock to hydrogen plants or being sent to a fuel system after necessary compression.

12.6.1 Detailed Simulation to Ensure Accuracy and Feasibility

For the above hydrogen pinch analysis and mathematical programming methods, there is one major assumption: Refinery gases are treated as a binary mixture of hydrogen and CH_4 by combining all of the impurities of hydrogen-containing gas streams as CH_4. This assumption can lead to infeasibility in the network after optimization because the hydrogen management technology is not able to capture the change in some importance performance parameters (e.g.,

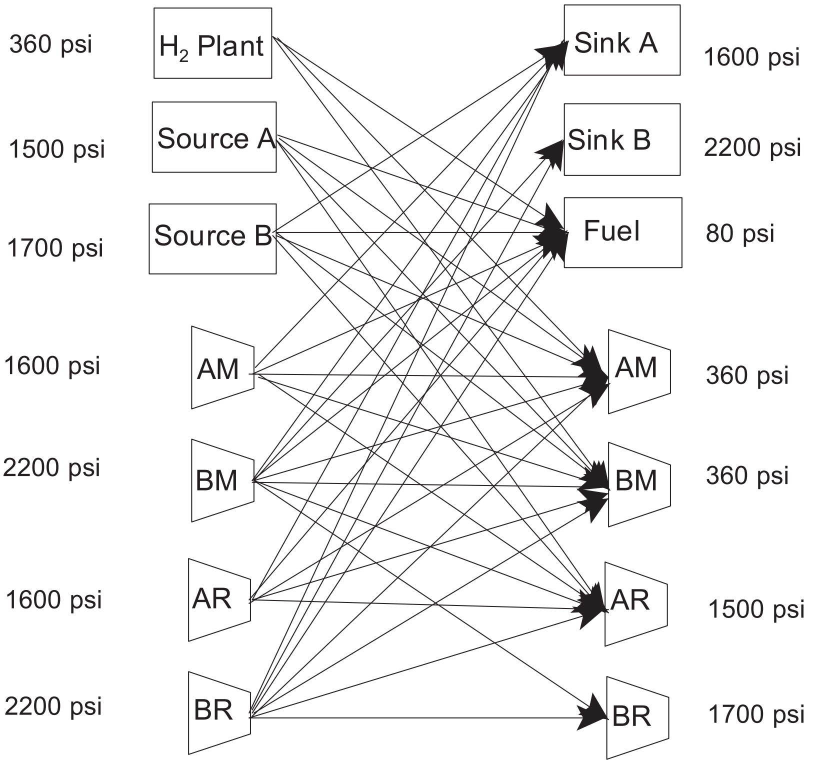


Figure 12.23—An example of reducible superstructure.

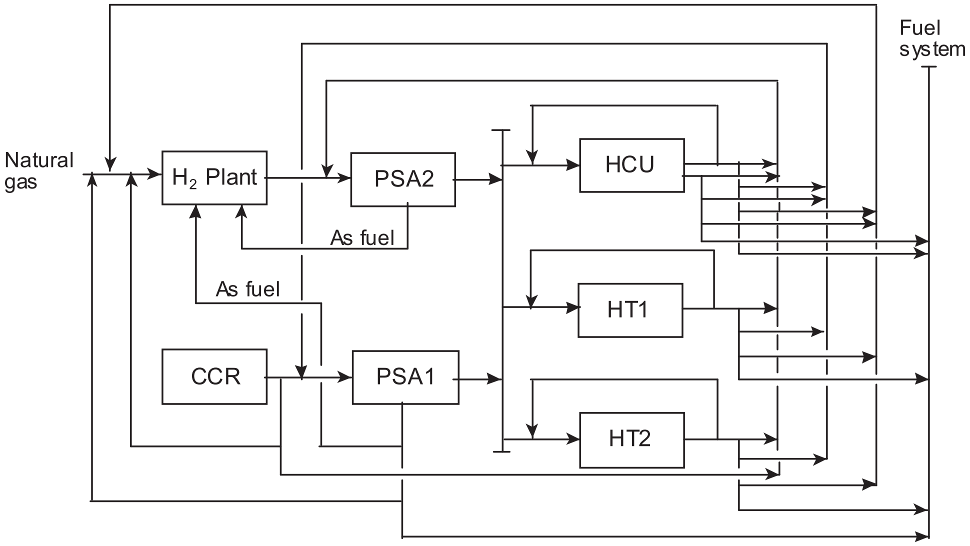


Figure 12.24—Superstructure—covering possible operating schemes.

hydrogen partial pressure, hydrogen-to-oil ratio, sulfur content, etc.) of hydrogen consumers because of changes in the impurity compositions of make-up streams. To obtain accurate solutions, there is a need for having a multicomponent methodology to represent hydrogen streams in hydrogen network management instead of lumping all impurities as CH_4 and treating hydrogen streams as a binary mixture of hydrogen and CH_4.

To take into account impurities, an integrated approach was developed by Zhang et al. [25]. A flash routine to calculate vapor-liquid equilibrium is required, together with the composition information of the vapor and liquid streams. Therefore, a new and more detailed consumer model can be built as shown in Figure 12.25. The simulation of individual units is still based on the assumption that there is no change in reaction by minimizing the change of the hydrogen-to-oil ratio and hydrogen partial pressure caused by the change in impurity composition. A whole hydrogen network can then be set up in a simulator for feasibility check using the extended hydrogen consumer model.

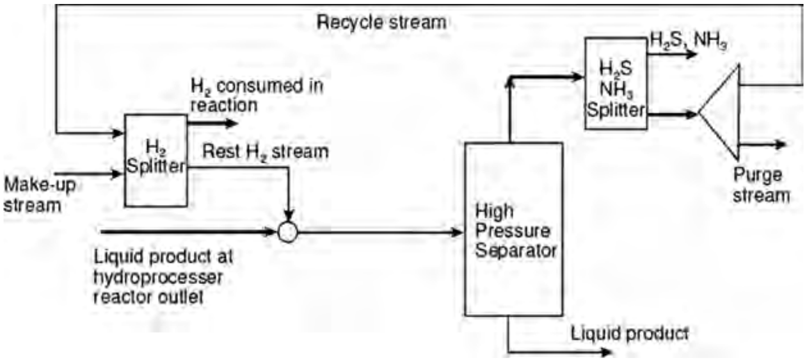


Figure 12.25—Extended hydrogen consumer model for impurity consideration.

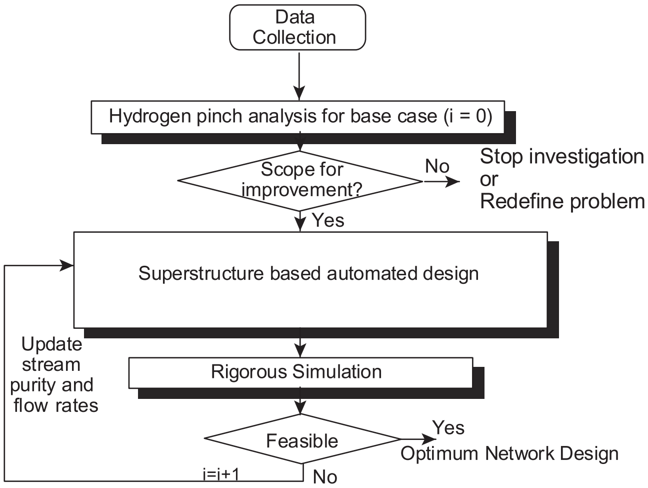


Figure 12.26—Overall methodology for refinery hydrogen management.

12.6.2 The Overall Methodology for Refinery Hydrogen Management

The advanced hydrogen management [25] follows the principles of the overall framework shown in Figure 12.26. Although the detailed simulation can also be supported with commercial simulation packages, the hydrogen pinch analysis is based on the graphical approach, and the automated design is performed using advanced mathematical programming methods (nonlinear programming and mixed integer linear programming).

12.7 CONCLUSIONS

Hydrogen supply has become one of the focal points in many refinery operations because of recent developments in environmental and fuel legislation. Therefore, it is important to raise the awareness of advanced techniques for hydrogen network management. The technology developed for refinery hydrogen management has been successfully applied in the refining industry. It not only helps in reducing hydrogen consumption, but it also keeps capital costs low in debottlenecking projects by identifying the most cost-effective revamping options through simple hydrogen pinch analysis for targeting and comprehensive mathematical programming methods for detailed solutions.

Although these approaches have been proven successful by many industrial projects, it needs to be pointed out that there is no general answer for hydrogen problems for all refiners. Each refinery has its particular process availability and constraints and maintains its own operating scheme. In today's business climate, the favorite solution is to increase saving and maximize effectiveness of investment. However, the intelligent applications developed from the approach discussed here can aid refiners in finding their optimal tailored solutions.

REFERENCES

[1] Haun, E.C., Anderson, R.F., Kauff, D.A., Miller, G.Q., and Stoecker, J., "The Efficient Refinery Hydrogen Management in the 1990's," presented at the Spring 1990 Technology Conferences, Des Plaines, IL, 1990.

[2] Aitani, A.M., and Ali, S.A., "Hydrogen Management in Modern Refineries," *Erdöl und Kohle,* Vol. 48, 1995, pp. 19–24.

[3] Rana, M.S., Sámano, V., Ancheyta, J., and Diaz, J.A.I., "A Review of Recent Advances on Process Technologies for Upgrading of Heavy Oils and Residua," *Fuel*, Vol. 86, 2007, pp. 1216–1231.

[4] McGrath, M.J., and Houde, E.J., "Upgrading Options for Processing Heavy Crudes," presented at the American Institute of Chemical Engineers Spring 1999 Meeting, March 14–18, 1999.

[5] Lamber, G.J., Schoeber, W.J.A.H., and van Helden, H.J.A., "The Hydrogen Balance in Refineries," presented at the Foster Wheeler Heavy Oil Processing and Hydrogen Conference, Noordwijk, The Netherlands, April 1994.

[6] Phillips, G., "Hydrogen—Innovative Business Solutions for 2005 and Beyond," presented at the European Refining Technology Conference—Process, Paris, France, November 1999.

[7] Gardner, A., "Refining Details—Hydrogen Production What's Available," *Today's Refinery*, February/March, 1998, pp. 27–31.

[8] Hiller, M.H., Lascatena, J.J., and Miller, G., "Hydrogen for Hydroprocessing Operation," presented at the 1987 National Petrochemical and Refiners Association Annual Meeting, San Antonio, TX, March 1987.

[9] Vervalin, C.H., Ed., "Gas Processing Handbook," *Hydrocarbon Process.*, Vol. 73, 1994, pp. 82–106.

[10] Boggs, B.K., King, R.L., and Botte, G.G., "Urea Electrolysis: Direct Hydrogen Production from Urine," *Chem. Commun.*, Vol. 32, 2009, pp. 4859–4861.

[11] Tao, Y., Chen, Y., Wu, Y., and Zhihua, Z., "High Hydrogen Yield from a Two Step Process of Dark- and Photo-Fermentation of Sucrose," *Int. J. Hydrogen Energy*, Vol. 32, 2007, pp. 200–206.

[12] Strik, D.P.B.T.B., Hamelers, H.V.M., Snel, J.F.H., and Buisman, C.J.N., "Green Electricity Production with Living Plants and Bacteria in a Fuel Cell," *Int. J. Energy Res.*, Vol. 32, 2008, pp. 870–876.

[13] Miller, G., and Stoecker, J., "Selection of a Hydrogen Separation Process," presented at the 1989 National Petrochemical and Refiners Association Annual Meeting, San Francisco, CA, March 1989.

[14] Spillman, R.W., "Economics of Gas Separation Membranes," *Chem. Eng. Prog.*, Vol. 85, 1989, pp. 41–62.

[15] Ratan, S., "Hydrogen Management System," *KTI Newsletter*, Fall, 1994, pp. 24–32.

[16] Pacalowska, B., Whysall, M., and Narasimhan, M.V., "Improve Hydrogen Recovery from Refinery Off-Gases," *Hydrocarbon Process.*, Vol. 75, 1996, pp. 55–59.

[17] Mintz, M., Folga, S., Molburg, J., and Gillette, J., "Cost of Some Hydrogen Fuel Infrastructure Options," Argonne National Laboratory, Transportation Technology R&D Center, January 2002.

[18] Gielen, D., and Simbolotti, G., "Prospects for Hydrogen and Fuel Cells," presented to the Transportation Research Board, Washington, DC, January 2006.

[19] Riis, T., Sandrock, G., Ulleberg, Ø., and Vie, P.J.S., "Hydrogen Storage—Gaps and Priorities," IEA Hydrogen Implementing Agreement, Paris, 2005.

[20] Alves, J., "Analysis and Design of Refinery Hydrogen Distribution Systems," Ph.D. thesis, Department of Process Integration, University of Manchester Institute of Science and Technology, 1999.

[21] Alves, J., and Towler, G.P., "Analysis of Refinery Hydrogen Distribution Systems," *Ind. Eng. Chem. Res.*, Vol. 41, 2002, pp. 5759–5769.

[22] Hallale, N., and Liu, F., "Refinery Hydrogen Management for Clean Fuels Production," *Adv. Environ. Res.*, Vol. 6, 2001, pp. 81–98.

[23] Liu, F., and Zhang, N., "Strategy of Purifier Selection and Integration in Hydrogen Networks," *Chem. Eng. Res. Des.*, Vol. 82, 2004, pp. 1–16.

[24] Liu, F., "Hydrogen Integration in Oil Refineries," Ph.D. thesis, Department of Process Integration, University of Manchester Institute of Science and Technology, 2002.

[25] Zhang, N., Singh, B.B. and Liu, F., "A Systematic Approach for Refinery Hydrogen Network Management," presented at PRES2008, Prague, Czech Republic, August 2008.

13

Design Aspects of Separation Units and Processing Equipment

M.C. Rodwell[1] and M.R. Riazi[2]

NOMENCLATURE

Symbols

A	Absorption factor defined in Eq 13.42, dimensionless
A	Surface area for heat transfer
A_c	Column cross sectional area, m^2
A_X	Cross sectional area
B	Rate of bottom product, mol/h
C_p	Specific heat capacity at constant pressure
C_v	Specific heat capacity at constant volume
D	Rate of distillate product, mol/h
D	Diameter of a separator
d_c	Column diameter
d_p	Packing particle diameter
E_M	Murphree efficiency in a distillation column defined in Eq 13.26, dimensionless
E_o	Overall column efficiency defined in Eq 13.15, dimensionless
E_i	Recovery factor for component i in a gas absorption column defined in Eq 13.43, dimensionless
F	Amount of feed, moles (rate in mol/h)
F	LMTD correction factor
F_T	Probability density function (PDF) for boiling point T (in Eqs 13.5 through 13.7)
g	Gravitational acceleration (9.80655 m/s^2)
GOR	Gas-to-oil ratio (scf/bbl)
H	Enthalpy (J/kg)
h	Column height used in Eqs 13.30 and 13.36
h	Local heat transfer coefficient ($W/m^2 \cdot K$) used in Eqs 13.70 and 13.72
h	Head of fluid used in Eqs 13.135 and 13.136
K	Souders-Brown factor, used in Eq 13.95
K_i	Equilibrium ratio in vapor-liquid equilibria ($K_i = y_i/x_i$), dimensionless
k	Thermal conductivity
L	Amount of liquid or reflux (for distillation column), moles (or rate in mol/h)
L	Length of a separator vessel, tangent to tangent
m	Mass fraction of a component
M_L	Molecular weight of liquid mixture
MW	Molecular weight
N	Number of actual or theoretical plates or equilibrium stages in a column
N	Number of moles
N	Speed, rpm
N_{SS}	Suction-specific speed
n	Polytropic exponent
Nu	Nusselt number, dimensionless
P	Pressure or partial pressure
Pr	Prandtl number
R	Reflux ratio (= L/D for distillation column), dimensionless
R	Hot fluid to cold fluid temperature change ratio, Eq 13.55
r	Radius
r	Pressure ratio
R_D	Fouling resistance for heat transfer
R_o	Universal gas constant (8.3144 kJ/kmol·K, 1.9859 Btu/lbmole·°R)
Ra	Rayleigh number
Re	Reynolds number
q	Heating rate for reboiler or condenser in a distillation column
Q	Heat transfer rate (MW, Btu/h)
Q	Volumetric flow (m^3/h, usgpm, acfm)
S	Stripping factor, dimensionless
SG	Specific gravity
T	Temperature
T_H	Time, hold-up volume
T_S	Time, surge volume
t	Temperature, air
u	Velocity
U	Overall heat transfer coefficient
V	Amount of vapor (or gas), moles (rate in mol/h)
V	Volume
T_F	Feed temperature, K
ΔT_{LMTD}	Log mean temperature difference, defined in Eq 13.51
W	Power (work)
x	Mole fraction of light component in liquid phase, dimensionless
y	Mole fraction of light component in vapor phase, dimensionless
Z	Compressibility factor

Greek Letters

α_{AB}	Relative volatility of component A to B, dimensionless
α_{AB}	Relative volatility of light key to heavy key in multicomponent distillation
Δ	Difference between two values of a parameter
θ	A dimensionless parameter defined in Eq 13.21
Θ	Time, settling or rising
γ	Ratio of specific heats, C_p/C_v
ε	Void fraction, used in Eq 13.111

---

[1] Fluor Canada, Ltd., Calgary, Alberta, Canada

[2] Kuwait University, Kuwait

η	Efficiency
ψ	A dimensionless parameter defined in Eq 13.22
μ	Dynamic viscosity
ν	Kinematic viscosity
π	Ratio of the circumference of a circle to its diameter
ρ	Density

Superscript

L	Value of a quantity for a liquid phase

Subscripts

A, B	Value of a quantity for component A in a binary mixture of A and B (A being the light component)
a	Air
avg	Average value of a quantity
B	Value of a quantity for the bottom product of a distillation column
$boot$	Boot of a horizontal separator
bp	Bubble point for a mixture (equivalent to boiling point)
C	Condenser for a distillation column
C	Continuous phase
$CMTD$	Corrected mean temperature difference
D	Value of a quantity for the distillate (overhead) product of a distillation column
DP	Dewpoint
E	Enriching section of a distillation column
eff	Effective
F	Value of a quantity for the feed
f	Fluid (in Eq 13.70)
f	Frictional (in Eq 13.128)
G	Greater, as in Eq 13.52
HK	Heavy key component in multicomponent distillation
LK	Light key component in multicomponent distillation
$LMTD$	Log mean temperature difference
L or l	Liquid phase
i	Inside of tube
i	Value of a quantity for component "i" in a mixture
min	Minimum
max	Maximum
mix	Mixture
m	Atomizing medium
O	Outside of tube
o	Initial value before a process begins
min	Minimum
P	Particle in dispersed phase
R	Reboiler for a distillation column
r	Radiant section
s	Superficial or per stage or stack
sat	Saturation condition
src	Source
T	Terminal
th	Theoretical value
V	Vapor phase
vap	Vapor, as in vapor pressure
w	Wall condition
20	Values of property at 20°C

Acronyms

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
GPSA	Gas Processors and Suppliers Association
HETP	Height equivalent to a theoretical plate
HLL	High liquid level
HILL	High interface liquid level
HVGO	Heavy vacuum gas oil
LHV	Lower (net) heating value
LHSV	Liquid hourly space velocity
LLL	Low liquid level
MOP	Maximum operating pressure
NLL	Normal liquid level
NPSH	Net positive suction head
SG	Specific gravity
SI	System International of Units
TEMA	Tubular Exchanger Manufacturers Association

13.1 INTRODUCTION

Petroleum refining and natural gas processing are complex industries composed of hundreds of various equipments and units. The major units involved in these industries may be categorized as separation, conversion, finishing, and support units. This chapter focuses on the design aspects of separation units, including desalting, distillation, absorption, extraction, and heat-transfer equipment such as fired heaters, heat exchangers or coolers, and pumps and compressors. In addition, design aspects of two- and three-phase separation units are also discussed in this chapter. Some design and operational aspects of conversion processes, natural gas processing, and control units are presented in chapters that cover these topics (see Chapters 5–12, 14–22, and 25–31). However, the units discussed in this chapter are used in various plants throughout refinery and natural gas processing industries.

13.2 CRUDE OIL DESALTING UNITS

Crude oil delivered to a refinery often contains small amounts of produced water, usually less than 1 vol %. Produced, or connate, water usually contains some quantity of dissolved ionic salts. Chlorides of sodium, magnesium, and calcium are the most common salts present in crude oils; other salts may be present depending on the geology of the reservoir from which the petroleum was sourced.

Removal of the salts from the crude oil is important because these salts can cause corrosion and fouling of units throughout the refinery. Hydrolysis of $MgCl_2$ and $CaCl_2$ in the presence of steam in the crude and vacuum distillation units will produce hydrogen chloride gas, which is a strong acid in the aqueous phase. Such strong acid condensation in the overhead systems of distillation columns can result in very severe corrosion. Sodium chloride tends not to hydrolyze and ends up in the bottoms products of the distillation process. High levels of sodium and calcium salts in the heavy products can promote fouling of furnace tubes in vacuum units, visbreakers, and delayed coking units. For these reasons, removal of these species from the feed oil is desired.

The inlet crude oil is mixed with clean wash water, which is usually steam condensate or the overhead water from the atmospheric and vacuum distillation units or perhaps phenolic sour water sourced from cokers or fluid catalytic cracking (FCC) units. The oil and water are mixed thoroughly via a static mixer and a special mix valve, which is usually specified by the desalter supplier. The mix valve usually will have a pressure drop of 70–200 kPa to ensure sufficient shear to mix the clean water with the connate water, diluting the salt in the water phase. The selection and tuning of this pressure drop is very important to the performance of the desalter. Too little shear will result in ineffective salt removal whereas too much will result in overly stable emulsions and rag formation.

The mixture is injected into the center of the vessel between two horizontal electrically charged grids. The electrical potential between the grids is usually in excess of 1000 V and is highly dependent on the electrical conductivity of the crude oil. The electric potential is an alternating current, and modern designs often use high frequencies (i.e., many multiples of the normal 50/60-Hz power supply). The purpose of the alternating electric potential is to vibrate the water droplets in the oil, causing them to contact each other and coalesce into droplets large enough to settle out of the hydrocarbon phase by gravity.

A schematic of an electrostatic desalter is shown in Figure 13.1, and a simplified flow diagram of a two-stage electrostatic desalter is shown in Figure 13.2.

Salt content in crude oils is usually quoted in units or pounds per thousand barrels (ptb) or parts per million by weight (ppmw). The conversion between the two can be calculated via

$$ppmw = \frac{2.853 \cdot ptb}{SG_{oil}} \tag{13.1}$$

for crude oils with small water contents. For larger water cuts, such as in production facilities, this needs to be adjusted to account for the volume and density of the connate water.

Predicting the performance of a one- or two-stage desalter can be modeled using a simple mass balance that depends on an empirical factor called the contact efficiency. The contact efficiency can be determined from pilot studies or evaluation of an operating unit. The authors' experience shows that contact efficiencies range from approximately 80 % for light crudes (>40° API) to as low as 25 % for very heavy, viscous crudes (<20° API). Because of this, wash

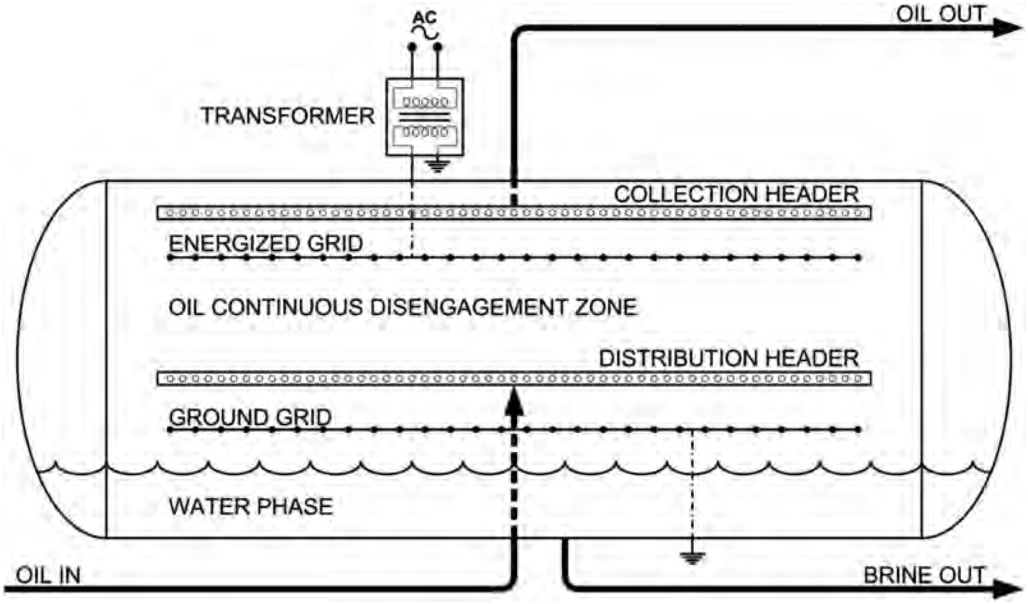


Figure 13.1—Electrostatic desalter schematic.

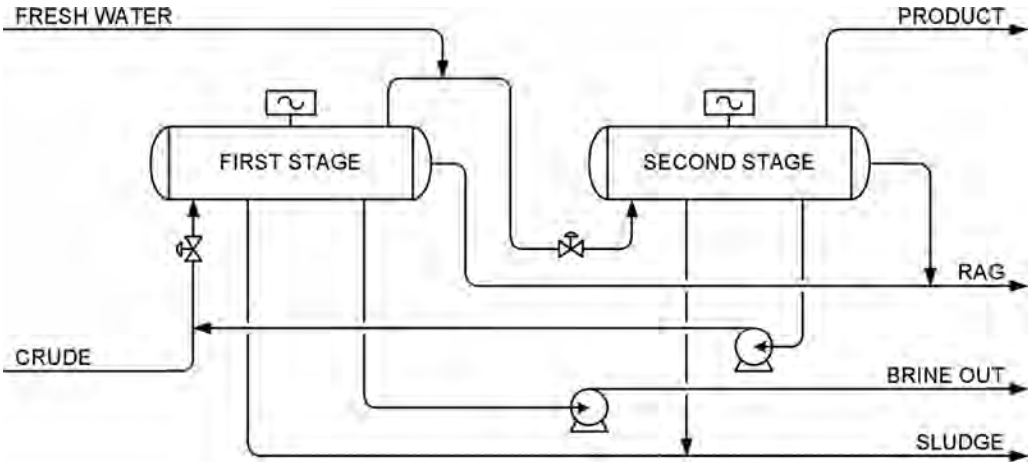


Figure 13.2—Desalting process flow diagram.

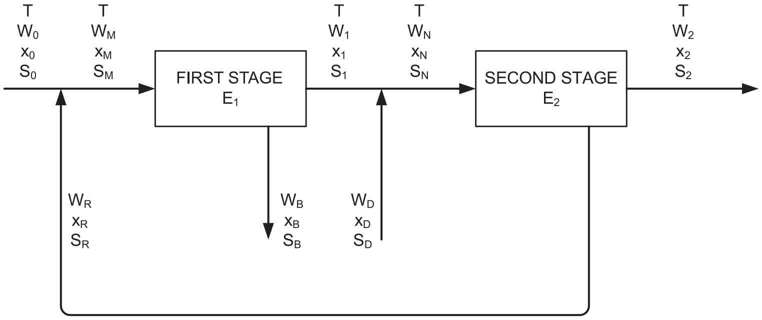


Figure 13.3—Two-stage desalter material balance.

water rates for light crudes can be as low as 3–5 % while achieving reasonable salt removal whereas heavy crudes may need up to 12 % wash water volume.

For a two-stage desalter, the performance can be estimated using the following equations. The equations are based on the mass balance diagram in Figure 13.3.

In the above figure, T is the volumetric flow of clean oil, W_x signifies the volumetric flow of water per 1000 bbl of crude, x_x is the water content (vol %) of the oil, and S_x is the salt content per volume of water (lb/bbl). The term W_xS_x therefore indicates the salt content of the oil in pounds per thousand barrels.

The water content of each stream in volume percent is related to the volumetric flow per thousand barrels by

$$W_x = \frac{1000 \cdot x_x}{(1 - x_x)} \tag{13.2}$$

First, we calculate the water recycle rate based on the expected dehydration performance of each stage:

$$W_R = W_B + W_D - W_C \tag{13.3}$$

Next, we calculate the water rates after the mixers:

$$\begin{aligned} W_M &= W_0 + E_1 W_R \\ W_N &= W_2 + E_2 W_D \end{aligned} \tag{13.4}$$

Next, we calculate the salt content of the recycle stream:

$$W_R S_R = \frac{W_1 W_0 S_0 (W_N - W_2) + W_M W_D S_D (W_N - E_2 W_2)}{W_M W_N + W_1 E_1 (W_2 - W_N)} \tag{13.5}$$

The salt content out of the first stage is determined via

$$S_1 = \frac{W_0 S_0 + E_1 W_R S_R}{W_M} \tag{13.6}$$

Finally, the salt content from the second stage can be found:

$$S_2 = \frac{W_1 S_1 + W_D S_D - W_R S_R}{W_2} \tag{13.7}$$

The derivation of these equations can be found in reference [1], as can further discussion of desalter mass balances and operation. One can rearrange the equations to solve for wash water rates (W_D), or one can use this method and iterate until the desired result is achieved.

The question of whether a single-stage or two-stage desalter arrangement is required depends on several factors, including the salt content, water content, and oil properties. A general rule of thumb is that reduction of the salt content to a level of 10 ptb (pounds per thousand barrels) can usually be achieved in a single stage. Reducing the level to a value closer to 1 ptb will require a second stage [2].

13.2.1 Fluid Properties

The density and viscosity of the inlet crude oil blend are the primary considerations of a desalter because these govern the separation of the oil and water phases in the vessel itself. To improve the difference between the oil and water phases, it is desirable to operate the desalter at as high of a temperature as possible. However, there are constraints that must be considered.

- The operating pressure must be greater than the vapor pressure of the crude oil feed at the desalter temperature because the desalter cannot operate with a vapor phase. Some suppliers do offer units that can handle small levels of vapor generation, but this is not recommended for most services.
- The seals around the electrical connections into the vessel are generally limited to a maximum operating temperature not greater than 149°C (300°F).
- Some high-fidelity-level instruments are limited to operating temperatures not greater than 130°C (266°F). It may be possible to mitigate this issue with cooling jackets to isolate the detector from the high-temperature process fluid.

Some very heavy crude oils (>940 kg/m^3; <19° API) may need to be diluted with a light cutter stock such as naphtha or kerosene to improve the density and viscosity to improve the oil/water separation. Because the hydrocarbon phase is the more viscous, the separation of water droplets from the oil will govern the size of the desalter vessel. The selection of the cutter stock should be made carefully to ensure that no asphaltenes are precipitated.

To determine if a crude blend will be challenging to separate, a drag calculation can be performed. This requires iteration of the vessel sizing and drag calculations (q.v., Section 13.7) to determine what size particles can be separated with respect to relative superficial velocities of the hydrocarbon and aqueous phases. If the water droplet size required to overcome the drag forces is larger than 500 μm, then separation will be challenging without very long residence times. There are usually two reasons this could be occurring. If the density of the oil and water are too similar, then there is not sufficient driving force for the separation. The other possibility is that the viscosity of the oil phase is too high, which restricts the movement of the water droplets. Either requires a change in operating temperature, dilution with cutter stock, or a different crude blend to improve the separation.

13.2.2 Emulsion Stability

Emulsion stability is usually affected by the presence of small solid particles in the oil or the presence of polar species in the petroleum, both of which will accumulate at the oil/water interface of droplets. These can prevent the water or oil droplets from coalescing, thus inhibiting the separation process.

Solid particles commonly found in crude oils can be asphaltenes, which may precipitate because of incompatibilities between crudes in the blend, and mineral solids such as fine clays. Crudes should be rigorously tested for compatibility to prevent asphaltene precipitation in the preheat train, which can foul exchangers and inhibit desalter performance.

Polar molecules can be any heteroatom containing molecules present in the oil, with oxygenates being the most surface active. Crudes with high naphthenic acid contents or containing lighter aliphatic acids may act as surfactants. Crudes with high calcium naphthenate content (e.g., Doba) are known to be particularly difficult to desalt because of emulsion stability issues in the desalter and brine treatment processes.

Chemicals are often added to the desalter fluids to assist in emulsion breaking and optimizing shear in the mixing valve, which is critical in reducing emulsion formation. Recent investigations in some high naphthenic acid heavy oils indicate that reduction in pH of the washing water can promote oil/water separation [2].

13.2.3 Hydrocarbon Conductivity

Some crude oil blends may have high conductivities, particularly those with high oxygen contents in the form of naphthenic and aliphatic acids. In some cases, two crudes that individually have low conductivity may have increased conductivity when they are blended; some have theorized that this is due to the lighter crude improving the "mobility" of polar species in the heavier crude, although this has not been substantiated in the literature.

High conductivity results in electrical current flowing through the hydrocarbon phase between the electrodes in the desalter. To maintain a high potential between the grids, a large current can flow, resulting in very high power requirements compared with a desalter operating in a low-conductivity crude. High conductivity can also result in "arcing" or "shorting" of the grids, resulting in a trip of the electrical supply, essentially shutting down the desalter.

13.2.4 Solids Content and Mud Wash

If the crude charge to the refinery is expected to have a high BS&W, particularly with an identified risk for high solids content, the desalter should be provided with mud wash connections and a mud wash pump. The desalter circulation pumps can be diverted for this purpose, but the ideal configuration has a dedicated mud wash pump.

The mud wash pump takes water from the last-stage desalter vessel or a clean water source and pumps it into the bottom of the vessel through a series of directional nozzles. This should be done in sequence from one end of the vessel to the other, washing the accumulated solids from the bottom of the vessel. The fluid velocity from the nozzles should be sufficient to entrain 1-mm sand particles. Water should simultaneously be withdrawn from the vessel, removing the entrained solids. This water stream should be quenched or cooled before routing to a tank or pond or centrifuged for solids removal.

13.2.5 Rag Formation

In many desalters, a layer of stable oil/water emulsion will accumulate over time between the oil and water phases. This rag layer can result intermittently from loss of chemical additives or changes in crude charge, or it can be due to continuous buildup as a result of fundamental properties of the crude oil. The rag layer is either a water continuous layer containing oil droplets or vice versa. Additionally, the droplets contained in the primary continuous phase may in turn contain an emulsion of the other phase. This makes the rag layer particularly difficult to treat chemically.

Because of the high water content of the rag layer, it has a very high electrical conductivity—essentially that of the desalter brine. If the rag layer builds up such that it contacts the electrical grids, it will short-circuit the system, resulting in a trip. Therefore, it is necessary to withdraw the rag layer from the desalter for treatment.

The rag layer draw is done simply through the use of nozzles between the grids. The rag should be drawn slowly, limiting the change at an interface level to less than 5 cm/min to prevent shorting of the grids. The rag can then be quenched or cooled before routing to a tank for treatment.

Determination of the rag layer thickness in the desalter is a challenging issue. It usually cannot be seen in a visual level gage glass, and the minimal density difference between the rag and water phase makes interface floats unreliable. This was traditionally performed by taking samples from various elevations of the vessel to determine the location of the interfaces. Modern capacitance probes can provide some guidance, but again the difference between the rag layer and brine can be difficult to see. Additionally, heavy, high-viscosity crudes can coat the probes, limiting their usefulness. Newer gamma-ray devices can provide very detailed information about rag distribution in the vessel.

13.2.6 Rag Processing

The rag layer drawn from a desalter can be difficult to process to recover clean oil and clean water. Chemical treatment and settling time in tanks can be effective in some circumstances. Flotation cells have shown some effectiveness for rag treatment, although for very heavy crudes this is unlikely to be effective because of the limited density difference of oil and water. Centrifuges can be very effective for separation of the rag layer, although high mineral content could result in high maintenance costs. Pilot testing of rag separation technologies is recommended.

13.3 DESIGN OF DISTILLATION COLUMNS

The distillation column was introduced in Section 5.5 of Chapter 5. In this section, we present design calculations for tray and packed columns for binary and multicomponent systems. Because distillation is based on the relative volatility of compounds and principles of vapor-liquid equilibrium (VLE) in the mixture, we begin this section with the generation of VLE data. Then we discuss fundamental design calculations for batch, flash, and continuous column distillation units. Details of design approaches and related developments are given in various available sources [3–6], and the most widely used methods that may be applicable to the petroleum industries are presented in this chapter. In general, design equations for all separation equipment (i.e., distillation, absorption, extraction, etc.) are based on two equations: material balance and phase equilibrium. Simultaneous solution of these equations leads to general design equations for these separation units.

13.3.1 VLE Data

Distillation is based on the separation of compounds through vaporization in which lighter (more volatile) components tend to vaporize at lower temperature in comparison with heavier (higher boiling point) compounds. Separation of compounds continues until the vapor and liquid phases in contact with each other reach an equilibrium state. Consider a multicomponent system under the condition of temperature T and pressure P at which vapor and liquid phases may coexist together at equilibrium. If the mole fraction of component i in the liquid is shown by x_i and in the vapor phase by y_i, then the equilibrium ratio (K_i) is defined as

$$K_i = \frac{y_i}{x_i} \tag{13.8}$$

K_i is a dimensionless parameter that depends on T, P, and the composition of both phases. The simplest form of K_i is obtained through Raoult's law, which gives $K_i = P_i^{vap}/P$, in which P_i^{vap} is the vapor pressure of component i at temperature T. Raoult's law is valid when the liquid is an ideal solution and the vapor phase is assumed to be an ideal gas such as benzene-toluene system under atmospheric pressure. Calculation of vapor pressure or K_i values for various systems of hydrocarbons as well as nonhydrocarbons is discussed in full detail in ASTM Manual 50 [7]. Examples of a nonideal system are ethanol-water or acetone-chloroform, in which they may exhibit azeotrope behavior. As pressure changes, so do the equilibrium curves and the boiling point diagram. In general, with an increase in pressure the equilibrium curves get closer to the diagonal and make separation by distillation more difficult. Knowledge of K_i values or the equilibrium curve is the first step in the design or operation of any type of distillation unit.

Equilibrium data may also be presented in terms of the relative volatility of A to B, α_{AB}. defined as the ratio of equilibrium ratios: $\alpha_{AB} = K_A/K_B$. At a given pressure, values of α_{AB} vary with temperature and decrease with an increase in temperature. For a binary system of A and B, the equilibrium relation can be expressed in the following form in terms of an average value of α_{AB}:

$$y_A = \frac{\alpha_{AB} x_A}{1 + (\alpha_{AB} - 1)\, x_A} \tag{13.9}$$

For systems that follow Raoult's law, the relative volatility can be calculated from vapor pressure data: $\alpha_{AB} = P_A^{vap}/P_B^{vap}$. As α_{AB} increases, the equilibrium curve gets farther from the diagonal line and separation by distillation becomes easier.

13.3.2 Flash Distillation

Flash distillation is the simplest form of distillation and is performed in a unit called a flash separator. The feed enters the separator at higher temperature (by passing through a heater) or at lower pressure (by passing through an expansion valve) in which part of the feed is vaporized. The condition of T and P in the separator is the key to determining the level of separation and the amount of vapor (V) and liquid (L) produced, as shown in Figure 13.4. It is assumed that the produced vapor and liquid phases are in equilibrium.

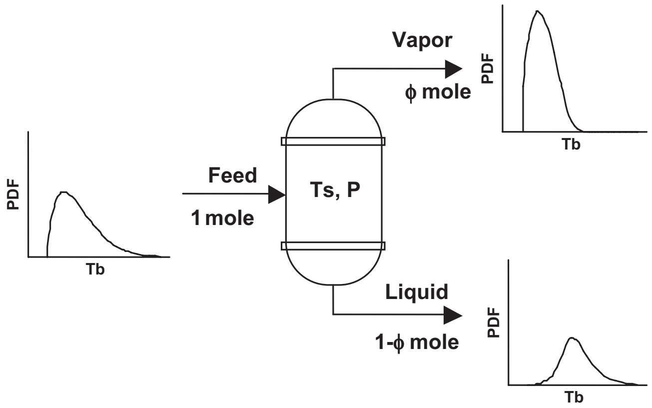


Figure 13.4—Schematic of a single-stage flash distillation unit.

For the system shown in Figure 13.4 and for a binary mixture, the material balance equation reduces to $y = (1 - 1/\phi)\, x + x_F/\phi$, in which ϕ is the fraction of feed vaporized ($\phi = V/F$) and is a number between 0 and 1. With the knowledge of the equilibrium relation between the y and x parameters, ϕ can be determined. If the feed is a continuous mixture such as crude oil, a probability distribution function (PDF) model can be used to express boiling point (T_S) distribution of feed, as shown in Figure 13.4. The amount of vapor (ϕ) produced and the PDF of products can be obtained from the following equations:

$$\int_{T_\circ}^{\infty} \frac{1 - K_T}{(1 - \phi) + \phi K_T} F_T^F \, dT = 0 \tag{13.10}$$

$$F_T^L = \frac{1}{(1 - \phi) + \phi K_T} F_T^F \tag{13.11}$$

$$F_T^V = \frac{K_T}{(1 - \phi) + \phi K_T} F_T^F \tag{13.12}$$

where:

K_T = equilibrium ratio of a component with boiling point T, and

F = PDF for boiling point.

Discussion about use of PDF in development of the above equations is given in Chapter 4 of ASTM Manual 50 [7]. A schematic of a three-stage separator is shown in Figure 13.5, where a crude oil pressure is reduced in three stages to atmospheric pressure. The details of calculations are discussed in Chapter 9 of reference 7. The composition of the liquid from the last stage is the same as crude oil ready as a feed to a refinery and was given in Chapter 1 (Table 1.1).

13.3.3 Batch Distillation

The simplest form of batch distillation, also known as differential distillation, consists of a heated kettle or boiler and a condenser to liquefy generated vapor [3–6]. There is no reflux, and once a certain amount of distillate is produced, the remaining liquid in the vessel can be withdrawn

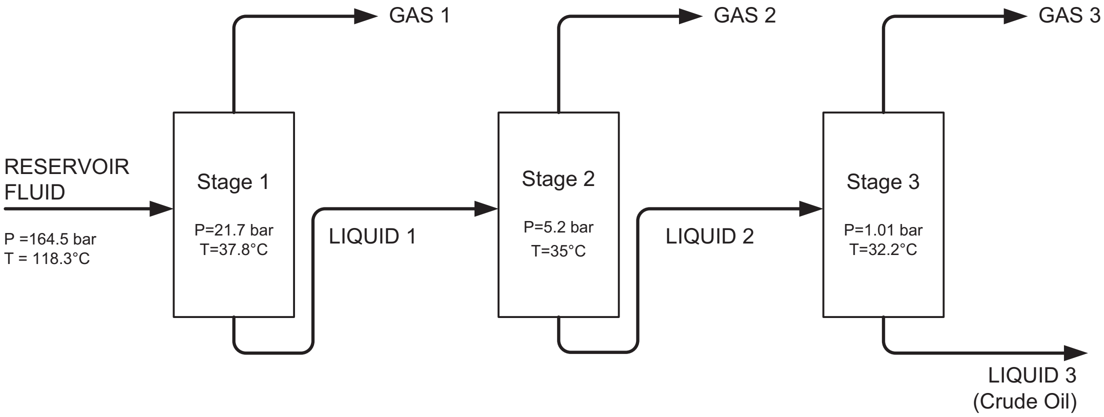


Figure 13.5—Schematic of a three-stage separator in a Middle East production field.

as a bottom product (rich in heavy compounds). Assume a binary liquid mixture of A and B exists in batch flask in which the initial amount of liquid is n_o moles with a composition of $x_{Ao} = n_{Ao}/n_o$ (mole fraction). At any time during the vaporization process, the number of moles of liquid remaining in the vessel is n with composition x_A and $n_o - n$ moles of distillate with an average composition of $y_{A,avg} = (n_{Ao} - n_A)/(n_o - n)$. The highest separation occurs at an initial time when $y_{A,avg}$ is at its highest value but the amount of distillate (product) is insignificant. Through material balance and equilibrium relation, we obtain the following relation for calculation of x_A.

$$\ln\frac{n_o}{n}=\frac{1}{\alpha_{AB}-1}\ln\left[\frac{x_A(1-x_{Ao})}{x_{Ao}(1-x_A)}\right]+\ln\left(\frac{1-x_{Ao}}{1-x_A}\right) \tag{13.13}$$

Another form of this equation can be derived between moles of A and B remaining in the vessel as

$$\ln\frac{n_A}{n_{Ao}}=\alpha_{AB}\ln\left(\frac{n_B}{n_{Bo}}\right) \tag{13.14}$$

For example, for an initial mixture of 60 moles benzene and 40 moles toluene distilled in a pot to reduce the benzene concentration to 30 mol % at 1 atm pressure, the temperature changes from approximately 85ºC to 105ºC, at which an average value of α_{AB} calculated from the vapor pressure is approximately 2.4. From the above relations, we get $n = 65.5$ moles and $x_A = 0.3$ whereas the distillate (34.5 moles) has a composition of $y_{A,avg} = 0.855$. If we had to use one-stage flash distillation to produce the same amount of distillate, then the composition would be $y_A = 0.731$. This indicates that batch distillation has better separation efficiency than flash distillation.

13.3.4 Distillation with Reflux—Binary Systems

The separation of components in a distillation process increases with returning a portion of liquid distillate to the distillation column, known as reflux, as shown in Figure 13.6. Distillation columns are designed with the use of equipment to promote contact between vapor and liquid in the column. These devices are various types of trays or packing. An ideal tray or a theoretical stage is a device at which vapor and liquid leaving the stage or tray are in equilibrium and the maximal separation of components can be achieved. A partial condenser (Figure 13.6) operates as an ideal stage whereas a total condenser does not increase purity of the distillate. Likewise, the reboiler acts as an ideal tray or stage because vapor returning to the column is in equilibrium with the bottom product (Figure 13.6).

The reflux ratio is the ratio of the rate of reflux to the rate of distillate ($R = L/D$), and with an increase in reflux the quality of product increases. However, as the rate of reflux increases, the amount of heat required for the reboiler also increases, which causes an increase in the operating cost while decreasing the capital cost. The optimal reflux is chosen when the total cost is at a minimum [4]. The operating reflux ratio is always greater than the minimum reflux at which the number of trays or the column height is infinity. The feed divides the column into two parts of enriching (above the feed) and stripping (below the feed) sections. The basic design of such columns involves the calculation of the number of trays and the height and diameter of the column. Calculations for determining the number of ideal trays (N_{th}) are available in various sources [3–6].

Selecting the operating conditions of a distillation column is a key part of the process. First, the operating pressure will fix the VLE data. As stated previously, lower operating pressures tend to make separation easier because the equilibrium curves are further apart, resulting in higher relative volatility. The following considerations should be evaluated when selecting the operating conditions of a distillation column:

- What condenser cooling medium will be used? The column top pressure will be the vapor pressure of the overhead product. It can be raised slightly with blanket gas or reduced slightly if a subcooling condenser is used. For most columns it is typical to set the overhead condensing temperature to no less than 10°C above the maximum supply temperature of the cooling medium. Using air-cooling will result in higher operating pressures than using cooling water. Refrigeration is not advisable unless absolutely necessary because of the high capital and operating costs.
- At the selected operating pressure, is the bottoms temperature required to boil the bottoms product (or feed in the case of a feed furnace heated column) compatible with the bottoms product? Could it result in decomposition via cracking or coking of the fluid? If so, reducing the operating pressure and temperature will be necessary either by using a colder condensing medium or operating at vacuum using ejectors or vacuum pumps.

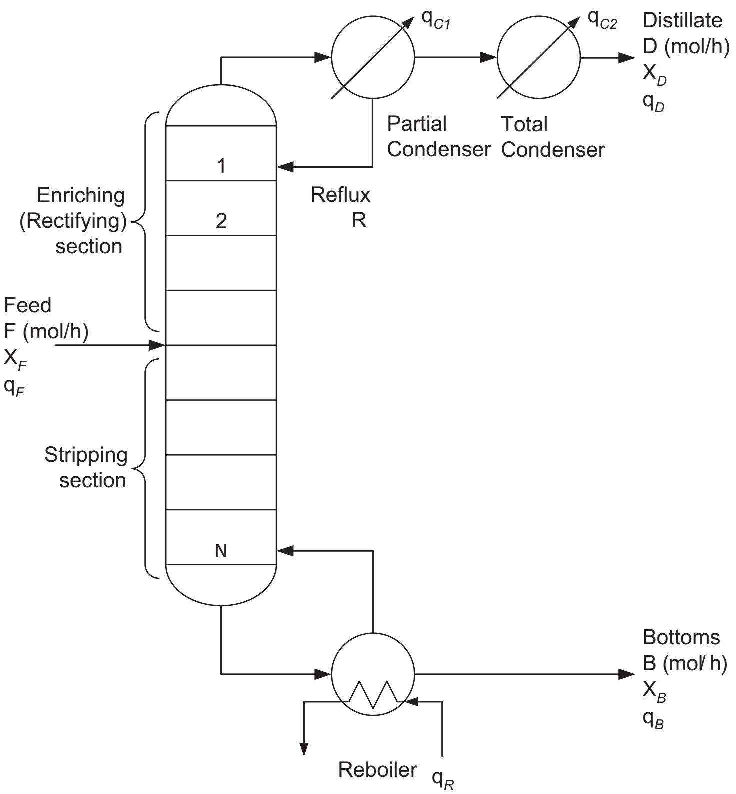


Figure 13.6—Continuous distillation column with reflux for a binary system with a partial condenser.

- What heating media are available for reboilers? If steam is available at 150°C and 250°C, then it is more energy-efficient to use the lower-pressure steam source; therefore, avoiding a pressure that results in a reboiler temperature of 155°C is advisable.
- Are there external constraints on operating conditions, such as major compression requirements (a la deep cut natural gas liquids [NGL] plants) that drive higher operating pressures? Caution is advised with columns that will operate near the cricondenbar because the latent heats are very small, the density difference between liquid and vapor are small, and relative volatilities are small. This is a common design consideration with cryogenic demethanizer columns.

The graphical method of McCabe-Thiele is most widely used to determine *N* for binary systems, as shown in Figure 13.7 for a benzene-toluene system at atmospheric pressure. The compositions (mole fraction of light

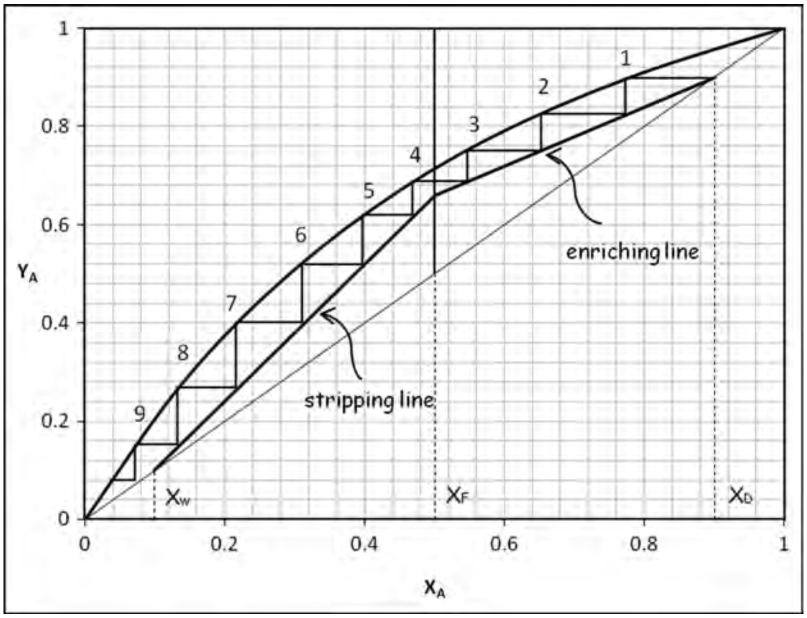


Figure 13.7—Number of theoretical trays in a distillation column according to McCabe-Thiele method for a binary mixture of benzene and toluene.

component) in the feed, distillate, and bottom products are shown by x_F, x_D, and x_B, respectively. In this example, the feed enters as saturated liquid with $x_F = 0.5$, and it is desired to have 50 % of feed as distillate with $x_D = 0.9$ and $R = 1.43$. Composition of distillate and bottom products can be determined from material balance. If molar rates (i.e., mol/h) of feed, distillate, and bottom products are shown by F, D, and B, respectively, then $F = D + B$ and $Fx_F = Dx_D + Bx_B$. From the material balance, the bottom composition is $x_B = 0.1$. The enriching operating line originates from the diagonal at x_D with a slope of $R/(R + 1)$ or an intercept of $x_D/(R + 1)$. This line intersects with the feed line, at which it is connected to the intersection of x_W with a diagonal. The feed line is originated from a diagonal (at x_F) with a slope of $q/(q - 1)$, where q is the feed quality and is defined as $q = (H_v - H_F)/(H_v - H_L)$, where H_F is the enthalpy of feed and $(H_v - H_L)$ is the heat of vaporization for the feed. If the feed enters as saturated liquid, then $H_F = H_L$ and $q = 1$ whereas if it enters as saturated vapor, then $q = 0$. According to Figure 13.7, the number of ideal stages is 8.6, and if a total condenser is used, then the number of ideal trays is determined by subtracting 1 for the reboiler and we obtain $N_{th} = 7.6$. Because actual plates are not ideal, the number of real plates (N) is greater than 7.6, and that depends on the overall efficiency of the column, E_O, as given in Eq 13.15:

$$N = \frac{N_{th}}{E_O} \tag{13.15}$$

In this equation, N_{th} represents the number of theoretical trays not counting the reboiler and partial condenser. Calculation of overall efficiencies (E_O) will be discussed later.

13.3.4.1 CALCULATION OF MINIMUM NUMBER OF TRAYS

As the reflux increases, the operating line of the enriching section approaches diagonal because the slope of the line $R/(R + 1)$ increases with an increase in the value of R. As the operating lines get closer to the diagonal (45° line), the number of trays gets smaller and smaller (see Figure 13.6). For total reflux that is $D = 0$, we have $R = \infty$, which corresponds to the operating line with a slope of unity. Therefore, for the case of minimum plates, both operating lines lie on the diagonal, and feed composition and its quality do not affect the minimum number of trays. For cases in which the equilibrium data can be represented by an average value of relative volatility (α_{AB}), the minimum number of theoretical stages can be calculated analytically through the Fenske equation, which was proposed in 1932 and is shown in Eq 13.16 [4].

$$N_{\min} = \frac{\ln\left[x_D\,(1 - x_B)\,/\,x_B\,(1 - x_D)\right]}{\ln\,(\alpha_{AB})} \tag{13.16}$$

To know the minimum number of ideal trays in the column excluding the reboiler, N_{min} as calculated from the above equation should be reduced by 1.

13.3.4.2 CALCULATION OF MINIMUM REFLUX RATIO

The optimum reflux can be determined by minimizing the total cost (operating + fixed capital costs). However, the actual and operating reflux is usually expressed in terms of the minimum reflux ratio R_{min}, at which the number of trays is infinity. The operating line in the enriching section at R_{min} can be drawn from a diagonal at x_D to the intersection of the q-line of the equilibrium curve. If this line continues, then it intersects with the y-axis, at a point that gives the value of $x_D/(R_{min} + 1)$ from the y-axis reading.

13.3.5 Distillation of Multicomponent Systems

If the feed to a distillation column has more than two components, then the procedure to determine the number of trays is somewhat different [3–6]. Separation of a mixture of three components (A, B, and C, in which C is the heaviest component) by two distillation columns in series is demonstrated in Figure 13.8, where C is mainly separated in the first column and A and B in the second column.

Consider that a mixture of four components, A, B, C, and D (ordered from light to heavy as boiling point increases or K value decreases), is fed to a distillation column with a reflux. The first step is to get the K values for all compounds at the operating pressure and temperature of the column on the basis of the methods available as given in Chapter 6 of ASTM Manual 50 [7]. As the temperature in the column varies, the K values may be determined at two temperatures: the temperature in the condenser (dew point of distillate) and in the reboiler (bubble point of bottom product). The second step in solving a multicomponent distillation problem is to identify two key components designated as a heavy key (HK) and light key (LK), which both appear in appreciable amounts in top and bottom products. Then, for all components, relative volatility with respect to HK should be determined as $\alpha_i = K_i/K_{HK}$, in which we always have $\alpha_{HK} = 1$, and for the LK $\alpha_{LK} = K_{LK}/K_{HK}$. Once the values of α_{LK} at the top and bottom temperatures of the column (at condenser and reboiler temperatures) are determined, the average value of α_{LK} can be determined from

$$\alpha_{LK,avg} = \sqrt{\alpha_{LK,top}\ \alpha_{LK,bottom}} \tag{13.17}$$

The Fenske equation (Eq 13.16) can then be used to calculate the minimum number of theoretical stages (at total reflux, $R = \infty$):

$$N_{\min} = \frac{\ln\left[(Dx_D/Bx_B)_{LK}/(Bx_B/Dx_D)_{HK}\right]}{\ln\,(\alpha_{LK,avg})} \tag{13.18}$$

After the initial round of calculations, the composition of top and bottom products can be modified using the following

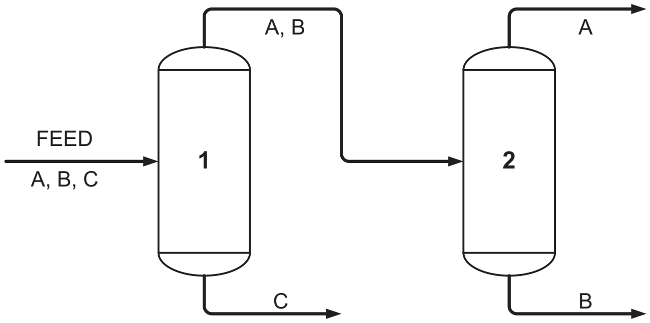


Figure 13.8—Separation of a three-component mixture by two distillation columns.

relation until no significant changes are observed in the composition:

$$\left(\frac{x_i}{x_{HK}}\right)_D = \left(\alpha_{i,avg}\right)^{N_{\min}} \left(\frac{x_i}{x_{HK}}\right)_B \tag{13.19}$$

To calculate the total number of theoretical stages at an operating reflux value of R, the method of Underwood can be used. In this method, R_{min} is calculated from

$$R_{\min} = \left[\sum_i \frac{\alpha_i\,(x_{iD})}{\alpha_i - \theta}\right] - 1 \tag{13.20}$$

in which parameter θ is determined from solving the following relation:

$$\sum_i \frac{\alpha_i x_{iF}}{\alpha_i - \theta} = q - 1 \tag{13.21}$$

where q is the feed quantity defined earlier. Once R_{min} is known, N_{th} can be determined from the Gilliland correlation using input data of N_{min}, the value of R at operating conditions, and R_{min}. The Gilliland correlation is usually expressed in a log-log graphical form, but the following relation developed based on the correlation represents the original data fairly well and can be used for practical purposes [6]:

$$\frac{N_{th} - N_{\min}}{N_{th} + 1} = 1 - \exp\left[\left(\frac{1 + 54.4\Psi}{11 + 117.2\Psi}\right)\left(\frac{\Psi - 1}{\Psi^{0.5}}\right)\right] \tag{13.22}$$

where:
$\Psi = (R - R_{min})/(R + 1)$ and
R_{min} is calculated from Eq 13.20.

The value of R is usually given in terms of R_{min} (i.e., operating reflux is 30–50 % higher than its minimum). Finally the feed-plate location is determined from

$$\log\frac{N_e}{N_s} = 0.206\,\log\left[\left(\frac{x_{HK,F}}{x_{LK,F}}\right)\frac{B}{D}\left(\frac{x_{LK,B}}{x_{HK,D}}\right)^2\right] \tag{13.23}$$

where:
N_e and N_s = number of theoretical stages in the enriching and stripping sections, respectively, and $x_{HK,F}$ = mole fraction of the HK component in the feed.

Other compositions are similarly defined. In Eq 13.23, N_e gives the number of theoretical stages above the feed tray and N_s does include a reboiler as one theoretical stage or tray. N_e and N_s can be determined from simultaneous solution of Eq 13.23 with $N_{th} = N_e + N_s$, where N_{th} is calculated from Eq 13.22.

As an example, consider the feed to a distillation column operating at 4 atm consisting of 100 mol/h of a mixture of 40 % n-butane, 25 % n-pentane, 20 % n-hexane, and 15 % n-heptane (all in mol %). The feed enters at its boiling point and is distilled so that 95 % of the n-pentane is recovered in the distillate and 95 % of n-hexane in the bottom product. The following should then be calculated: (1) the amount and composition of distillate and bottom products, (2) N_{min} and R_{min}, and (3) N_{th} and the feed-tray location at an operating reflux ratio 30 % higher than R_{min}. To solve this problem, we assume that all butane appears in the distillate and all heptane appears in the bottom product. Pentane is the LK and hexane is the HK component. From material balance calculations, the compositions of distillate and bottom products are calculated as given in Figure 13.9.

Top and bottom temperatures are then calculated from dew point and bubble point calculations as T_{top} = 64°C and T_{bottom} = 133 °C. Therefore, the average column temperature is 98.5°C. At this temperature, we obtain $\alpha_{LK,avg} = 2.3$. Using Eq 13.18, we calculate $N_{min} = 7.2$ and from Eq 13.20 we obtain $R_{min} = 0.505$. At $R = 1.3$, $R_{min} = 0.657$, and from Eqs 13.22 and 13.23 we get $N_{th} = 16.8$, $N_e/N_s = 1.187$, and $N_e = 9.1$ (feed enters on the 10th tray). Similar calculations can be performed by a HYSYS simulator [8] with use of the Peng-Robinson equation of state. With this, we obtain bottom product $B = 35.25$ mol/h, $x_{A,B} = 0.00019$, $x_{B,B} = 0.03552$, $x_{C,B} = 0.539$, $x_{D,B} = 0.4253$, T_{bottom} = 130.5 °C, $R_{min} = 0.485$, $N_{min} = 7.4$, $N_{th} = 17.5$, and $N_e = 9.4$, which are close to the values calculated through the above methods. If the feed to the column is a crude oil or an undefined petroleum mixture, then a distribution model can be used to represent the mixture with several pseudocomponents with known composition and characteristic properties as discussed in Chapter 4 of ASTM Manual 50 [7].

13.3.6 Energy Requirement for a Distillation Column

The main operating cost for a distillation column is the cost for the energy required in the reboiler. High-pressure steam is typically used in the reboiler to partially vaporize the liquid from the bottom of column. The rate of energy required is designated by q_R (e.g., kJ/h, kW, MMBtu/h) and can be determined through overall energy balance around the column shown in Figure 13.6. If the enthalpy of feed, distillate, and bottom products are shown by h_F, h_D, and h_B (i.e., kJ/mol), respectively, and the energy removed from the condenser is shown by q_C, then the overall energy balance gives the following relation for calculation of q_R:

$$q_R = Dh_D + Bh_B + q_C - Fh_F \tag{13.24}$$

h_D and h_B are enthalpies of saturated liquid as they leave condenser and reboiler at the corresponding temperatures. Calculations of the enthalpy of petroleum fractions are discussed in Chapter 7 of ASTM Manual 50 [7]. The mass rate of saturated steam required for the reboiler can be calculated from q_R/λ_s, in which λ_s is the latent heat of steam. The amount of energy removed from the condenser (e.g., via cooling water), q_C, can be calculated through an energy balance around the total condenser as

$$q_C = D\,(R + 1)\,(H_1 - h_D) \tag{13.25}$$

where H_1 is the enthalpy of saturated vapor leaving the top of the column and entering the condenser (Figure 13.6), which has the same composition as distillate product (x_D). In fact, in the above equation, $(H_1 - h_D)$ is the latent heat of product D in kilojoules per mole. $D(R + 1)$ is equivalent to V_1 or the molar rate of vapor entering the condenser. The mass rate of cooling water required depends on the decrease in temperature of water (ΔT) and can be calculated through water heat capacity as $q_c/(C_p\Delta T)$.

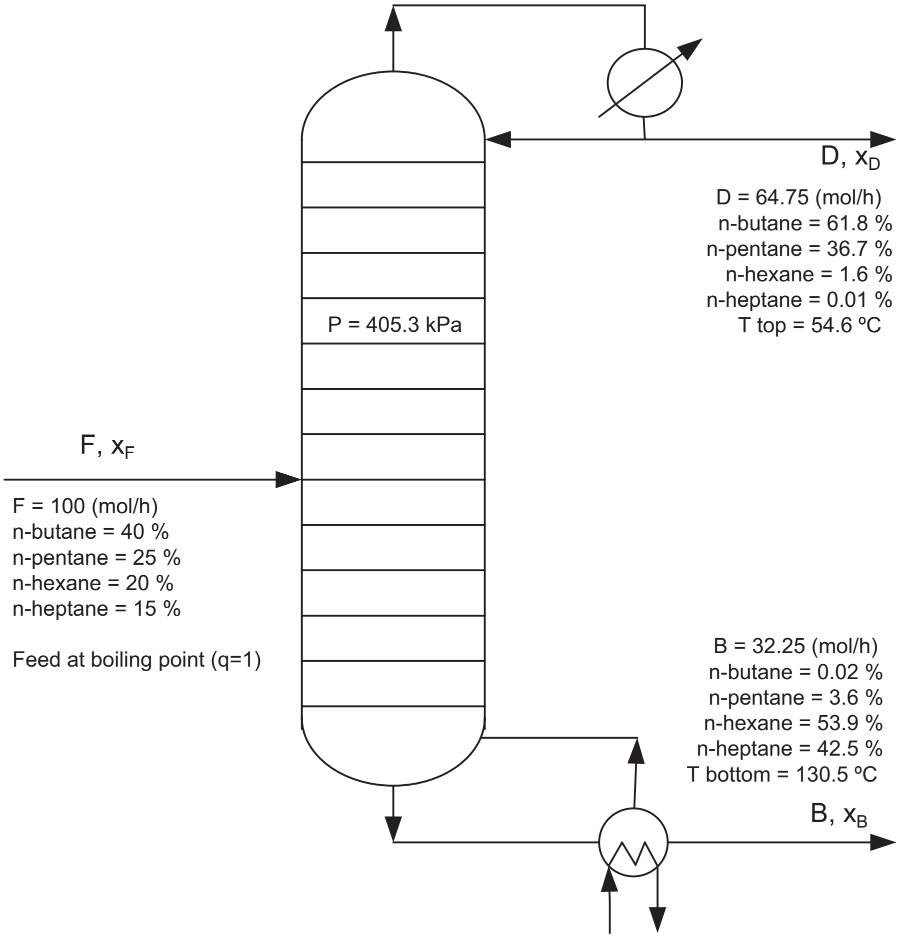


Figure 13.9—Material balance calculations for multicomponent distillation column design.

As an example, consider a distillation column operating at atmospheric pressure with a feed of 100 moles of equimolar mixture of benzene and toluene with $x_D = 0.9$, $x_F = 0.5$, and $x_B = 0.1$ as presented in Figure 13.6.

Enthalpies of saturated liquid and vapor for a benzene-toluene binary system are given in reference 5. On the basis of such data, the following expression can be obtained for the enthalpy (H) of saturated vapor of a mixture of benzene-toluene with a mole fraction of benzene as y $H = 38.45 - 7.246y - 0.396y^2$, where H is in kilojoules per mole. Likewise, for a saturated liquid mixture, the following expression well represents the data: $h = 5.1 - 8.0816x + 2.99x^2$, where h is the liquid enthalpy. At $x_D = 0.9$, $x_F = 0.5$, and $x_B = 0.1$, we get $H_1 = 31.6$, $h_F = 1.81$, $h_D = 0.248$, and $h_B = 4.32$ kJ/mol. The reference state for the enthalpy values is saturated liquid benzene ($x_D = 1$) at 1 atm in which enthalpy is considered as zero. From Eq 13.25 with $R = 1.43$ and $D = 50$ mol/h, $q_C = 3809$ kJ/h (1.06 kW) and from Eq 13.24 we get $q_R = 3856$ kJ/h (1.07 kW).

The heat input to the reboiler (q_R) and the heat removal (q_C) from the condenser are among the variables that can be manipulated to control the column. In general, in a distillation column, the variables that can be manipulated to control the column are R, D, B, $q_{R,}$ and q_C. With $q_{R,}$ one can control the bottoms composition (x_B) and temperature whereas with q_C the tower pressure can be controlled. With the distillate rate (D), the distillate product composition (x_D) and liquid level in the accumulator is controlled and with the bottom rate (B) the liquid level in the column can be controlled to avoid flooding. The distillate product quality and composition are controlled by manipulating the reflux ratio (R) as discussed in reference 5.

13.3.7 Column Efficiency

As was stated through Eq 13.15, the number of trays calculated through the above methods is based on the assumption that each tray or each stage (for the case of packed columns) behaves as an ideal stage. Vapor and liquid leaving an ideal tray are in equilibrium; however, for an actual tray as shown in Figure 13.10 the vapor phase is not in equilibrium with liquid on the tray. For example, consider a tray column as shown in Figure 13.6 or Figure 13.10 in which vapor comes to the *nth* tray from the lower tray ($n + 1$) with composition y_{n+1} and leaves the *nth* tray with composition y_n. If the liquid leaving the *nth* tray has a composition of x_n and the composition of vapor in equilibrium with this liquid is shown by y_n^*, then for an ideal or theoretical tray $y_n = y_n^*$. However, in practice, trays are not ideal and vapor composition is less than the equilibrium composition: $y_n < y_n^*$. This is the basis for the definition of tray efficiency known as Murphree efficiency (E_M), defined as

$$E_M = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}} \tag{13.26}$$

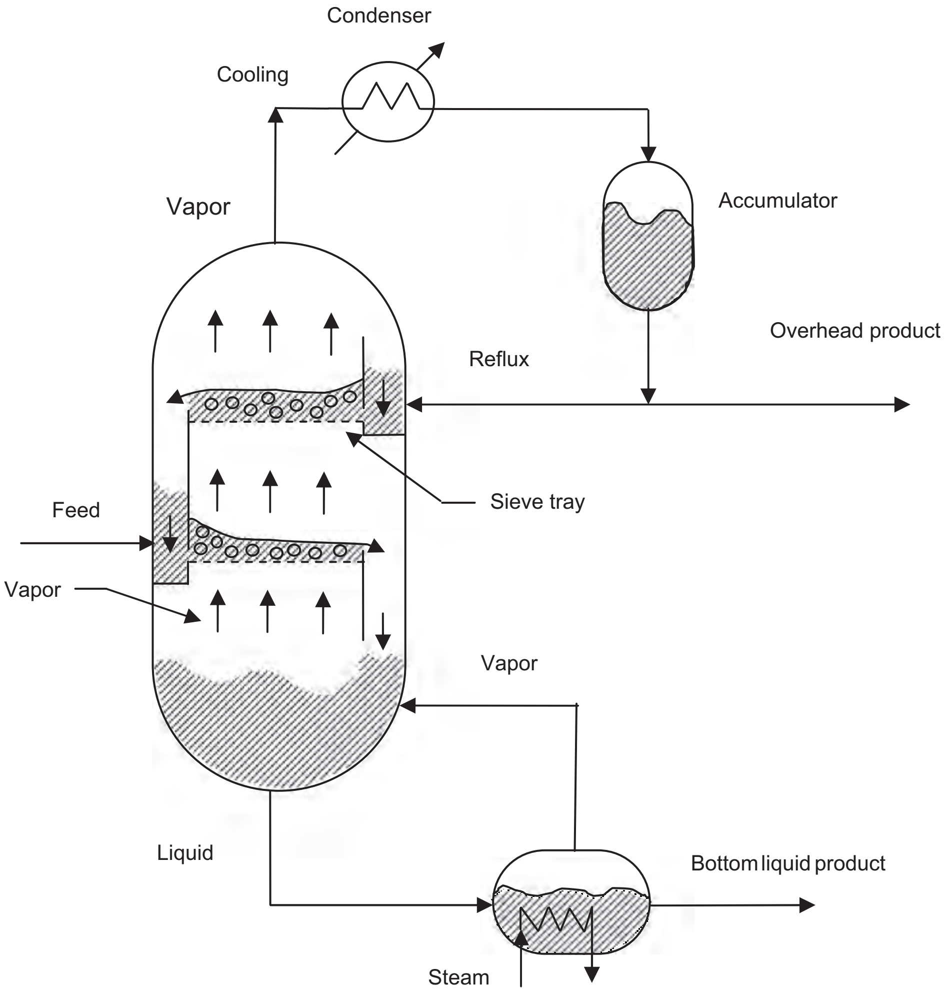


Figure 13.10—Vapor liquid contact in a sieve tray distillation column.

Murphree efficiency varies from tray to tray and is different from the overall column efficiency, defined as the number of theoretical trays to the actual tray (see Eq 13.15). The Murphree efficiency can be used to construct a curve that represents the actual y_n and not the equilibrium curve presented by y_n^*. This is demonstrated in Figures 13.7 and 13.11, where the McCabe-Theile method is used to obtain the actual number of trays. For example, if $E_M = 0.5$ and a quasi-equilibrium curve is used instead of a real equilibrium curve, we get 17.5 – 1 or 16.5 actual trays without including the reboiler step, which is always equivalent to one theoretical step as shown in Figure 13.10. In this way, we obtain $N = 17$ and $N_{th} = 7.5$ (without reboiler). The actual number of trays should always be rounded to the higher number. For example, for this example it is 17 trays plus a reboiler.

Because this method of determining the actual number of trays is tedious, inconvenient, and not practical for multi-component systems, a simple analytical expression of Bradford, Drickamer, and O'Connell is recommended as [3,9]

$$E_o = 0.492(\mu_L \alpha_{LK,avg})^{-0.245} \tag{13.27}$$

where:

μ_L = viscosity of liquid feed and

$\alpha_{LK,avg}$ = average relative volatility of light to heavy component.

The above equation is suitable for sieve and valve tray columns and gives an average error of ±10 %. Typical values of column efficiency for tray columns are between 40 % and 80 %. Another widely used empirical correlation to estimate the overall efficiency is

$$E_o = 19.2–57.8\log(\mu_L) \tag{13.28}$$

For absorption tray columns, the overall column efficiency E_o (in %) can be estimated from

$$\log E_o = 1.597 - 0.199\log(mM_L\mu_L/\rho_L) - 0.0896[\log(mM_L\mu_L/\rho_L)]^2 \tag{13.29}$$

where:

μ_L = average viscosity of liquid in cP (mPa.s),

ρ_L = liquid density in $\mathrm{lb_m/ft^3}$ at average tower temperature (if ρ_L is in $\mathrm{kg/m^3}$, then it should be divided by 16.02 to have it in $\mathrm{lb_m/ft^3}$),

M_L = average molecular weight of liquid, and

m = slope of the equilibrium curve (or line).

The above equation cannot be applied to distillation columns because m is not constant along the tower. The average error for this equation is approximately 16 %. Typical values of E_o for absorption columns are between 10 and 30 % and are normally within the range of 1–50 % [10]. The efficiency of packed columns is discussed in the next Section 13.3.8 where height equivalent to a theoretical plate (HETP) is discussed.

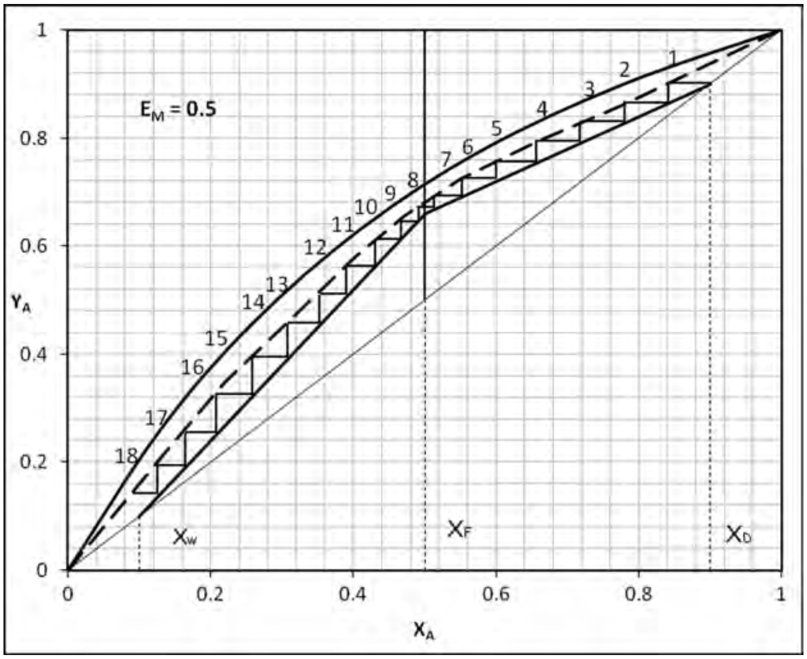


Figure 13.11— Use of Murphree efficiency in the calculation of the actual number of trays for the distillation column of Figure 13.10.

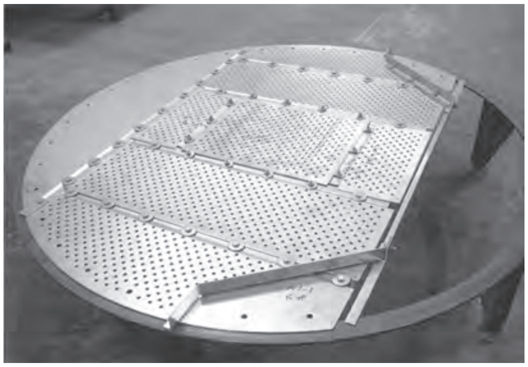
A recent article by Kister [11] examines factors that affect overall tray efficiency when designing a new distillation column or revamping an existing commercial-scale fractionator. In summary, parameters that affect tower efficiency include VLE data such as relative volatility, reflux ratio, viscosity of fluid, tower geometry such as flow path length, fractional hole area, hole diameter, and weir height. Most efficiency test data reported in the literature were obtained at total reflux; however, the reflux ratio has been reported to have a small effect on tray efficiency. In general, tray efficiency increases with lower viscosity and relative volatility (see Eq 13.27). Viscosity is important because of diffusivity because more turbulent mass transfer, thinner liquid, and vapor films give better liquid mass transfer coefficients. At very low relative volatility ($\alpha < 1.2$), small errors in VLE data have a huge effect on tray efficiency. For instance, at $\alpha = 1.1$, a –3 % error gives a tray efficiency 40–50 % higher than its true value. Because the accuracy of VLE data is seldom better than 2–3 %, in low-volatility systems tray efficiencies become meaningless unless accompanied by actual VLE data. However, for $\alpha > 1.5$–2.0, VLE errors have a small direct effect on tray efficiency. This applies to tray and packed columns. Pressure also has little effect on tray efficiency; for example, as column pressure increases from 10 to 30 bar for isobutane-*n*-butane systems, efficiency decreases from 105 to 90 %. Literature sources also indicate that tower geometry has a major effect on the efficiency. For example, as flow path length increases from 300 to 1500 mm, the overall tray efficiency for a cyclohexane-*n*-heptane system increases from 65 to 100 % [11].

13.3.8 Column Types and Operational Aspects

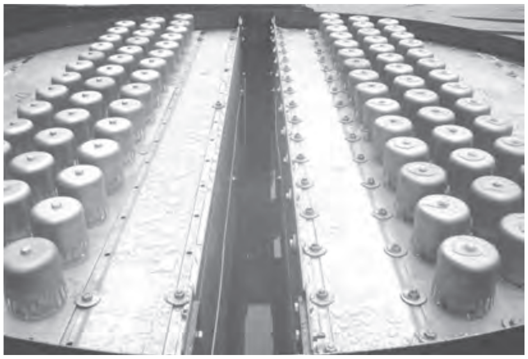
A schematic of a distillation column with a partial condenser is shown in Figure 13.6. The top condenser is a partial condenser to obtain liquid for the reflux, and the product is condensed in a second condenser. The first condenser plays like a single equilibrium stage or a tray. The bottom liquid is also partially vaporized in a reboiler, and a further separation can occur in the reboiler because it acts like an ideal stage. Having a higher reflux rate can increase the purity of top products; however, it reduces the rate of product and requires higher energy in the reboiler. When the column is operating at total reflux, the number of trays becomes a minimum and column length is minimized whereas the operating cost is infinity.

Performance of a distillation column largely depends on the type of equipment used to bring into contact vapor and liquid along the column. This can be done through trays or packings. Behavior of a sieve tray column is shown in Figure 13.10. Trays are made of metal plates with holes on them for passing vapor. Liquid on a tray is held by weir and moves downward from one tray to the lower tray through the downcomer at the end side of the tray and by gravity force. The minimum height of weir is approximately 0.5 in. whereas 1- to 3-in. height is quite common. The height of the downcomer and weir has a direct effect on column flooding and overall efficiency. An ideal tray is a tray in which the vapor and liquid leaving from that tray are in thermodynamic equilibrium and the maximal possible exchange of components has occurred on that tray. Because there is no ideal tray, the efficiency of a tray is defined so as to quantify how far a tray is from an ideal tray. For this reason, the number of actual trays is always greater than the number of ideal or theoretical trays determined based on the assumption that trays are ideal. There are different types of trays, with the most common types being sieve trays, bubble-cap trays, and valve trays. In an industrial scale, sieve and bubble-cap trays are shown in Figure 13.12a [12,13]. Sieve trays cost less than valve trays by 20 %, and bubble-cap trays normally cost 3–4 times more than valve trays. The major difference in a valve and sieve tray is the pressure drop across the plate. As shown in the figure, the size of the hole in the sieve tray is approximately ⅛ to ½ in. with ⅜ in. as an average size of a hole. As a rule of thumb for sieve trays, the total hole area of a plate is approximately 5–15 % of the total column area. In bubble-cap trays, there is a riser in

(a)



Sieve Trays, 1800mm Ø Dephosgenation Column



Bubble Cap Trays, 1800mm Ø Vacuum Flash Tower

(b)

Pall Rings in Metal

Pall Rings in Plastic

DMR High Performance Random Packing in Metal

DMTP High Performance Random Packing in Metal

Ceramic Saddles

Figure 13.12—(a) Two types of industrial scale trays and (b) various packings for industrial use [12]. With permission from [12].

the middle of the cap in which gas passes through. The size of a bubble cap is a design parameter, but 3 and 6 in. are common sizes, and for a column of 7 ft. approximately 22 rows of 3 in. or 8 rows of 6-in. caps are needed. However, 3-in. caps are more efficient, but because of cost considerations 6-in. caps are preferable [14].

As the name implies, a sieve tray is a simple plate with a series of holes on the tray where the gas goes through. In valve trays, a contact device moves with the gas and if there is no gas, then the valves are closed, preventing liquid from dropping through the holes. One problem with sieve and valve trays is weeping, which is flow of liquid through gas-opening holes. Weeping is mainly associated with sieve trays and reduces the tray efficiency when it occurs. In general, sieve and valve trays are more efficient than bubble-cap trays and less expensive, but weeping is a problem. Sieve trays are the least expensive kind of trays; however, the liquid flow and gas flow rates must be under control and within a narrow range to prevent weeping.

An alternative to tray columns is packed towers, which are filled with particles called packing. Columns can have structured or random packing. These kinds of columns are usually used for columns with diameters less than 2 ft (0.6 m) and usually for absorption columns, although they can also be used for distillation columns. The most common types of packings are raschig ring, berl saddle, intalox (metal), intalox saddle (ceramic), tellerette, or pall ring, as discussed in reference 6. Samples of such packings are shown in Figure 13.12b [12]. Usually 1.5- and 2-in. (37 and 50 mm) sizes are used, but they should always be less than 1/10 of the column diameter.

The main characteristic of a packing is to have high surface area with less volume. Liquid flows over packings and forms a thin film in which gas passes over the film and exchange of components occurs. Packings are made of ceramics, plastics, or metals with good mechanical strength so that they do not crush or powder. Metallic packings are mainly used in petroleum and natural gas units, whereas plastics are used in absorption and stripping columns operating below 120°C. They must be resistant to thermal degradation and not reactive to gas and liquid flowing in the column. Packed columns are less expensive than tray columns and must show low pressure drop and liquid hold-up. On top of a packed column there is a distributor to distribute liquids and prevent channeling within the column. Some advantages of packed columns over tray columns are discussed in Section 13.3.9.3.

A new distillation column should go through "column commissioning," which is a series of operations before column startup. These include removing undesirable materials in the column through air or N_2 blowing, pressurizing the column to detect any leaks, and washing to remove dirt. After commissioning, the column is brought to its normal pressure followed by heating (if needed) and then feed is introduced gradually to a normal feed rate. One major problem during the operation of a distillation column is flooding, which is due to accumulation of liquid on trays. Flooding can be detected when there is a drop in the bottom product and a sudden increase in pressure drop along the column. Once flooding occurs, the liquid must be removed as liquid (pumped off), as it will not be possible to boil off the excess [15].

Sometimes it is necessary to operate the column with total reflux, which means no product with feed interruption. This is done from a few minutes to several days and is needed to stabilize the column, condenser, and reboiler. Some common problems during operation of a distillation column are [16]

- Tray damages due to corrosion or poor installation.
- High liquid level in the column and flooding. For this reason, the lower trays must be made with extra strength.
- Water comes from feed or steam injected into the column and causes problems such as corrosion, pressure surges, flooding, and hydration.
- Hydrate (loosely bonded mixtures of hydrocarbons and water) formation causes problems such as plugging of tubes. Hydrates are solids, and low temperature, high pressure, and turbulence promote formation of hydrates. Usually when a column is operating at 30–40°F, hydrates may form, and dehydration equipment or materials are needed. A similar problem exists with wax formation at low temperatures, and adding components to the feed to lower the freezing point will help to prevent hydration or wax formation.
- Leaking in heat exchangers, which sometimes cause reactions with other streams and difficulties in operation of the column.
- During flooding, the plant must be shut down to clean the column and to remove blockages. Online cleaning includes use of antifoam injection and solvent injection to dissolve frozen particles. Changes in feed composition and reducing the plant load may also help to prevent flooding.
- Foaming is a problem with formation of foams. These are vapors that do not separate from liquid and usually occur in the stripping section of a distillation column as well as absorption columns. The life of a foam is just few seconds, and antifoam materials (such as dimethylsilicons) may be used to prevent foaming. If the bottom product of a distillation column has lower surface tension than its top product, then foaming is unlikely.

13.3.9 Column Size Calculations

Design calculations for a distillation column mainly involve calculation of the height and diameter of the column. The way these column dimensions can be calculated for tray and packed columns is summarized below.

13.3.9.1 TRAY COLUMNS

For tray columns, the height is calculated from the following relation:

$$h_c = (N_{act} - 1)\, h_s + \Delta h \qquad (13.30)$$

in which h_c is the height of the column, N_{act} is the actual number of trays in the column, and h_s is the tray spacing. Δh is the additional height required for the top and bottom of the column and should not be less than $2h_s$. Tray spacing varies with the column diameter and number of trays. It usually varies from 0.15 m (6 in.) to 0.9 m (36 in.). For columns more than 1 m in diameter, a spacing of 0.3–0.6 m will be normally used. A typical value for tray spacing is 0.5 m; however, when the number of trays is so large, the height should be limited because of external constraints such as the ceiling of a building. For small column diameters, a smaller tray spacing may be used. A larger spacing is required between certain plates that feed enters or there is a side stream product and for manways into the column [10].

To calculate the diameter of a tray column, the maximum allowable vapor velocity (v_{max}) in the column is first determined from

$$v_{\max} = K_v \left(\frac{\sigma}{20}\right)^{0.2} \sqrt{\frac{\rho_L - \rho_V}{\rho_V}} \qquad (13.31)$$

where:

σ = surface tension of liquid in dyn/cm (mN/m),

ρ_L = liquid density in kg/m^3 or lb$_m$/ft^3, and

ρ_V = vapor density in kg/m^3 or lb$_m$/ft^3.

A typical value of σ for organic liquids is approximately 20–25 mN/m and for water is 72 mN/m. Calculations of σ, ρ_L, and ρ_V are discussed in ASTM Manual 50 [7]. At moderate column pressures, ρ_V can be calculated from the ideal gas law using the average molecular weight of gas and the column temperature. The value of K_V is in ft/s and should be obtained from Figure 13.13, where L and V are the flow rates of liquid and vapor, respectively, in the column in kg/h or lb$_m$/h. Another relation for approximate calculation of v_{max} without use of the figure is given as [10]

$$v_{\max} = (-0.171\, h_s^2 + 0.27\, h_s - 0.047) \sqrt{\frac{\rho_L - \rho_V}{\rho_V}} \qquad (13.32)$$

where:

h_s = tray spacing (m), and

v_{max} = maximum vapor velocity (m/s).

The calculated vapor velocity (v_{max}) from Eq 13.32 should be revised for the downspout area (91 %), foaming (95 %), and flooding (80 %) as follows:

$$v_{max,\, design} = (0.91)\,(0.95)\,(0.8)\, v_{max} \qquad (13.33)$$

The tower cross-sectional area (A_c) is then calculated from the vapor flow rate (V) and vapor density (ρ_V) as

$$A_c(m^2) = \frac{V\ (kg/h)}{3600\ (s/h)} \times \frac{1}{\rho_V (kg/m^3)} \times \frac{1}{v_{\max,design}(m/s)} \qquad (13.34)$$

Finally, the column diameter, d_c, is calculated from A_c as

$$d_c = \sqrt{\frac{4A_c}{\pi}} \qquad (13.35)$$

13.3.9.2 PACKED COLUMNS

For packed columns, the height is calculated from the following relation:

$$h_c = N_{th}(HETP) \qquad (13.36)$$

in which N_{th} is the theoretical number of stages (excluding reboiler) and is basically calculated the same way as the number of theoretical trays. HETP is the height equivalent to a theoretical plate and is in fact the height of the packed column, which can give a separation equivalent to one theoretical plate. In Eq 13.36, h_c is in fact the height of the column that is filled with packing. The real height of the column is higher considering the top and bottom portions of the column. HETP depends solely on the packing size as given in Eq 13.37 in SI and English unit systems for random-packed towers [3]:

$$\begin{aligned} HETP\ (m) &= 0.018\ d_P(mm) \\ HETP\ (ft) &= 1.5\ d_P(in) \end{aligned} \qquad (13.37)$$

in which d_P is the packing diameter. If the tower diameter is less than 0.6 m but not less than 0.3 m, then it can be assumed that $HETP = d_c$. For vacuum distillation, it is suggested to add 0.15 m to the predicted values of HETP. Some other researchers have developed slightly different relations in which HETP is predicted from the column diameter (d_c) as given in Eq 13.38 [9]:

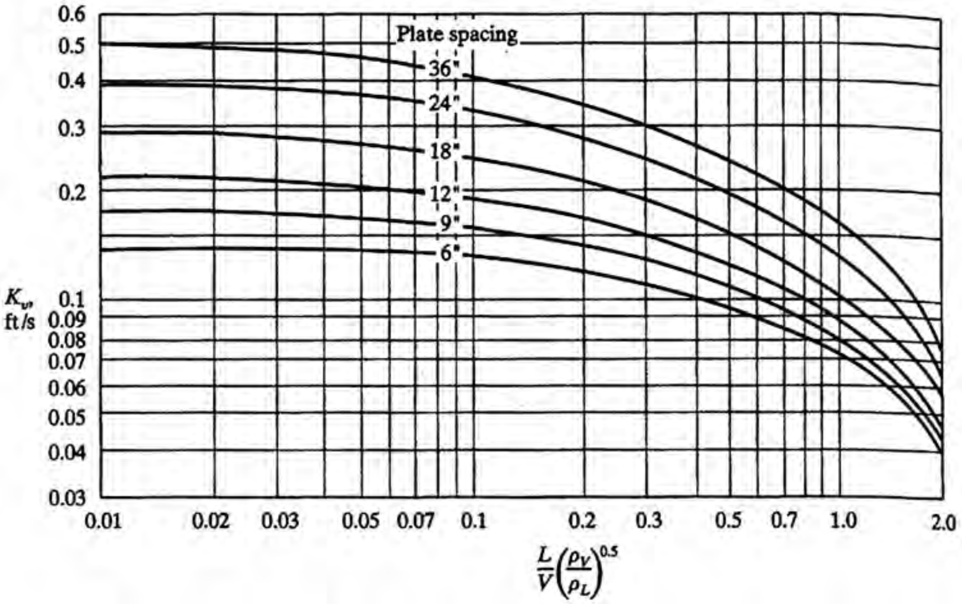


Figure 13.13— Estimation of K_v for tray columns [10].

$$HETP = \begin{cases} d_c & \text{for } d_c \le 0.5\,\text{m} \\ 0.5 d_c^{\,0.3} & \text{for } d_c > 0.5\,\text{m} \\ d_c^{\,0.3} & \text{for absorption columns} \\ & \text{with } d_c > 0.5\,\text{m} \end{cases} \tag{13.38}$$

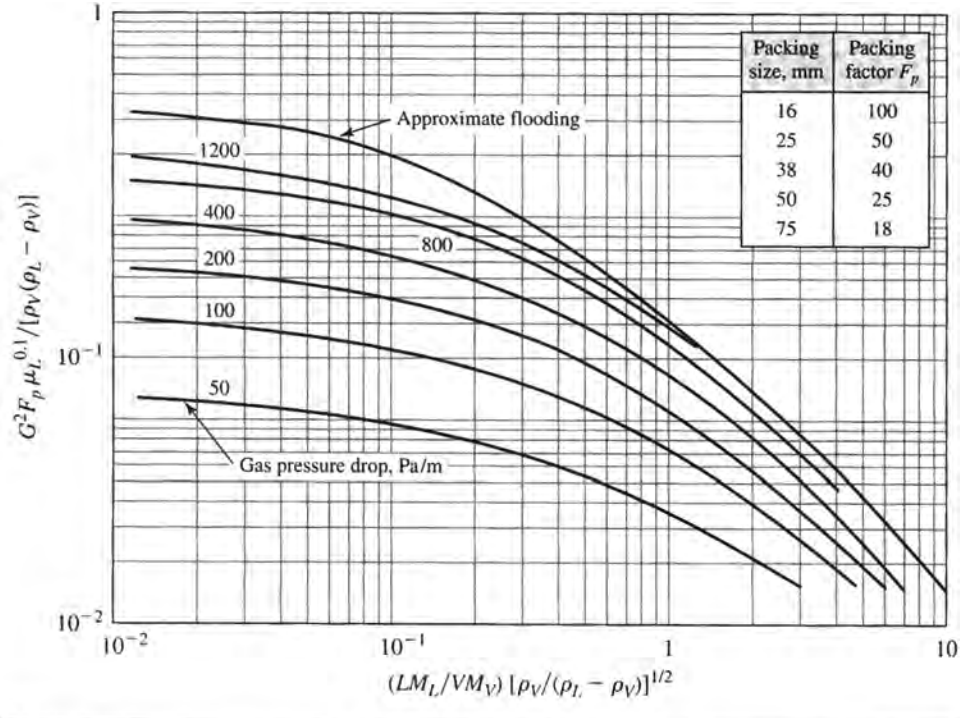
where HETP and d_c are both in metres. Again, for vacuum distillation 0.15 m should be added to the predicted values of HETP. For structured-packed towers the relation is

$$HETP = 100/a + 0.1 \tag{13.39}$$

in which *HETP* is in metres and *a* is the surface area of packing in metres squared per cubic metres. HETP in structured-packed towers is usually less than that of random-packed towers and is in the range of 0.3–0.6 m (1 to 2 ft). Values of *a* depend on the type of packings and vary from 200 to 700 m^2/m^3 for structured packing as given in reference 3. For random packing, values of *a* are less than those for structured packing. However, most structured packings have surface areas in the range of 200–300 m^2/m^3 and for random packing in the range of 100–200 m^2/m^3. The void fraction (volume of empty space to volume of column) for various packings is in the range of 0.9–0.97.

To calculate column diameter for packed columns, a similar method as that of tray columns may be used but using different correlations for gas-phase mass flux (*G*) and pressure drop in the column. According to this method, if pressure drop is known, *G* can then be calculated from the gas flow rate (*V*), and the area of cross section A_c can be calculated as indicated in Figure 13.14. The column diameter can then be calculated from Eq 13.28. The properties of gas and liquid phases needed for use of Figure 13.14 can be estimated from the composition through methods provided in ASTM Manual 50 [7]. For the cases in which these values significantly vary from top to bottom of the column, a separate diameter can be calculated for the bottom that is different from the top.

To calculate A_c from Figure 13.14, the pressure drop in the column for the gas phase per unit length of packed column must be known. The recommended pressure drop in packed columns for atmospheric- and high-pressure separations ranges from 400 to 600 Pa/m, for vacuum operation between 4 and 50 Pa/m, and for absorption/stripping columns between 200 and 400 Pa/m [9]. The conversion factor for such pressure drop from an English-unit system is 1 in. H_2O/ft height = 83.33 mm H_2O/m height = 817.13 Pa/m height [7]. For absorption columns, a typical value for pressure drop is 0.25 in. H_2O/ft, which is nearly equivalent to 200 Pa/m. The minimum pressure drop is approximately 50 Pa/m, and the packing factor, F_p, given in Figure 13.14 mainly varies with packing size; however, it also slightly varies with packing type. More data on packing factor are given in reference 5.



Packing size, mm	Packing factor F_p
16	100
25	50
38	40
50	25
75	18

where

$G = VM_V/A_c$, superficial gas mass flux, kg/(s·m^2)

F_p = packing factor, dimensionless; see insert

μ_L = liquid viscosity, Pa·s

ρ_V = gas density, kg/m^3

ρ_L = liquid density, kg/m^3

L = liquid flow rate, kg mol/s

A_c = column cross-sectional area, m^2

M_V = molecular weight of vapor, kg/kg mol

M_L = molecular weight of liquid, kg/kg mol

V = gas flow rate, kg mol/s

Figure 13.14—Flooding and pressure drop correlation for packed columns—calculation of column diameter [9].

13.3.9.3 ADVANTAGES AND DISADVANTAGES OF TRAY AND PACKED COLUMNS

Advantages of tray columns can be summarized as follows [9,10]:

- Design calculations for tray columns are more reliable than those for packed columns.
- Tray columns can be used to handle a wide range of liquid and vapor rates without flooding.
- Plates are more accessible for cleaning than packings, especially when liquid contains dispersed solids.
- The total weight of a dried tray column is less than that of a packed column.
- It is easier for tray columns to make provisions for side streams.
- Packed columns are not used when the column diameter is larger than 1.5 m, and tray columns are not used when the diameter of the column is less than 0.6 m (2 ft).
- Packed columns are less expensive than tray columns and easier to construct, especially when handling corrosive liquids.
- Packed columns are preferred when the liquid has a tendency to foam.
- The amount of liquid hold-up in packed columns is less than that of tray columns.
- The pressure drop in packed columns is less than that of tray columns and is more suitable for vacuum columns.

Use of a packed column is more common in gas absorption towers than distillation columns.

13.3.10 Commercial Simulation Tools

The aforementioned methods are manual but are still a valuable toolkit for engineers to understand how distillation calculations are performed. However, for many designers and operators, commercial simulation and modeling tools are available to overcome the sheer volume of calculations required for a multicomponent column. A very good text on this subject is by Kaes [17], which covers many of the common refinery units that can be modeled in commercial thermodynamic simulators. Many of these simulators also have shortcut methods to estimate the dimensions of the column using various published correlations such as those discussed above.

Additionally, many suppliers of column internals offer software for rating or sizing columns using their proprietary internals. An independent option is available for firms that are members of Fractionation Research, Inc. (www.fri.org), which has data and software available for many systems and internals designs.

13.4 ABSORPTION AND STRIPPING

The design of absorption columns is mainly similar to those of distillation columns. Absorption columns can be designed as a tray or packed column. However, because the gas and liquid flow rates in absorption processes are usually less than those for distillation columns, packed columns are more common than tray columns. The main difference with distillation is that there is no condenser, reflux, and reboiler in the column as shown in Figure 13.15. In addition, in many practical cases the equilibrium curve for gas absorption systems is usually a straight line with a slope of m: $y_i = m_i x_i$. In cases in which the amount of solute in the solvent is small and Henry's law can be applied, m_i is the same as Henry's constant (k). However, in general, the relation between y_i and x_i is given through the equilibrium ratio $y_i = K_i x_i$ as defined in Eq 13.8. K_i varies with temperature, pressure, and composition, although for hydrocarbon mixtures, composition dependency may be neglected. Estimations of K_i, and k_i have been discussed in detail in ASTM Manual 50 [7].

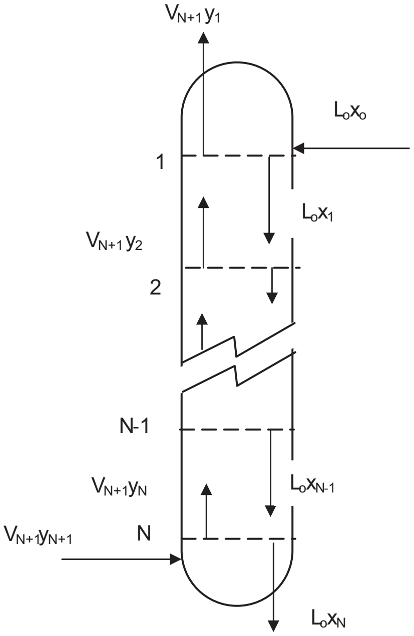


Figure 13.15—General schematic of a multistage gas absorption column.

As shown in Figure 13.15, gas enters at the bottom at a rate of V_{N+1} (mol/h) with a composition in terms of mole fraction (y_{N+1}). The solvent (usually pure) enters from the top of the column at a rate of L_0 (mol/h) with composition x_1 and leaves at a rate L_1 (mol/h) with composition x_1. Compositions x and y represent mole fractions of a component distributed in the liquid and vapor phases, respectively. The overall and component material balances (in moles) can be written as

$$L_0 + V_{N+1} = L_N + V_1 \tag{13.40}$$

$$L_0 x_0 + V_{N+1} y_{N+1} = L_N x_N + V_1 y_1 \tag{13.41}$$

If the solvent is pure, then $x_0 = 0$, in which x represents the mole fraction of a component that is being absorbed from the gas phase by liquid solvent. Usually V_{N+1}, L_0, y_{N+1}, x_0, and y_1 are known whereas L_N, V_1, and x_N are unknown. For a multistage unit, the above equations can be written for any stage (i.e., *nth*), and through simultaneous solution of these two equations a linear equation for the operating line can be obtained. By drawing the operating line and equilibrium line and using a step-by-step procedure similar to the McCabe-Thiele approach, the number of stages (N) can be determined [3]. Analytically and for constant m, this leads to the Kremser equation for calculation of the number of theoretical stages N:

$$N = \frac{\ln\left[\frac{y_{N+1} - m x_0}{y_1 - m x_0}\left(1 - \frac{1}{A}\right) + \frac{1}{A}\right]}{\ln A} \tag{13.42}$$

where A is the absorption factor defined as $A = L/mV$ and is dimensionless. Because L, V, and m may vary from top to bottom of the column average, A may be calculated as $A = \sqrt{A_1 A_N}$, where $A_1 = L_0/m_1V_1$ and $A_N = L_N/m_NV_{N+1}$. For a single-stage unit, Eqs 13.40 and 13.41 can be solved together, with $y_N = m_i\ x_N$ through equilibrium relation in which $N = 1$.

Another example of gas absorption units in refinery gas plants is to remove heavy hydrocarbons from a hydrocarbon gas mixture using a solvent that has a good absorbing power for hydrocarbons. Oils are obviously good solvents to absorb a hydrocarbon compound from a gas mixture, especially if they are from the same hydrocarbon family. In such cases, it is usually desired to remove a certain fraction of a compound from a gas mixture, which is defined as recovery, E_i:

$$E_i = \frac{n_{i,inlet} - n_{i,outlet}}{n_{i,inlet}} \tag{13.43}$$

where:

$n_{i,inlet}$ = number of moles of component i in the gas entering the column,

$n_{i,outlet}$ = gas leaving the column, and

$n_{i,inlet} - n_{i,outlet}$ = amount of component i absorbed by the oil or removed from the gas.

In this definition, it is assumed that the solvent entering the column is free of component i, the absorbing species. Using definition E_i, Eq 13.43 can be rearranged to be written as

$$E_i = \frac{A_i^{N+1} - A_i}{A_i^{N+1} - 1} \tag{13.44}$$

where A_i is the absorption factor defined in Eq 13.43. In finding N (number of theoretical stages) from the above equation, component i must be a component for which A_i is close to unity and is referred as a key component.

To recover solvent from the absorption column, the lean oil is usually sent to a stripping column as shown in Figure 13.16. The stripping process is opposite of gas absorption, and absorbed components in the liquid phase are stripped by a gas that is usually nonsoluble in the solvent. For example, for the case of rich oil (oil with absorbed gases), the best stripping gas is steam, which cannot be absorbed by oil but it can take some light hydrocarbon gases out of oil. A stripping column is best operated at low pressures and high temperatures (opposite to the conditions in an absorption column). When pure steam is used to strip light hydrocarbon gases out of oil, the number of theoretical stages can be calculated from [5].

$$1 - \frac{n_{i,outlet}}{n_{i,inlet}} = \frac{S_i^{M+1} - S_i}{S_i^{M+1} - 1} \tag{13.45}$$

in which $n_{i,outlet}$ is the moles of i in the stripped lean oil leaving the stripping column and $n_{i,inlet}$ is the moles of i in the rich oil entering the stripper. S_i is the stripping factor and is defined as K_iV_0/L_{M+1}. V_0 is the moles of stripping medium entering the column (i.e., moles of steam entering), and L_{M+1} is the moles of rich oil entering the stripping column. M is the number of theoretical stages in the column (similar to N for an absorption column). The left side of the above equation is equivalent to the recovery factor (fraction of i removed from rich oil) in the stripper.

A recent article by Binous [16] shows how computer software such as MATLAB and MATHEMATICA can be used to make calculations related to equilibrium-stage separations and to obtain the number of equilibrium stages for processes such as distillation, absorption, stripping, and extraction.

13.5 LIQUID-LIQUID EXTRACTION

For liquid systems in which distillation cannot be used to separate the key component from a liquid mixture because of low relative volatility, component sensitivity to the high temperatures, or a small amount of solute present in the feed, an extraction process using a solvent is an alternative process. In this process, a solvent (C) is added to a liquid mixture (A + B) in which C is mainly insoluble in B and forms two phases (both liquid); however, component A is the solute and can be dissolved in solvent C. Component A is the key component that has to be separated from B. The

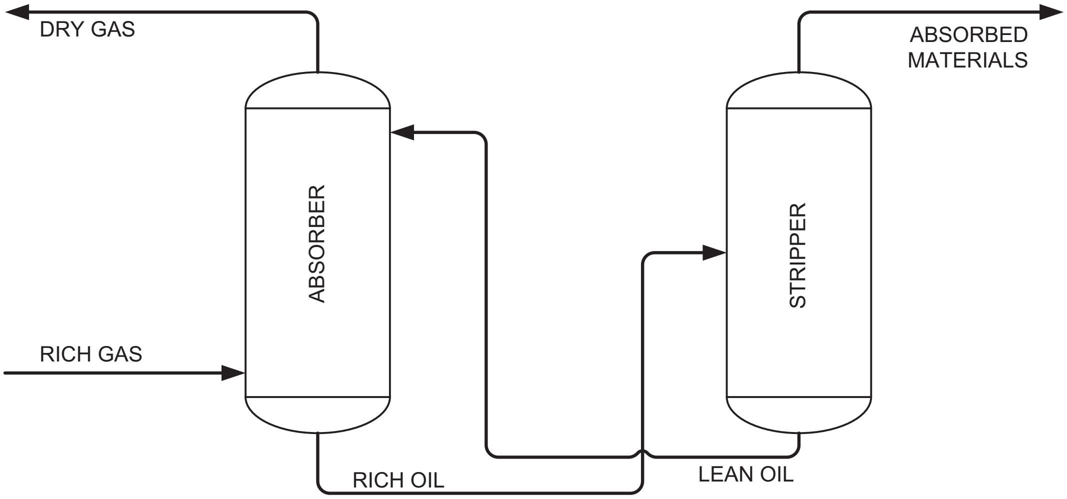


Figure 13.16—Absorption and stripping columns in series.

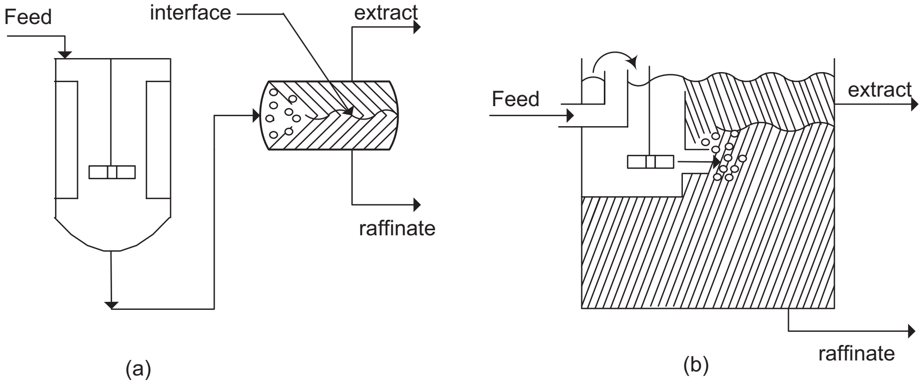


Figure 13.17—Schematic of a single-stage extraction unit with two different configurations.

mixture of A and C (overflow) is the extract phase (solvent-rich phase) and the underflow is the raffinate, as shown in Figure 13.17 [3]. In this figure, two different configurations are shown for an extraction unit in which the feed and solvent are first mixed and then remain to be separated into two phases. Separation of A is determined when the two liquid phases reach equilibrium. The composition of each phase at equilibrium conditions can be determined from liquid-liquid equilibrium (LLE) calculations or from experimental data as discussed in reference 7. Because in each phase there are three components, the composition of each mixture can be shown on a triangular coordinate system so that $x_A + x_B + x_C = 1$. For liquid systems, all compositions are expressed in terms of weight fraction (wt % /100). The equilibrium data are presented on a triangular diagram by a series of tie lines that connect the composition of two phases in equilibrium as shown in Figure 13.18. In this figure, data on the LLE of a ternary system of ethylbenzene-styrene-diethylene glycol are presented that can be used to separate styrene from ethylbenzene [18].

For this system, the solvent is diethylene glycol and styrene is to be removed from the ethylbenzene-styrene solution. Any mixture that has a composition in the area inside of the dashed equilibrium curve splits into two phases in equilibrium with each other with a composition known from ends of the tie-line. The raffinate phase is the ethylbenzene-rich phase (higher concentration of B and the lower part of the equilibrium curve) whereas the extract phase is solvent rich (higher concentration of C), which is the upper part of the curve. The point where the length of a tie-line becomes zero is the plait point. Any mixture with a composition outside of the envelope cannot be separated by phase split.

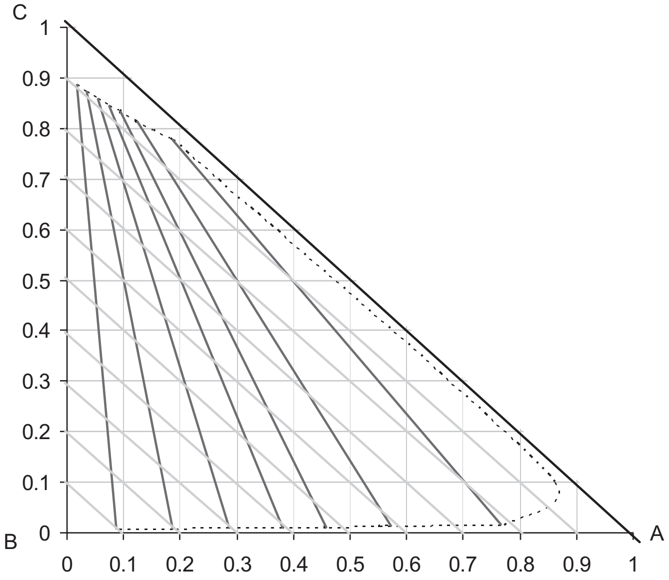


Figure 13.18—LLE data (in weight fraction) for styrene (A), ethylbenzene (B), and diethylene glycol (C).

As in the case of distillation and absorption, design calculations involve the number of stages required for a certain degree of separation and solvent-to-feed ratio. A solvent rate is similar to reflux in distillation, and at the minimum solvent rate the number of stages will be infinity. A general schematic of a multistage extraction unit showing the raffinate and extract phases is shown in Figure 13.19. The same schematic also applies to a single-stage unit with $N = 1$. A multicontact extraction unit is usually built as a vertical column similar to gas absorption columns in which the feed (heavier liquid phase) enters from the top and solvent (lighter liquid phase) is introduced from the bottom. The raffinate phase (heavier phase) leaves from the bottom, and the extract (solvent rich) phase leaves the column from the top. This is to imagine that the schematic shown in Figure 13.19 is rotated 90º in a clockwise direction. The extract phase can be taken in a distillation column for separation and recovery of solvent.

Design equations can be developed based on material balance and equilibrium relations. If the weight fraction of each component in the extract phase (V phase in Figure 13.18) is shown by y and in the raffinate phase (L phase) is shown by x, then the overall material balance and component material balances for A and C can be written as

$$\begin{aligned} &\mathrm{L_o(feed) + V_{N+1}(solvent) = V_1(extract)} \\ &\quad \mathrm{+ L_N(raffinate) = M} \end{aligned} \tag{13.46}$$

$$\begin{aligned} &\mathrm{x_{Ao}L_o(A\ in\ feed) + y_{A,N+1}V_{N+1}(A\ in\ solvent)} \\ &\mathrm{= x_{A,N}L_N(A\ in\ raffinate) + y_{A,1}V_1(A\ in\ extract)} \\ &\mathrm{= M\ x_{A,M}} \end{aligned} \tag{13.47}$$

$$\begin{aligned} &\mathrm{x_{Co}L_o(C\ in\ feed) + y_{C,N+1}V_{N+1}(C\ in\ solvent)} \\ &\mathrm{= x_{C,N}L_N(C\ in\ raffinate) + y_{C,1}V_1(C\ in\ extract)} \\ &\mathrm{= M\ x_{C,M}} \end{aligned} \tag{13.48}$$

where M is a mixture (with composition of x_M) formed by adding the entering feed (L_o) and solvent (V_{N+1}) streams. By

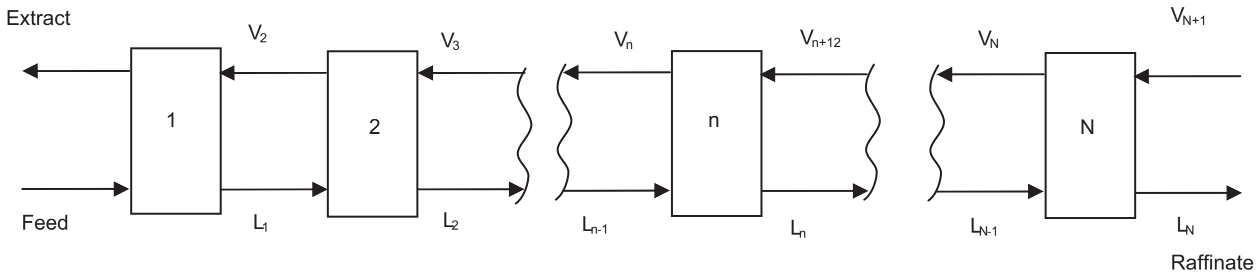


Figure 13.19—General schematic of a multistage extraction unit.

simultaneous solution of these equations, M, $x_{A,M}$, and $x_{C,M}$ can be determined as

$$x_M = (L_o x_o + V_{N+1} y_{N+1})/M \qquad (13.49)$$

To determine the number of stages, the operating lines can be developed based on the difference between the raffinate and extract phase, which remain constant in each cross-sectional area of the extraction column; that is, $L_N - V_{N+1} = L_o - V_1 = L_1 - V_2 = L_n - V_{n+1} = \Delta$. The difference point Δ can be best determined graphically by the intersection of a line connecting L_N to V_{N+1} and a line connecting L_o to V_1. The number of stages can be determined from a series of operating lines connecting Δ to L_1, L_2, etc., and corresponding tie-lines. Likewise, by determining point Δ_{min}, one can determine the minimum solvent required for extraction purposes. This can be demonstrated in the following example.

For the ternary system of acetic acid (A), water (B), and ether (C), the solvent is ether and acid is to be removed from the aqueous solution. Based on data taken for this system from reference [3], the LLE envelope is developed as shown in Figure 13.20. Consider 100-kg/h feed of aqueous solution of acetic acid (30 wt %) is being extracted by the pure solvent isopropyl ether. It is desired to calculate the minimum solvent required to have water phase at 2 wt % acid concentration when it leaves the unit.

With respect to the symbols used in Figure 13.19, we have $L_0 = 100$ kg/h, $x_{A0} = 0.3$, $x_{C0} = 0$, $y_{A,N+1} = 0$, $y_{C,N+1} = 1.00$, and $x_{AN} = 0.02$. The feed is located on the BA coordinate (Figure 13.20) at $x_{A0} = 0.3$. The tie-line passing through this

Figure 13.20—Calculation of minimum solvent and number of theoretical stages for LLE.

point gives $V_{1,min}$ on the envelope, which, if connected to point L_N (at $x_A = 0.02$), intersects with the line from L_0 to V_{N+1} at point M as shown in Figure 13.20. Reading from the figure for this coordinate is $x_{AM,min} = 0.115$ and $x_{CM,min} = 0.58$, and substituting into Eq 13.42 gives $V_{N+1,min} = 160$ kg/h. At this solvent rate, the number of theoretical stages is infinity; however, at a solvent rate greater than this number, x_{AM} is calculated from Eq 13.49 with point M on the figure, in which point V_1 can be determined from connecting L_N to M and its intersection with the upper portion of the equilibrium curve in Figure 13.20. By connecting L_0 to V_1 and its intersection with the $L_N V_{N+1}$ line, point Δ is determined and can be used to determine the number of ideal units.

13.6 HEAT TRANSFER EQUIPMENT

13.6.1 Heat Exchangers

Heat exchangers are used to transfer energy from a hot fluid to a cold fluid by indirect contact. The hot fluid can be a process fluid, steam, or a heat transfer medium such as hot oil. The cold fluid can be a process fluid, cooling water, sea water, a refrigerant, or a heat transfer medium such as a glycol solution.

Shell and tube exchangers are those in which one fluid flows through the tubes whereas the other flows through a shell around the tubes; heat then transfers through the metal tube walls. These are the most common exchangers in refinery applications because they can be constructed to withstand high pressures and temperatures. They also provide good heat transfer in most applications.

Plate exchangers are those in which the fluids flow between layers of corrugated plates. The plates are corrugated to induce turbulence in the fluids, thus increasing heat transfer. Plate exchangers can be either gasketted or welded, depending on the service. Gasketted plate exchangers (commonly called plate and frame) are those in which polymer gaskets are used to isolate the fluids from each other and the external environment. These exchangers can be easily disassembled for cleaning or maintenance and are often used in refinery applications for services involving water or amine.

Welded (or brazed) plate exchangers are usually used in very clean services. A block-type plate exchanger can have multiple process streams, such as those used in liquefied natural gas (LNG) liquefaction, NGL recovery, and air separation facilities. These are not common in refinery applications.

Spiral exchangers are a special type of plate exchanger in which the process fluids flow through spiral paths between two plates that have been rolled into such a shape. These exchangers are particularly good for services prone to plugging, such as slurries. They are most common in food-processing facilities, but their use in refineries for streams such as visbreaker and FCC bottoms products is not unknown and can provide significant benefits [19].

All heat exchangers are governed by the basic energy balance and heat transfer equations, with the differences in the details. The heat transfer in a heat exchanger is described by

$$Q = U_o A_{Eff} \Delta T_{LMTD} \quad (13.50)$$

The log-mean temperature difference (LMTD) is calculated via

$$\Delta T_{LMTD} = \frac{\Delta T_G - \Delta T_L}{\ln\left(\frac{\Delta T_G}{\Delta T_L}\right)} \quad (13.51)$$

where:
ΔT_G = greater terminal temperature difference, and
ΔT_L = lesser terminal temperature difference.

Figure 13.21 displays the temperature differences for countercurrent and co-current exchangers.

For the countercurrent exchanger, the terminal temperature differences are calculated as

$$\Delta T_G = T_2 - t_1 \qquad \Delta T_L = T_1 - t_2 \quad (13.52)$$

whereas for co-current exchangers they are calculated as

$$\Delta T_G = T_2 - t_2 \qquad \Delta T_L = T_1 - t_1 \quad (13.53)$$

For shell and tube exchangers, which make up most exchangers in a refinery, flow on either the shell or the tube side will be a combination of countercurrent and co-current flow. Therefore, it is necessary to correct the pure countercurrent LMTD. Many correction methods have been published over the years, including those of Underwood [20], Bowman et al. [21], and Maxwell [22]. Wales [23] revised the equations of Bowman et al., providing a clearer relationship.

For tubular exchangers, the corrected LMTD replaces the LMTD in Eq 13.50:

$$\Delta T_{LMTD} = F \cdot \Delta T_{LMTD} \quad (13.54)$$

The correction factor, *F*, is calculated via the following method. It can also be read from charts published by the Tubular Exchanger Manufacturers Association (TEMA) [24]. From reference 21, the hot-fluid-to-cold-fluid temperature change ratio is

$$R = \frac{T_1 - T_2}{t_2 - t_1} \quad (13.55)$$

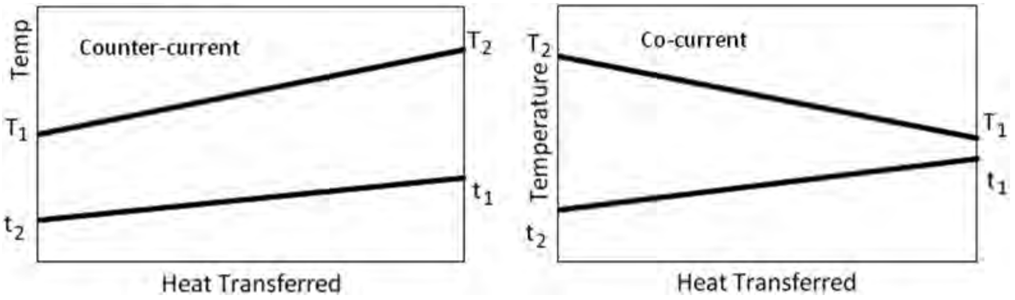


Figure 13.21—Mean temperature difference.

Instead of the cold-fluid temperature efficiency used in reference 21, reference 23 proposed the use of the outlet temperature gap to inlet temperature gap ratio:

$$G = \frac{T_2 - t_2}{T_1 - t_1} \tag{13.56}$$

Values of G also indicate how much heat exchange is occurring. When G equals +1, there is no heat exchanger possible; when $G = -1$ there is maximum heat exchange occurring. If the outlet temperatures are equal, then $G = 0$. A negative G value indicates a fluid temperature cross.

For an exchanger with one shell pass and two tube passes,

$$F_{1,2} = \frac{\left(\frac{(R^2+1)^{1/2}}{R-1}\right) \cdot \ln\left(\frac{R+G}{1+GR}\right)}{\ln\left(\frac{C+D}{C-D}\right)} \tag{13.57}$$

where C and D are defined as

$$C = (R + 1)(1 + G) \tag{13.58}$$

$$D = \sqrt{(1-G)\,(R^2-1)} \tag{13.59}$$

Additionally, for an exchanger with two shell passes and four tube passes,

$$F_{2,4} = \frac{\left(\frac{(R^2+1)^{1/2}}{2(R-1)}\right) \cdot \ln\left(\frac{R+G}{1+GR}\right)}{\ln\left[\frac{C+2\cdot\sqrt{(R+G)\,(1+GR)}+D}{C+2\cdot\sqrt{(R+G)\,(1+GR)}-D}\right]} \tag{13.60}$$

Note that Eqs 13.57 and 13.60 are indeterminate for the rare case of $R = 1$. In this situation, one can replace part of the numerator via

$$\frac{1}{(R-1)} \ln\left[\frac{(R+G)}{(1+RG)}\right] = \frac{(1-G)}{(1+G)} \tag{13.61}$$

For exchangers with more passes, Bowman et al. [21] provided a generalized form for a given R and number of shell passes, N. Wales [23] adjusted this in terms of the value G:

$$G_{N,2N} = 1-(1+R)\left\{\frac{\left[\frac{1+RG_{1,2}}{R+G_{1,2}}\right]^N - 1}{\left[\frac{1+RG_{1,2}}{R+G_{1,2}}\right]^N - R}\right\} \tag{13.62}$$

In the rare case of $R = 1$, the equations are again indeterminate. In this situation,

$$G_{N,2N} = \frac{G_{1,2}+1-N\cdot(1-G_{1,2})}{G_{1,2}+1+N\cdot(1-G_{1,2})} \tag{13.63}$$

$G_{N,2N}$ can be substituted into Eq 13.57 to obtain a correction factor for a three-six, four-eight, five-ten, or six-twelve exchanger.

Wales took this one step further and identified an approximation of Eq 13.57 accurate to 1 % when $G \geq -0.05$ (which would mean F < 0.75) and $0.33 < R < 3.00$:

$$F_{1,2} \cong \frac{2.0619 \cdot \ln\left[\frac{(2.15+G)}{(1+2.15\cdot G)}\right]}{\ln\left(\frac{5.5212+0.7788\cdot G}{0.7788+5.5212\cdot G}\right)} \tag{13.64}$$

Equation 13.64 can be combined with Eq 13.63 for approximations of more complex exchanger configurations.

For most heat exchangers, an F correction factor above 0.8 is desired. The reason is that F can be considered a measure of the efficiency of the surface area used (and capital expended). An F factor below 0.8 indicates that the surface area is not being put to good use. The curvature of these equations is such that as G declines, F declines even faster. This indicates a risk that if you have a heat exchanger with a low F correction factor (i.e., below 0.8), small changes in process temperatures can result in very little heat transfer occurring because of inefficient use of surface area. Plots of these equations can be found in references 21 and 23 as well as many textbooks on heat transfer.

If the F factor falls below 0.8, it is recommended to increase the number of shells (or shell passes) to improve the overall factor. Most commercial process simulators can calculate the F factor for a heat exchanger (given the number of passes on each side).

It must be noted that the prior method of determining the corrected LMTD only applies if the process flows are constant, the specific heats of the fluids are relatively insensitive to temperature, no phase change occurs, and the overall heat transfer coefficient is constant through the exchanger. If there is a phase change, or the specific heats of the fluids change significantly with temperature, the heat curves will not be straight lines. For such considerations, it is necessary to use a weighted LMTD calculation. Methods for this have been published, including reference [25].

The effective surface area, A_{Eff}, is the tube surface area that is useful in transferring energy. This means that portions of the tube area that is concealed by the tubesheet are excluded, as is the area of the return bends in a U-tube exchanger if the shell side fluid does not actively flow through the head of the shell (i.e., the shell side fluid around the return bends is essentially stagnant as is often the case).

The overall heat transfer coefficient, U_O, can be determined via

$$U_O = \frac{1}{\left(\frac{1}{h_o} + \frac{1}{h_i}\frac{A_o}{A_i} + \frac{D_o}{2k}\ln\left(\frac{D_o}{D_i}\right) + R_{D_o} + R_{D_i}\frac{A_o}{A_i}\right)} \tag{13.65}$$

In most applications, the surface areas of each side of the heat exchanger are the same; therefore $A_o/A_i \approx 1$, and the resistance of the metal tube is very small, leaving the form

$$U_O = \frac{1}{\left(\frac{1}{h_o} + \frac{1}{h_i} + R_{D_o} + R_{D_i}\right)} \tag{13.66}$$

where the values denoted h are the heat transfer coefficients on the inside and outside of the clean tubes, and the values denoted *R* are the fouling resistances (factors) on the inside and outside of the tubes. Note that in mild fouling services, the fouling resistance changes the overall coefficient by a few percent, and very fouling services can reduce it by a factor of 10.

A heat transfer text or exchanger design manual should be consulted for more details on how the local heat transfer coefficients are calculated. Typical overall heat transfer coefficients (fouled) are shown in Table 13.1.

When specifying a heat exchanger, the overall heat transfer coefficient will be calculated rigorously by the heat transfer engineer. For these cases, the process engineer should provide the fouling factors that the heat transfer engineer should use. Some operating companies or engineering firms have their own data on recommended fouling factors. TEMA [24] also publishes recommended design fouling factors in their standards. A small excerpt of these is provided in Table 13.2.

TABLE 13.1— Typical Refinery Heat Transfer Coefficient

Hot Fluid	Cold Fluid	Overall Coefficient[c], W/m²·K
Steam	Water	1400–4200
No Phase Change		
Water	Water	900–1700
Organic	Water	300–900
Gases	Water	30–300
Light hydrocarbons[a]	Water	300–900
Heavy hydrocarbons[b]	Water	100–300
Water	Brine	200–500
Heavy hydrocarbons[b]	Heavy hydrocarbons	30–300
Condensing		
Light hydrocarbons[a]	Water	500–900
Organic solvents	Water	300–700
Heavy hydrocarbons[b] at vacuum	Water	100–200
Steam, vacuum	Water	900–2600
Ammonia	Water	740–1500
Vaporization		
Steam	C_2–C_8	430–1100
Steam	Light hydrocarbons[a]	280–900
Steam	Heavy hydrocarbons[b]	60–500
Dowtherm	Heavy hydrocarbons[b]	50–200

Notes

[a] Light hydrocarbons are defined as materials with normal boiling points below 300°C. Heat transfer coefficient is a function of viscosity, and lower viscosities (i.e., lower boiling materials) will generally have U-values at the higher end of the range given.

[b] Heavy hydrocarbons are defined as materials with normal boiling points above 300°C.

[c] For heat transfer coefficients in Btu/ft²·h·°F, divide these values by 5.678.

When specifying a heat exchanger, the process engineer should also specify the allowable pressure drop for the heat transfer engineer. The allowable (and eventually the calculated) pressure drops are always specified as "clean" (i.e., without fouling).

In Table 13.2, the "Pressure Drop Factor" column is a multiplier that should be considered in the design of hydraulic systems and prime movers, such as pumps and compressors. The factor should be multiplied by the clean pressure drop of the exchanger.

When specifying a heat exchanger, the allowable pressure drop should be selected based on the fouling tendencies and viscosities of the fluids. This is because the heat transfer coefficient is dependent on these values. Higher pressure drops allow for higher fluid velocities, which can counteract the negative aspects of high viscosity fluids. Table 13.3 provides some recommended allowable pressure drops based on fluid viscosity.

The pressure drops in Table 13.3 are recommended because they should provide reasonable fluid velocities in the exchanger.

One alternative to designing heat exchangers with fouling factors is for the exchangers to be designed using the so-called "no-foul" design method [26]. This method uses high fluid velocities to reduce the fouling tendencies of the system. This can be beneficial because the fouling factor for some services can add significant surface area over the clean requirement. If one is planning to utilize the no-foul design method, it is recommended to add 50–100 % to the allowable pressure drops shown in Table 13.3. However, the pressure drop factors shown in Table 13.2 for severe fouling services should not be reduced because predicting fouled pressure drop is still very much a guess. For the design and rating of other types of heat exchangers in refineries, such as plate and spiral exchangers, the design is usually proprietary and the supplier should be contacted for assistance in rating the performance.

13.6.2 Air-Cooled Exchangers

Air-cooled heat exchangers, often called fin-fan or aerial coolers, are very common in many refineries, especially those where access to raw water for makeup to a cooling tower or sea water are not readily available. Air-cooled exchangers function by having a fan blow atmospheric air through a bundle of (usually) finned tubes through which the process fluid passes. The configuration is cross flow because the air flows perpendicular to the process fluid. Air-cooled exchanger design is usually performed by the engineering contractor or manufacturer.

An evaluation of an air-cooled exchanger can be performed using Eq 13.50, with the condition that the terms U and A_{Eff} are both on the same basis, either on the bare tube area (excluding the fins) or on the finned area. The former is the usual basis. Heat transfer coefficients on a bare tube basis are given in Table 13.4.

To perform a preliminary design of an air cooler, it is necessary to estimate the air-side outlet temperature [27]:

$$(t_2 - t_1) = 8.8 \times 10^{-4} \cdot U \cdot \left[\frac{(T_2 + T_1)}{2} - t_1 \right] \tag{13.67}$$

The air-side temperature rise, $(t_2 - t_1)$, is corrected using the following:

TABLE 13.2—Recommended Fouling Factors

Fluid	Design Fouling Resistance		Pressure Drop Factor
	h·ft²·°F/Btu	m²·K/W	
Acid gases	0.002	0.00035	1.1
Amine/glycol solutions	0.002	0.00035	1.1
Light hydrocarbon vapors	0.001	0.00018	1.1
Vacuum overhead vapors	0.002	0.00035	1.1
Crude oil (<350°F)	0.002–0.003	0.00035–0.00053	1.2
Crude oil (>350°F)	0.003–0.005	0.00053–0.00088	1.2
Crude oil with salt	0.002–0.007	0.00035–0.00123	1.5
Naphtha	0.002	0.00035	1.1
Light gas oil	0.003	0.00053	1.1
Heavy gas oil	0.003–0.005	0.00053–0.00088	1.2
Atmospheric residue	0.007	0.00123	1.5
Vacuum residue/visbreaker tar	0.010	0.00176	1.5
FCC light cycle oil	0.002–0.003	0.00035–0.00053	1.1
FCC heavy cycle oil	0.003–0.004	0.00053–0.00070	1.2
Light coker gas oil	0.003–0.004	0.00053–0.00070	1.2
Heavy coker gas oil	0.004–0.005	0.00070–0.00088	1.2
Lubes solvent	0.001	0.00018	1.1
Lubes extract	0.003	0.00053	1.2
Lubes product	0.001	0.00018	1.1
Water, boiler feed	0.0005–0.001	0.00009–0.00018	1.0
Water, condensate	0.0005	0.00009	1.0
Water, cooling tower	0.001–0.002	0.00018–0.00035	1.1
Water, river	0.003	0.00053	1.2
Water, sea	0.0005–0.001	0.00009–0.00018	1.1
Water, silty or hard	0.003–0.005	0.00053–0.00088	1.2

TABLE 13.3—Allowable Pressure Drop

Viscosity (mPa·s/cP)	Allowable ΔP (kPa/Shell Side)	Allowable ΔP (kPa/Tube Side)
<1.0	35	35–70
1–5	35–70	70–100
5–10	70–100	100–150
10–25	100–150	150–210
>25	Heat transfer engineer to recommend	

$$(t_2 - t_1)_{corrected} = (t_2 - t_1) \cdot (0.0026) \cdot (T_2 - T_1) + 0.886 \quad (13.68)$$

This corrected value is then used to determine the LMTD of the exchanger via Eq 13.51. Similar to shell and tube exchangers, because the flow is not countercurrent, we must correct the LMTD using a correction factor. Various manufacturers publish correction curves. Generally, air-cooled exchangers with four or more tube passes are essentially countercurrent and the LMTD correction factor can be assumed to be 1.0. For fewer tube passes, the curves should be consulted. Most air coolers are designed for an LMTD correction factor of greater than 0.8. For quick evaluations, an assumption of 0.9 is reasonable.

13.6.3 Heating Coils

Heating coils are often provided inside tanks where there is concern about the fluid in the tank becoming very viscous or even freezing if the temperature in the tank were to drop because of ambient cooling. The heat loss from the tank is most precisely determined using the method published by Kumana and Kothari [28]. This method is somewhat involved and requires iteration; however, it provides better results than other methods. An example set of data is provided in Figure 13.22.

Once the heat loss from the tank is determined, one can determine the size of the heating method required to

TABLE 13.4—Typical Heat Transfer Coefficients for Air-Cooled Exchangers

Hot Fluid	Overall Coefficient[a], W/m²·K
Condensing	
Ammonia	550–700
Refrigerant (i.e., propane)	500–650
Naphtha	400–600
Diesel/light gas oil	250–300
Reactor effluent	450–600
Steam	550–900
Gas cooling	
Air	50–200
Hydrocarbon gases	150–200
Hydrogen	20–100
Liquid cooling	
Heavy fuel oil	30–100
Residue	60–100
Vacuum gas oil	60–300
Diesel/light gas oil	150–400
Naphtha	300–500
Glycol Solution	550–700
Water	650–800

Notes
[a] For heat transfer coefficients in Btu/ft²·h·°F, divide these values by 5.678.

maintain the tank temperature. There are several methods for heating a tank, including

- A heating coil containing steam or other heating medium within the tank,
- An electric immersion heater,
- A circulation loop in which the fluid is pumped through an external heat exchanger or fired heater and returned to the tank, and
- A fire tube inside of the tank where a fuel is combusted and the heat of the flue gases heats the tank contents through the wall of the fire tube.

Electric immersion heaters are best suited to small heat requirements, and fire tubes are typically only used where other heating media are not available (such as at remote oil production facilities). In refineries, the most common options are in-tank heating coils and circulation loops through external heaters. The former are best utilized for lighter materials in which mixing in the tank is provided by convection resulting from heating or from movements of product in and out of the tank (i.e., diesels and vacuum gas oils). The latter are best suited to high-viscosity materials in which mixing is not sufficiently provided by convection or oil movements (i.e., atmospheric and vacuum residues).

The sizing of an external heat exchanger is no different than sizing any other heat exchanger in the refinery. This method, with circulation, is the most effective for keeping large tanks warm, especially for fluids with high viscosities in which allowing the tank to cool would result in it being very difficult to pump out the tank. If the heat duty required to maintain tank temperature, or to reheat the tank, is larger than approximately 0.3 MW (10^6 Btu/h), an external heat exchanger is recommended.

Heating coils inside a tank are best used for smaller tanks with lighter materials (i.e., diesel) or for tanks where

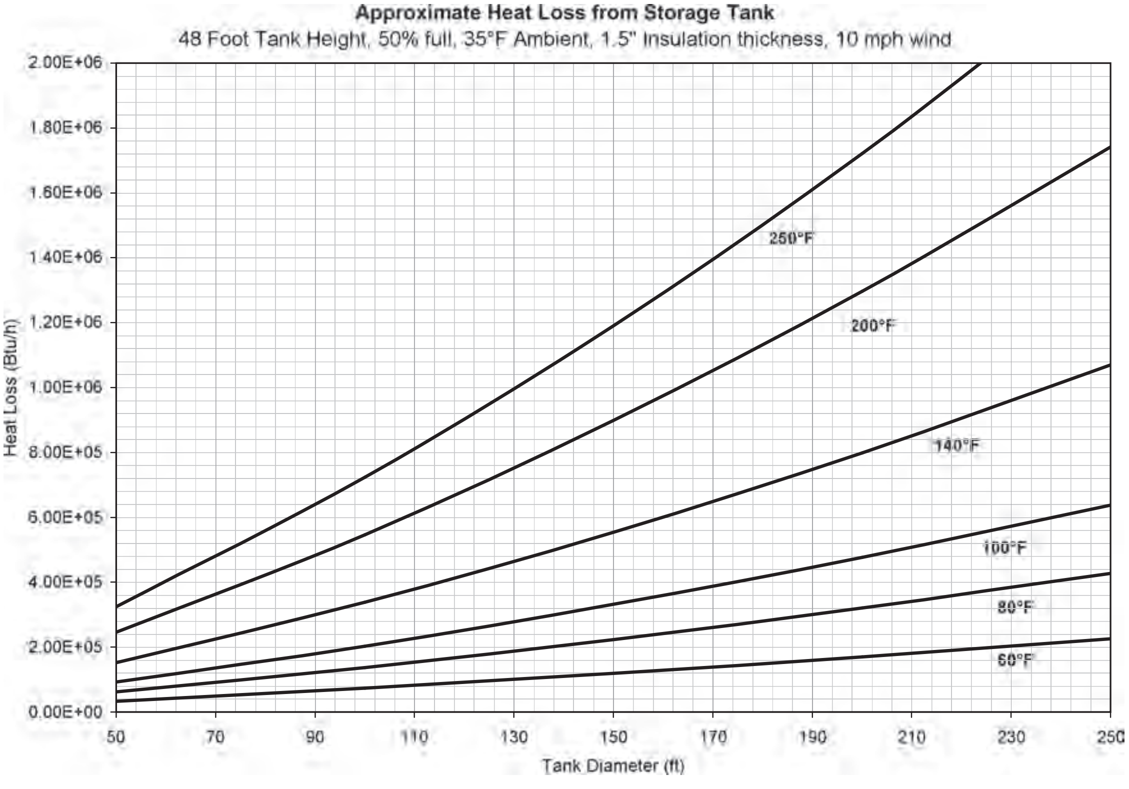


Figure 13.22—Example curves for heat loss from a tank.

some water is expected to decant in the bottom of the tank. The heating coil can then be used to keep the water in the tank from freezing, or perhaps to keep the diesel from falling below the pour point in cold weather. Heating coils inside of tanks are usually heated with steam, although hot oil can and should be used if the fluid in the tank is to be stored at temperatures above 95°C. This is because a steam coil can leak water into the tank contents and, if the temperature were to rise above 100°C, a boil-over event could occur in which the water flashes and pushes hydrocarbon over the top of the tank.

The heating coil can be sized using a typical heat transfer equation for cylinders. The overall heat transfer from the coil to the tank is described by

$$Q = U_o A_{coil}(T_S - T_\infty) \tag{13.69}$$

where:
T_h = average temperature of the heating medium, and
T_∞ = bulk temperature in the tank.

The overall heat transfer coefficient, U_o, is determined via

$$U_o = \left(\frac{1}{h_o} + \frac{1}{h_f} + \frac{t_m}{k_m} + \frac{1}{h_i}\right)^{-1} \tag{13.70}$$

If the heating medium is steam, then the external resistance is orders of magnitude greater than the internal or wall resistance, and even the fouling term is negligible. In this case, just the external coefficient is required and $U_o = h_o$.

If jet-mixers are provided along the walls of the tank, then the heat transfer becomes forced convection, and the equation of Churchill and Bernstein [29] can be used:

$$\overline{Nu_D} = 0.3 + \frac{0.62 \cdot Re_D^{1/2}\, Pr^{1/3}}{[1 + (0.4/Pr)^{2/3}]^{1/4}} \cdot \left[1 + \left(\frac{Re_D}{2.82 \times 10^5}\right)^{5/8}\right]^{4/5} \tag{13.71}$$

where the average Nusselt number is defined by

$$Nu_D = \frac{hD}{k} \tag{13.72}$$

and the Prandtl number is defined by

$$Pr = \frac{C_P k}{\mu} \tag{13.73}$$

The area of the coil used in Eq 13.69 should be limited to those portions that experience fluid velocities above 0.3 m/s (1 ft/s), below which free convection is essentially occurring.

If there are no jet mixers, then one relies on free convection in the tank fluid. This is very ineffective at transferring any significant heat to the tank, but it can still be sufficient to prevent water from freezing. For free convection from a coil, the correlation of Churchill and Chu [30] can be used:

$$\overline{Nu_D} = \left\{0.6 + \frac{0.387\, Ra_D^{1/6}}{\left[1 + (0.559 / Pr)^{9/16}\right]^{8/27}}\right\}^2 \tag{13.74}$$

The Rayleigh number is defined as

$$Ra_D = Gr_D Pr = \frac{g\beta C_P \rho^2}{\mu k}(T_w - T_\infty)\, D^3 \tag{13.75}$$

For Eqs 13.71 and 13.74, the properties of the fluid should be determined at the wall temperature of the tube. For tubes heated with steam, it can be safely assumed that this is essentially the temperature of the steam.

For most tank coils, the overall heat transfer coefficient determined will range from 4.0 W/m²·K (free convection) to 24 W/m²·K (forced convection) (0.7 – 4.3 Btu/h·ft²·°F). The internal heat transfer coefficient can be estimated for steam and liquid heat transfer fluids; however, for steam it is almost unnecessary because it will be orders of magnitude better than for the outside coefficient.

For condensing steam, where the velocities are low (Re < 35,000), Chato [31] recommends

$$\overline{h_D} = 0.555 \cdot \left[\frac{g\rho_l(\rho_l - \rho_v)\, k_l^3 \Delta H_f'}{\mu_l\,(T_{sat} - T_w)\, D}\right]^{1/4} \tag{13.76}$$

where $\Delta H_f'$ is the modified latent heat of the steam:

$$\Delta H_f' = \Delta H_f + \frac{3}{8} C_{P,l}\,(T_{sat} - T_w) \tag{13.77}$$

The wall temperature, T_w, must be determined via iteration.

For a liquid heat transfer fluid, the Dittus-Boelter equation [32] can be used over a narrow range of conditions:

$$\begin{aligned} &Nu_D = 0.023\, Re_D^{0.8} Pr^n \\ &n = 0.3 \text{ for cooling of the tubeside fluid} \\ &0.7 \le Pr \le 160 \\ &Re_D > 10^4 \end{aligned} \tag{13.78}$$

This equation can have errors as large as 25 % [33]; therefore, caution is recommended. More recent correlations by Petukhov [34] and Gnielinski [35] can be used over wider ranges of Reynolds number with higher accuracy, but they require estimation of a friction factor inside of the pipe.

13.6.4 Fired Heaters

Fired heaters, or furnaces, are used in refining applications in which the heat input required is too large to be economical with steam or hot oil heat (i.e., many exchanger shells, plus large boilers) or in which the heat input temperature is higher than is feasible with steam or hot oil. This section deals with process fired heaters and does not discuss boilers or heat-recovery steam generators.

This section defines what fired heaters are and why they are used. It also explains how to perform simple performance calculations for a fired heater. The detailed design of fired heaters is beyond the scope of this text.

13.6.4.1 INTRODUCTION

In many refineries, steam pressures greater than 4500 kPag/650 psig (saturation temperature 260°C/500°F) are often unavailable. In addition, one should remember that higher pressure reduces the latent heat of water, requiring larger flows to obtain a given heat flow. At 334°C (650°F), the latent heat is half that at 300 kPag (44 psig), and at 374°C (705°F) the latent heat of steam is zero. Also, note that a saturation steam temperature of 334°C occurs at 13,500 kPa (1960 psig).

Hot oils can be used to obtain high temperatures at lower pressures than are required for steam. Dow's Syltherm® 800 offers a maximum supply temperature of 400°C (750°F), but this is a liquid phase (sensible heat) medium. Dowtherm® A and Solutia's Therminol® VP-1 offer maximum operating temperatures of 400°C (750°F) in vapor phase operation, but the latent heat is only approximately 200 kJ/kg (86 Btu/lb). Using sensible heat or low latent heat fluids will require very large flows to obtain large duties. Therefore, such heat-transfer fluids are usually restricted to smaller heating requirements.

Fired heaters are generally of a design as shown in Figure 13.23 and are usually designed to API Standard 560, which is also numbered as ISO 13705. Older furnaces and those in regions that did not historically use API standards may not be designed in complete accordance with the standard, but the same methods can be used to evaluate performance.

The parts of the fired heater shown above are described below.

The radiant section or firebox is that part of the heater where the process tubes are heated primarily by radiation from the flame in the furnace. In most fired heaters, 50–70 % of the heat released by combustion of the fuel is recovered in the radiant section.

The convection section is the part of the heater where process tubes are heated by convection from the hot gas leaving the radiant zone. This section usually recovers approximately 10–30 % of the heat released by combustion.

The air preheater is an optional part of the heater that can be used to recover low-grade heat from the flue gas to preheat the combustion air. This is usually economical on heaters larger than 10 MW (30 MMBtu/h), but it is dependent on fuel value and current market capital costs. This can increase the overall efficiency of the furnace to approximately 90 %.

The selective nitrogen reduction section is an optional part of the heater that may be required if limitations on oxides of nitrogen (NO_x) emissions require it. This is briefly described later.

Flue gas cleanup or capture absorbers are uncommon, but they can be required to capture sulfur dioxide (SO_2) or carbon dioxide (CO_2) from the flue gas. The process tubes are the tubes that contain the process fluid(s) inside of the furnace and are exposed to the radiant or convective sections. Process tubes are usually bare tubes, but extended-surface tubes (e.g. fins) are sometimes used in convection sections to obtain higher heat transfer rates.

A return bend or header is a piece of tubing that is bent to 180°, or is cast or forged, to connect two tubes in the furnaces. The burners introduce the fuel and air mixture to the firebox, where the fuel is ignited. Burners can range from simple gaseous fuel nozzles to complex devices that utilize recycled flue gas for NO_x reduction, atomize liquid fuels, or handle particulate solid fuels.

The pilots are small burners, usually operated on an independent fuel supply, which provide the ignition energy for the main burners. Sootblowers are devices used to inject steam or air into the furnace to clean soot from the heat transfer

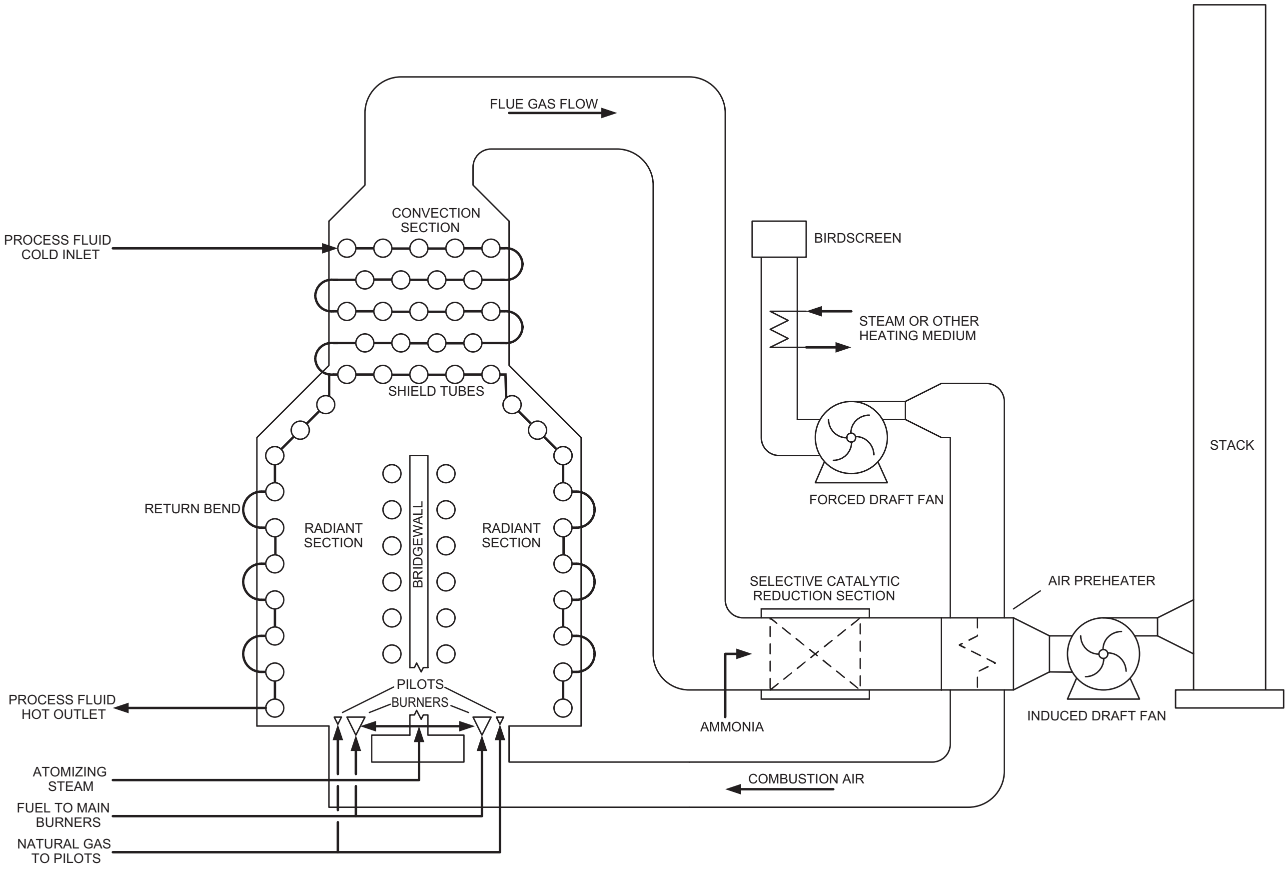


Figure 13.23—Schematic of a refinery fired heater.

surfaces. These are only required on furnaces burning liquid or solid fuels. The casing is the metal covering of the furnace.

The forced- or induced-draft fans provide the motive force to create a pressure profile through the furnace. These are not necessarily required and depend on the size and complexity of the furnace. Such fans are common for large furnaces with air preheaters, selective nitrogen reduction systems, or flue gas capture systems. A furnace with both fans is called a balanced-draft furnace whereas one with no fans is called a natural-draft furnace.

The stack provides two key functions for the furnace. The first is to provide draft, or the induced-pressure profile of the furnace (for furnaces without fans). Because the hot flue gas has greater buoyancy than the cooler atmosphere, the pressure at the bottom of a stack is lower than that at the top of the stack (i.e., atmospheric pressure). This pressure profile (from atmospheric pressure to the lower pressure at stack bottom) is called draft. The second function of the stack is to disperse the flue gas into the atmosphere. The exit temperature, velocity, and elevation of the stack top all affect how the flue gas is dispersed and what the concentration of contaminants in the flue gas (i.e., oxides of sulfur [SO_x] and NO_x) is at grade around the facility.

13.6.4.2 CONFIGURATIONS

Vertical (or helical) cylindrical heaters are generally used for small duties under 10 MW (34 MMBtu/h). These are tall cylinders with a single row of vertical tubes against the wall of the cylinder. A single burner or small pattern of burners is located on the floor of the furnace. In some designs, the tubes are oriented in a helix rather than a bank of vertical tubes. For cylindrical furnaces, the flow to the individual tube passes is usually not controlled. These furnaces are often natural draft and do not have air preheaters, and sometimes they do not have even have convection sections. However, if fuel prices are high, convection sections and air preheat on small furnaces may become more common.

Cabin (or box) heaters are used for larger duties. For very large duties (>30 MW), a multiple cabin heater will likely be selected for constructability and process control reasons. In these furnaces, the process tubes run either vertically or horizontally along the walls of the firebox, and sometimes they run between the rows of burners (double-fired tubes). The burners are either on the floor of the furnace or on the walls. This is the type of furnace depicted in Figure 13.23. The selection of vertical or horizontal tubes is dependent on the process requirements. Double-fired tubes are used when it is desired to keep heat fluxes low. Because these furnaces are large, the feed is usually split into multiple tube passes in the radiant section. The choice to independently control each pass is usually up to the preference of the owner and operator. However, as discussed below, there are good reasons to independently control each pass in some services.

13.6.4.3 APPLICATIONS OF FIRED HEATERS

Fired heaters are often used for the following applications in a refinery:

- Atmospheric and vacuum distillation charge furnaces,
- Delayed coking charge furnaces,
- Visbreaker charge furnaces,
- Hydrotreater/hydrocracker feed furnaces,
- Hydrocracker hydrogen heaters,
- Hydrotreater/hydrocracker fractionation charge furnaces,
- Catalytic reforming charge furnaces,
- Thermal oil heaters (for indirect heat transfer loop),
- Steam superheaters (for superheating steam generated in by the process), and
- Steam-hydrocarbon reformer furnaces (for hydrogen or synthesis gas production).

Charge furnaces for crude and vacuum distillation units are complex units because the feed is vaporizing at high temperatures. Outlet temperatures greater than 360°C (680°F) for atmospheric and 400°C (750°F) for vacuum distillation furnaces are not advised because undesirable cracking reactions and coking/fouling of the tubes are likely at such conditions. Mass fluxes of the process fluid should be kept high to prevent fouling. The high pressure drop and low outlet pressures, particularly in vacuum service, result in the tube passes increasing in size through the furnace because of the increase in volumetric flow. In a new design or evaluation, it is critical to check the velocities throughout the tube passes to ensure that low velocities do not occur (i.e., tube size increases early). These furnaces often have velocity steam injected with the feed to provide additional volume, increasing the fluid velocities in the tubes. To avoid coking problems, average heat fluxes should not exceed 35 kW/m². For furnaces processing very refractory feedstocks (e.g., Athabasca), lower values are recommended.

These furnaces are usually cabin-type heaters (because of the scale) and can have the tubes vertically or horizontally oriented. Vertical tube orientation in vacuum furnaces is not desirable [36] because it forces the process fluid to pass through the highest flux zone multiple times, increasing the chances of coking. The control of the feed to each tube pass is critical in these furnaces because the pressure drop per pass can vary because of varied fouling or heat fluxes.

Delayed coking and visbreaking charge heaters are very specialized designs because the process temperatures are often greater than 480°C (900°F) because the intention is to crack the feedstock. These furnaces are often designed for steam or air spalling and even pigging. In a large delayed coker unit, the furnace may have eight or more cells so that a cell can be taken offline and pigged while the unit is in operation. This spalling or pigging is required because of the buildup of coke and other scale (because of minerals in the feed) on the tubes. For the design or evaluation of a delayed coker furnace, it is recommended to contact the technology licensor. The control of the feed to each tube pass is critical in these furnaces because the pressure drop per pass can vary because of varied fouling or heat fluxes.

Hydrotreater charge furnaces are generally less severe than other furnace applications, except in the case of residue hydrocrackers in which temperatures are high and the feedstock will tend to crack. These furnaces can range in size from small cylindrical furnaces to very large cabin types. Average radiant heat fluxes can range from 30 to 40 kW/m² (lower for heavier materials and higher for naphtha).

For naphtha and kerosene hydrotreaters, a key parameter that must be considered is that the feed to the furnace should be 100 % vapor phase. Having a two-phase feed to the furnace with a 100 % vapor outlet means that somewhere in the furnace tubes there will be a dry point where the last liquid evaporates. At this point in the furnace, the tube metal temperature profile will have a step increase, resulting in very high stresses in the tube. This can result in catastrophic tube failures and should therefore be avoided.

The control of the feed to the individual passes of the furnace is up to the licensor and owner. For a vertical tube furnace, individual pass control is recommended. If the individual passes are not controlled, symmetrical piping on the inlet and outlet of the furnace is critical. If the furnace is single phase (i.e., naphtha), individual pass control is not warranted.

Hydrogen heaters are usually only found in high-severity hydrocrackers. These units are fairly simple, except that process temperatures can reach 538°C (1000°F) with very high hydrogen partial pressures. Additionally, because the heat transfer coefficient on the process side is low, the tube metal temperatures can be very high. All of this requires special metallurgies (e.g., 347H Stainless) and careful monitoring of tube metal temperatures.

Hydrotreater and hydrocracker fractionation furnaces are less severe than crude distillation furnaces, except in the case of residue hydrocrackers. These furnaces can be of whichever configuration is the most economic, although horizontal cabin types are recommended. Average radiant tube fluxes can be from 38 to 50 kW/m^2. For units producing diesel, lower fluxes and lower tube wall temperatures may be desired because temperatures above 360°C (680°F) have been known to result in cracking and undesirable color in the product.

Catalytic reforming furnaces heat the feed to the endothermic reforming reactor. Such furnaces are often designed similarly to naphtha hydrotreater furnaces and are usually vertical cylindrical type.

Thermal oil furnaces are usually vertical cylindrical units, sometimes with convection boxes. The heat fluxes and tube wall temperature requirements are specific to the thermal oil used. These data are readily available from the thermal oil suppliers (e.g., Dow Chemical, Solutia). If the thermal oil is being vaporized, then individual pass control should be considered (unless it is a thermosyphon-type vaporizer with a drum).

Steam superheaters are mostly vertical cylindrical units, usually without convection boxes. The heat fluxes are similar to those of boilers. Because the process-side heat transfer coefficient is low, the tube metal temperatures can be high, requiring special metallurgy.

Hydrogen reformers are very specialized units that can be fired from the top, side, or bottom, and can have vertical or horizontal tubes.

13.6.4.4 COMBUSTION CALCULATIONS

Combustion calculations provide key information about a fired heater design. The first is to determine how much air is required to burn the fuel, and the second is to determine the energy available in the flue gas.

There are two ways to perform combustion calculations. The first is using traditional combustion equations using the stoichiometry of the combustion reactions and the heats of combustion. An adiabatic flame temperature calculation can be used to determine the theoretical flame temperature.

The stoichiometry of combustion can be shown as

$$\mathrm{C}_x\mathrm{H}_y\mathrm{O}_z\mathrm{S}_w\mathrm{N}_v + \left(x + w + v + \frac{y}{4} - \frac{z}{2}\right)\cdot \mathrm{O}_2 \rightarrow$$

$$x \cdot \mathrm{CO}_2 + \frac{y}{2}\cdot \mathrm{H_2O} + w \cdot \mathrm{SO}_2 + v \cdot \mathrm{NO} \qquad (13.79)$$

This is feasible for liquid and solid fuels in which the atomic composition of the fuel is known. In such cases, the fuel composition is usually known on a mass basis and must be converted to molar. For the purposes of combustion calculations, it is safe to assume that sulfur and nitrogen oxidize to the forms shown here because they are small portions of the overall heat of combustion (some of the nitrogen in the fuel will actually reduce to N_2). The nitrogen content of the fuel can simply be ignored in most cases because it has minimal effect on the flue gas composition.

For gaseous fuels, one usually knows the composition on a molecular basis, such as hydrogen, methane, propane, etc. For such fuels, it is easier to use the stoichiometry per component. Here, methane is shown as an example:

$$\mathrm{CH_4} + 2 \cdot \mathrm{O_2} \rightarrow \mathrm{CO_2} + 2 \cdot \mathrm{H_2O} \qquad (13.80)$$

For each reaction, the heat of combustion is known, allowing the total heat of combustion to be calculated:

$$\Delta H_{LHV} = \sum_i x_i \Delta H_{LHV,i} \qquad (13.81)$$

where i is the fraction of a given component in the fuel.

Using this stoichiometry and heats of combustion, we can determine the composition of the flue gas and the heat release of the combustion. A selection of heat of combustion data is provided in Table 13.5.

The heating value of fuel oils can be estimated using the following correlation, which was curve-fitted from data in Chapter 27 of reference 6.

TABLE 13.5—Heat of Combustion Data for Selected Fuels

Fuel	Lower Heating Value (MJ/kg)
Hydrogen	121
Carbon monoxide	10.9
Methane	50.0
Ethane	47.8
Propane	46.4
Butanes	45.8
Gasoline	44.4
Kerosene/jet fuel	43.0
Diesel	43.0
Heavy (No. 6) fuel oil	38.0
Petroleum coke (dry basis)	36.0
Anthracite coal	35.0
Bituminous coal	26–32
Subbituminous coal (range of volatiles)	14–21
Lignite (range of water contents)	5–10
Peat, wet	2.5

$$\Delta H_{LHV} = -12.649 \cdot SG^2 + 9.3575 \cdot SG - 0.275 \cdot (wt\%\ \mathrm{S}) \cdot SG^{-0.75} + 43.9893 \tag{13.82}$$

This equation provides lower heating values (LHVs) in megajoules per kilogram. Conversion to British thermal units per pound is obtained by multiplying the result by 429.9.

The heating value of a gaseous fuel can be estimated from molecular weight if the composition is not available:

$$\Delta H_{LHV} = 5.775 + 1.829 \cdot MW \tag{13.83}$$

This equation provides LHVs in megajoules per Newton-cubic metre and should be considered accurate to ±1.5 MJ/Nm³ for gases with molecular weights below 44.

It is important to account for the inert and excess species in the combustion air and fuel, such as nitrogen (N_2), argon (Ar), water (H_2O), excess oxygen (O_2), and carbon dioxide (CO_2). The last may be present in the fuel at a concentration that is significant (~2 %). The quantity of water vapor present in the combustion air can be determined using a psychrometric chart or simulator. The composition of dry air is approximately 78.08 % N_2, 20.95 % O_2, 0.93 % Ar, and 0.04 % CO_2 (molar basis). The water content in atmospheric air can be significant (6.4 vol % at 100 % relative humidity at 100°F).

Excess oxygen is provided as excess air. Most furnaces are designed for 10–30 % excess air, with the lower end used for gas-fired balanced draft furnaces and the higher end for oil-fired natural draft furnaces. The purpose of excess air is to ensure that combustion is complete, leaving only parts-per-million levels of CO and hydrocarbons remaining. Furnaces operating with sufficient excess air should have at least 2 mol % O_2 remaining in the flue gas.

One aspect that is often overlooked is that the heats of combustion available in the literature are generally at a standard temperature (T_o)—either 298 K (25°C / 77°F) in scientific literature or 60°F (15.56°C/288.7 K) in engineering literature. The heat of combustion values should be net, or LHVs, in which the latent heat of the water in the flue gas is not included. To determine the flame temperature, we must consider the enthalpy present in the combustion air and fuel as well as the heat of combustion:

$$\Delta H_T = \sum_i m_i \int_{T_\circ}^{T_{IN}} C_{P,i}(T)\, dT + \sum_j m_j\, \Delta H_{LHV,j} \tag{13.84}$$

where the ΔH_T term is the total enthalpy change from the inlet air and fuel conditions to the flame. The summation subscript *i* indicates all of the species present in the fuel and combustion air, including inerts. The subscript *j* indicates the reactants in the combustion.

Determining the theoretical flame temperature means that we must assume that the combustion is adiabatic (i.e., no heat losses):

$$0 = \Delta H_T - \sum m_k \int_{T_F}^{T_\circ} C_{P,k}(T)\, dT \tag{13.85}$$

where the appropriate thermodynamic model is used to calculate the specific heat of each component of the flue gas. The subscript *k* indicates all of the species present in the flue gas, including inerts. This equation must be solved for T_F, which is iterative, because of the dependence of the heat capacities, $C_{P,k}$, on temperature.

A commercial simulator makes these calculations much easier than doing so manually because integrating the specific heat functions can be quite involved. The reader is advised to review a thermodynamics text for more on this calculation [37].

A second method of performing a combustion calculation is possible for fuels when the exact composition is known (i.e. gases), using a commercial simulator. Combustion is a free-energy minimization reaction, or at least very close to reaching the minimum free energy of the system. Most commercial simulators have a unit operation called a Gibbs reactor (or something similar) that performs a free-energy minimization calculation by changing the composition of the stream. By inputting all of the reactants and allowing all of the possible combustion products, a Gibbs reactor can accurately estimate the flue gas composition and the theoretical flame temperature (if you make the reactor adiabatic). This method is usually faster, but it should be used with care. The tolerances of the simulators can result in small percentages of unburned fuel (usually hydrogen) and higher than real levels of CO (if it is allowed in the model). It is also not recommended to include species such as nitric oxide (NO), nitrogen dioxide (NO_2), and sulfur trioxide (SO_3) because these reactions are kinetically limited and will not go to a free-energy minimum.

Once the theoretical flame temperature and composition of the flue gas are known, the calculation of the heat available through the radiant and convective sections of the furnace can be determined by calculating the enthalpy available between the flame temperature and the bridgewall temperature (i.e., exit of the radiant section) and then down to the gas flue temperature leaving the convection section. This is again most easily accomplished with a commercial simulator. For a well-designed furnace, the bridgewall temperature should be between 800°C and 1000°C for most services [38].

The design or rating of the radiant heat transfer requires a more detailed analysis than this text can provide. The reader is advised to review the publications by Lobo and Evans [39], Cross [40], Mekler and Fairall [41], and the Heater Design website [42] for more of the detailed heat transfer calculations. The four-part dissertation by Berman [43–46] is also recommended for a complete review of furnace design considerations.

13.6.4.5 EFFICIENCY

A key parameter of fired heater design and evaluation is the efficiency of the furnace. There are two efficiencies often referenced with regard to furnaces: (1) fuel efficiency, which considers only that energy present in the fuel (ΔH_{LHV}), excluding any energy input (or shortage) from the ambient air (if ambient is different than 60°F) or an atomizing medium such as steam, and (2) thermal efficiency, which considers all energy inputs. The thermal efficiency is shown here (from reference 47):

$$\eta = \frac{\Delta H_{LHV} + H_a + H_f + H_m - (Q_r + Q_s)}{\Delta H_{LHV} + H_a + H_f + H_m} \tag{13.86}$$

where:

H_a = enthalpy correction of the combustion air,
H_f = enthalpy correction of the fuel, and
H_m = enthalpy correction of the atomizing medium.

Each value is usually expressed in terms of energy per mass of fuel (MJ/kg fuel, Btu/lb fuel). Alternatively, the calculation can be done on total energy flow (i.e., GJ/h, MMBtu/h) for the furnace.

The values Q_r and Q_s are the heat losses due to radiation to the environment and the heat losses in the stack gas, respectively. The heat losses due to radiation for a furnace will usually be between 1 % and 4 %, with the low end of the range on furnaces that have better casing insulation. The stack losses are directly related to the stack temperature.

The stack losses should be determined via the following equation:

$$Q_s = \frac{1}{m_f} \sum_k m_k \int_{T_s}^{T_\circ} C_{P,k}(T)\, dT \qquad (13.87)$$

There are two choices for performing this calculation. A process simulator can be used to determine the heat available in the flue gas (from stack temperature to reference temperature). This is done by modeling a cooler on the flue gas with the outlet conditions set at 60°F (15.556°C) and a vapor fraction of 1.0. This is necessary to avoid condensing the water in the flue gas. The simulator will predict a pressure much below atmospheric, but this is acceptable because the heat energy is not very pressure dependent.

The second choice is to follow a tabular method, as is presented in Appendix G of reference [47] or as presented in reference [48]. Both references provide an example calculation.

Using an air preheater, it is possible to achieve thermal efficiencies in excess of 92 % in a modern furnace. The limitation on furnace efficiency is usually due to the minimum stack temperature acceptable to avoid sulfuric acid (H_2SO_4) deposition.

13.6.4.6 ACID DEWPOINT

The minimum stack temperature when burning clean fuels, containing no sulfur, is limited simply by the dewpoint of the water vapor in the stack. This water vapor condensing can result in corrosion because dissolved O_2 and CO_2 can attack economizer tubes, air preheaters, and the stack itself. However, few fuels contain no sulfur.

Combustion of fuels containing sulfur result in SO_2. SO_2 can dissolve in condensed water, but it is a weak acid and does not significantly affect the dewpoint in the stack. However, a small portion of the sulfur in the fuel will oxidize to SO_3, which is highly hygroscopic and condenses as H_2SO_4 at temperatures above that of water. Hot H_2SO_4 is corrosive to almost all metals (Ta and Pt excepted). Operating a furnace below the dewpoint of H_2SO_4 will quickly destroy economizer tubes, air preheaters, dampers, and even the stack walls.

The dewpoint of H_2SO_4 can be predicted using the correlation developed by ZareNezhad [49]:

$$\begin{aligned} T_{DP} = 150 + 11.664 \cdot \ln(P_{SO_3}) + 8.1328 \cdot \ln(P_{H_2O}) - \\ 0.383226 \cdot \ln(P_{SO_3}) \cdot \ln(P_{H_2O}) \end{aligned} \qquad (13.88)$$

where T_{DP} is the dewpoint in degrees Celsius and the partial pressures of water and SO_3 are expressed in millimetres of mercury.

The problem of course is to predict the concentration of SO_3 in the flue gas. Oxidation of SO_2 to SO_3 is not well understood. The activation energy required is high, but it is influenced by several factors, such as excess oxygen, flame temperatures, and the presence of catalytic metals in the flame, such as nickel or vanadium from the fuel. Various sources [50,51] indicate that measured levels of SO_3 in flue gas range from 0.1 % to 3 % of the SO_2 concentration. Design guidelines at some engineering firms and boiler manufacturers assume 5 % for design purposes. Additionally, in the design of a fired heater, it is recommended that the flue gas temperature always should exceed the predicted acid dewpoint temperature by at least 25°C (45°F) to account for uncertainties.

A warning for furnaces in cold climates: An uninsulated stack can result in low stack wall temperatures. For one furnace the author assessed, the stack gas exit temperature was 115°C, and the predicted acid and clean water dewpoints were 93°C and 45°C, respectively. With an ambient temperature of –40°C and a wind, the stack wall metal temperature fell to just 32°C. In this case, operators continuously drained acidic water from the stack bottom. If the stack metal temperature is expected to fall below the dewpoint, then an acid-resistant lining (polymer or ceramic) is recommended.

13.6.4.7 SELECTIVE NITROGEN REDUCTION

As environmental regulations are tightened around the world, the implementation of selective nitrogen reduction to obtain very low NO_x emissions is becoming more common. In many jurisdictions, NO_x limits can be achieved using low-NO_x or ultra-low-NO_x burners; however, the strictest rules require greater effort.

Selective noncatalytic reduction (SNCR) is generally performed at a flue gas temperature between 870°C and 1150°C (bridgewall temperature). Urea or ammonia is injected into the flue gas at this point, whereby the ammonia reacts with NO_x to form molecular nitrogen, N_2. Although in theory this can achieve up to 90 % reduction in NO_x, problems of mixing, residence time, and temperature gradients mean that performance is usually limited to 30–40 %.

Selective catalytic reduction (SCR) is generally performed inside of or after the convection section. It requires a flue gas temperature of 230–450°C (450–840°F), with temperatures below 360°C (680°F) requiring longer residence times in the catalyst bed. The catalyst is a ceramic (often TiO_2) support, with an active catalytic layer that can be a base metal oxide (i.e., vanadium or tungsten), a zeolite, or a precious metal (i.e., platinum group). The base metal oxide catalysts are the least expensive, but they have the problem of catalyzing the oxidation of SO_2 to SO_3. Zeolites have a wider range of temperature stability with reduced catalytic activity for SO_x. Platinum-group metals are of course very expensive. The catalyst is usually of a honeycomb or plate configuration, with the former providing smaller units but with higher pressure drop and higher fouling potential.

Other problems with SCR include the potential formation of ammonium sulfate in fuels with high sulfur contents, which can precipitate and plug the SCR and the air preheater. Another problem with coal, coke, and heavy fuel oil-fired furnaces can be the presence of arsenic oxide (As_2O_3) in the flue gas. This gaseous form of arsenic will poison the SCR catalyst.

13.7 TWO- AND THREE-PHASE SEPARATORS

Two- and three-phase separators are a key part of any oil production, upgrading, refining, or chemical synthesis process. This section discusses the design of gravity separators used to separate gas-liquid, liquid-liquid, and gas-liquid-liquid separators. Solids separation is not discussed. A typical example in refining applications is the separation of gas, hydrocarbon liquid (oil), and water.

Separators may be oriented in either the horizontal or vertical; the latter is generally only applicable where the quantity of liquids is small (<10 % by mass) compared with the vapor phase, or where plot space limitations are a factor.

Separator vessels are generally sized based on the disengagement of the phases, with the hold-up volume (time) being secondary. However, the hold-up time, particularly in high liquid rate applications, can govern the sizing of a vessel. This will also be considered herein.

13.7.1 Disengagement Theory

Separator calculations are based on determining the velocity of particles of a dispersed phase from the forces exerted on said particles rising or falling through a continuous phase. Three forces act on a particle moving in a fluid: gravity, drag, and buoyancy. The derivation of these equations has been shown elsewhere and need not be repeated here. Solving these equations for the particle velocity results in the following:

$$u_T = \sqrt{\frac{4 \cdot gD_P(\rho_P - \rho_C)}{3 \cdot C_D \rho_C}} \tag{13.89}$$

The actual settling velocity depends on the drag coefficient (C_D), which is dependent on the Reynolds number of the particle as it moves through the fluid.

$$Re = \frac{\rho_C D_P u_T}{\mu_C} \tag{13.90}$$

The relationship between the drag coefficient and Reynolds number is shown by three equations [6], depending on the Reynolds number:

TABLE 13.6—Settling Regime

Newton's regime	$Re > 1000$	$C_D = 0.44$ (13.91)
Intermediate regime	$1 < Re < 1000$	$C_D = \left(\frac{24}{Re}\right) \cdot \left(1 + 0.14 \cdot Re^{0.7}\right)$ (13.92)
Stokes' regime	$Re < 1$	$C_D = \frac{24}{Re}$ (13.93)

The terminal velocity of the falling (or rising) particle is calculated and then compared with the superficial velocity of the continuous phase.

$$u_S = \frac{Q_C}{A_X} \tag{13.94}$$

If the terminal velocity is higher than the superficial velocity of the continuous phase, then the particle will fall (or rise) against the continuous phase motion. If not, then it will be carried with the continuous phase.

Many published methods for sizing separators use the Souders-Brown equation, which uses the empirical factor K to relate the allowable superficial velocity of the continuous phase to the difference in fluid densities:

$$u_a = K\sqrt{\frac{\rho_P - \rho_C}{\rho_C}} \tag{13.95}$$

Separation device vendors often have values of K available for their specific equipment, but a typical published source is available in the Gas Processors and Suppliers Association (GPSA) Engineering Databook. Table 13.7 is taken from this source:

TABLE 13.7—GPSA *K* Values

Separator Type	Pressure (psig)	*K* Factor (ft/s)
Horizontal with vertical pad		0.40–0.50
Vertical with horizontal pad	Atmospheric	0.35
	300	0.33
	600	0.30
	900	0.27
	1500	0.21
	Vacuum	0.20

Notes:
K = 0.35 at 100 psig; subtract 0.01 for every 100 psi above 100 psig.
For glycol or amine solutions, multiply the above K values by 0.6–0.8.
Typically use one half of the above K values for approximate sizing of vertical separators without mist eliminators. For compressor suction scrubbers and expander inlet separators, multiply K by 0.7–0.8.

The K value can be related to the particle size and drag coefficient by setting the Souders-Brown allowable velocity equal to the terminal velocity determined in Eq 13.89:

$$K = \sqrt{\frac{4 \cdot gD_P}{3 \cdot C_D}} \tag{13.96}$$

This allows one to use the K-value method for sizing of a separator and then checking the minimum particle size that would disengage in the given dimensions (or vice versa).

13.7.2 General Assumptions and Clarifications

In general, the equations provided for disengagement are based on a dilute suspension of small, rigid, spherical particles falling (or rising) through a stagnant Newtonian medium. There are several situations in which this is not the case.

If the continuous phase is non-Newtonian (i.e., viscosity is shear-dependent), then the reader is directed to Perry's Handbook [6] for guidance on such separations. If the particle sizes are very small (< 0.5 micron), then

Brownian motion can control the separation because the particles are influenced by individual molecule motion, which can overcome the force of gravity. If the particles (droplets/bubbles) are large enough to become distorted from spherical, then this will change the drag equations. Distortion from spherical is probable if the Eötvös number (N_{EO}) falls below 0.4:

$$N_{EO} = \frac{gD_P \cdot |\rho_P - \rho_C|}{\sigma} \tag{13.97}$$

where σ is the interfacial tension between the phases. If the particles are likely to be nonspherical, then the correlations of Clift [52] or Hu and Kintner [53] should be considered. If the dispersed phase is not dilute in the continuous phase (<5 vol %), then two possible problems arise with the aforementioned equations. The comparison between the particle's terminal velocity was made with the superficial velocity of the continuous phase. If the dispersed phase is not dilute, then the comparison should be made against the actual (local) velocity of the continuous phase, which would have to take into account the space occupied by the particles. Second, in a nondilute suspension, the particles may affect settling. Unlike the setting of solid particles, coalescence becomes important and will affect the drag coefficient of the droplets/bubbles, increasing the terminal velocity but potentially changing the sphericity of the droplets. If particles resist coalescence, then the terminal velocity will decrease (the droplets behave like solid particles) and the particles may hinder movement. Hindered settling can be estimated by the Maude-Whitmore [54] equation, although it and other hindered settling methods contain terms that requires empirical data.

13.7.3 Liquid Hold-Up

The liquid hold-up volumes of vessels may govern the sizing, depending on the application. The calculation of liquid hold-up is simply the multiplication of the liquid-phase flow rate by the hold-up time desired. The geometry of the vessel can then be determined based on that volume. Liquid hold-up is often separated into two categories: hold-up and surge.

Hold-up time is the time it takes to reduce the liquid level from normal (NLL) to low (LLL) at normal outlet flow rates with zero inlet flow. This time should be set considering the quality of control and reliability of the upstream facilities and the requirements of downstream equipment. For vessel feeding pumps, one should also consider the potential risk to the pump should the vessel go empty.

Surge time is the time it takes to increase the liquid level from NLL to HLL at normal inlet flow rates with zero outlet flow. This time should be set considering the need to insulate the upstream facilities from disruptions downstream. In combination, the hold-up and surge times should provide sufficient time for the control system to react to changes and adjust before the separator becomes full or empty. Some operating companies like to ensure that the surge time is sufficient for an alert human operator to react to the situation.

Liquid hold-up times for typical applications are shown in Table 13.8. Different refinery operating companies or engineering firms may use different values. Unless the operating company has specific rules, surge time should be set to 25–50 % of the hold-up times shown here.

TABLE 13.8—Typical Hold-Up Times for Separators

Service	Hold-Up Time (min)
Uncontrolled feed to units	
Wide variation in operations, batch operations.	30–300
Minor variation in operations, predictable variability	20–30
Controlled feed from other process units	
Upstream unit has poor control (yield variation)	15
Upstream unit has poor control (unsteady flow on level control)	10
Upstream unit has good control (steady flow on flow control)	5
Equipment inside of a process unit	
Column sump feeding another column	5
Feed to a distillation column	5
Feed to a series of distillation columns	10
Column reflux drum (depending on control scheme)	2–5
Feed to a fired heater	10
Feed to a low head charge pump	5
Feed to a high head charge pump	10
Liquid knockout drum	5
Refrigerant flash drum	2
Product directed to off-plot storage	5
Reboilers (kettle-type)	2
Steam drums	15

During the design of a new separator, the hold-up volumes are generally assumed to be between the tangent lines of the vessel, and the volumes (or partial volumes) of the heads are ignored; this may not be prudent in the case of a revamp or when generating data for dynamic simulations or controller tuning in which the actual liquid volume in the vessel needs to be considered.

The equations for the liquid volume in a vertical vessel are simply that of a cylinder:

$$V_L = \pi \cdot r^2 \cdot h_L \tag{13.98}$$

The value of h_L should be the distance between the liquid level of interest and the bottom tangent line.

For a horizontal cylinder, the volume of liquid in the vessel is only that of a partial cylinder. The equation for the partial volume of a horizontal cylinder is shown here:

$$V = L \cdot \left(r^2 \cos^{-1}\left(\frac{r-h}{r}\right) + (h-r) \cdot \sqrt{2hr - h^2} \right) \tag{13.99}$$

This equation is valid for values of h above or below the centerline of the vessel as seen in Figure 13.24. The cross-sectional area can be obtained by solving only the portion within the parentheses (i.e., divide volume by length).

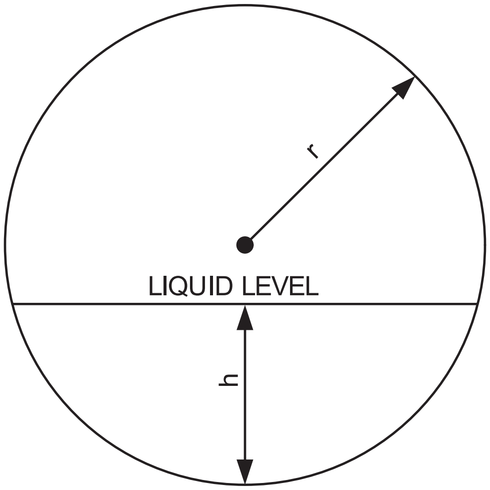


Figure 13.24—Partial section of a circle.

13.7.4 *Vertical Separator Procedure*

The sizing of a vertical gas-liquid separator is the most basic case. The liquid droplets will separate from the gas phase if their terminal velocity downward exceeds the superficial velocity of the gas flowing up the vessel, as shown in Figure 13.25. As noted previously, vertical separators are selected when there is minimal liquid volume and vapor-liquid separation governs.

- The particle size of the desired separation should be selected. This is the minimum particle size that should be carried over from the separator. A reasonable particle size for most separators is 500 μm. Smaller values (200–400 μm) are often used for flare or vent knockout drums to prevent liquid carryover into the stack or in compressor suction drums to prevent liquid ingress to the machine.
- The Reynolds number of the selected particle size should be determined per Eq 13.90.
- The drag coefficient of the selected particle size should be determined with the appropriate equation from Table 13.6.
- The *K* value can be determined from Eq 13.96 and compared with typical values or values specific to the type of internal (i.e., mesh pad, vane separator) to be used. If the *K* value is significantly lower than the typical values, this indicates that your particle size separation is aggressive compared with typical petroleum industry separators.
- Use the terminal velocity of the particle as the superficial vapor velocity, and determine the required cross-sectional area of the separator via Eq 13.94. From this, calculate the inside vessel diameter.
- Using the required hold-up time, calculate the hold-up volume from the liquid rate flowing into the separator. Divide by the cross-sectional area of the vessel to determine the height of liquid between the HLL and LLL. If this value is very large (>3D), consider a horizontal vessel or make the vessel diameter larger (i.e., liquid hold-up governs).
- Determine the overall dimensions of the vessel with the following rules. The recommended lengths for each section of the vessel are shown in Table 13.9 and Figure 13.5.

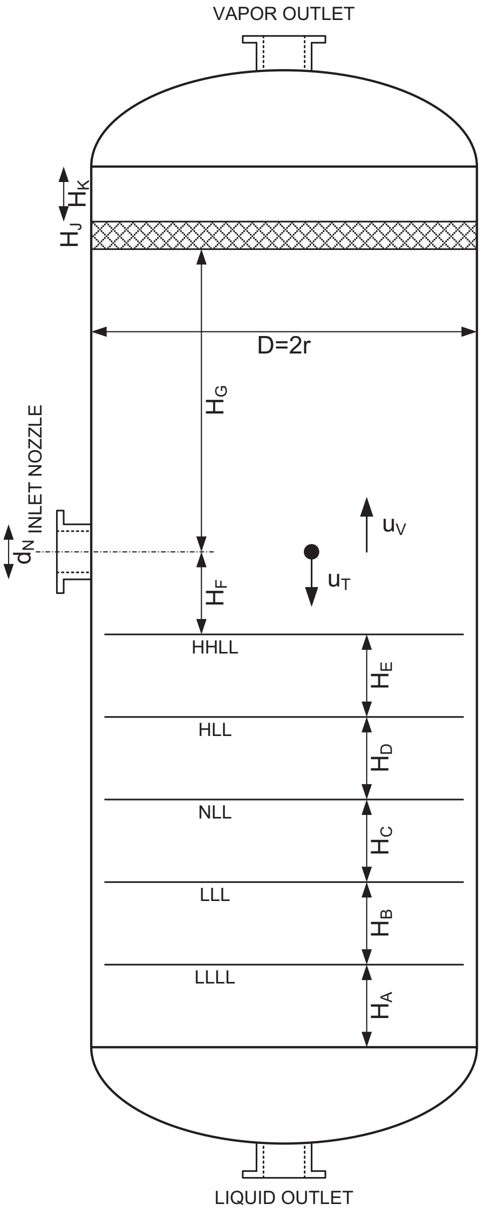


Figure 13.25—Vertical separator schematic.

The total height of a vessel should be between 3 and 6 times the vessel diameter. The optimal length/diameter (L/D) ratio is an economic factor related to the specifics of the situation. Parameters affecting the optimization include

- Operating and design conditions,
- Weight,
- Capital cost,
- Metallurgy,
- Plot space available, and
- Transportation limitations of fabricator to site.

A simple rule of thumb that is based on the weight of the vessel is that higher pressures justify higher L/D ratio. A typical set of values for carbon steel vessels are

TABLE 13.9—Vertical vessel dimension

Dimension	Recommended Length
H_A	Bottom tangent to LLLL (shutdown) should be ≥ 500 mm (10″). The minimum connection distance of a level instrument from the bottom line is approximately 300 mm. Therefore, the lowest control point should be slightly above this.
H_B	LLLL and LLL should be minimum 300 mm (6 in.) or 1–2 minutes of hold-up time.
$H_C + H_D$	LLL and HLL as calculated in step 6.
H_E	HLL and HHLL (shutdown) should be minimum 300 mm (6 in.) or 1–2 min of hold-up time.
H_F	HHLL (maximum liquid level) and inlet nozzle centerline should be ½*D* + ½ d_N
H_G	Inlet nozzle centerline and mesh pad or vane device should be ≥½*D*
H_J	Mesh pad thickness is usually 300 mm (6 in.), but other devices may be more or less.
H_K	From mesh pad/vane device to top tangent should be ≥½*D*.

TABLE 13.10—Optimal L/D Ratios

Design Pressure (kPag)	L/D at Minimum Weight
<1000	2–3
~2000	3–4
~4000	4
>8000	5+

A larger diameter than that required for vapor-liquid separation is acceptable if required to optimize the vessel cost and weight. Using the equations provided in reverse, one can estimate the size of particles that would carry over a larger diameter vessel.

13.7.5 Vertical Three-Phase Separator Procedure

In some rare cases, a vertical separator may be specified for three-phase (gas-liquid-liquid) separation. This is not common because a horizontal separator provides a longer separation flow path and will perform better as a liquid-liquid disengagement device. However, in situations with low liquid flows and plot space (e.g., offshore) limitations, a vertical three-phase separator may be necessary.

The procedure for sizing such a separator is the same as above, except that the engineer must check the disengagement of the two liquid phases. In most refinery applications this is the separation of oil and water. The disengagement calculations must be performed using oil and water as the continuous phase to check the rate at which water droplets fall through oil and to check the rate at which oil droplets rise through water.

The terminal velocity of the droplets of the dispersed phase must be checked against the superficial velocity of the continuous phase, using Eqs 13.89 through 13.93. Liquid-liquid separations almost always fall in the Stokes' law range. Because each separation is based on the same density difference, the more difficult separation (assuming the same superficial velocities and droplet sizes) will be that in which the continuous phase has the higher viscosity. For naphtha- through diesel-range materials, this means that separating oil from water is more difficult, whereas for heavier cuts the separation of water from the oil phase is more difficult. Likewise, the high viscosity of amine solutions can make separation of hydrocarbon droplets difficult.

Droplet size selection for liquid-liquid separation can be difficult. For low-viscosity systems, separation of droplet sizes of 100 μm can be expected. For high-viscosity systems (>50 cP), it can be difficult to separate droplets smaller than 1000 μm (0.04 in.) in a reasonably sized vessel.

For the rare case of a two-phase liquid-liquid separator (no vapor), the sizing calculations are done using the same methods except that the superficial velocity of each phase must be less than the terminal velocity of the desired particle size to be separated. Whichever continuous-phase superficial velocity results in the larger vessel diameter governs. Additionally, one must consider whether the feed should be above or below the interface-level control range. In general, the feed should be above the high interface level if the separation of the light-phase droplets from the continuous heavy phase is more difficult (i.e., more residence time for the heavy liquid) and below if the reverse is true. However, if the ratio of the flows is quite different or the desired hold-up time would result in a very large vessel, one could consider the alternative.

For a three-phase vertical separator, the light liquid draw must be from the side of the vessel or from a standpipe inside of the vessel that extends above the high interface level. Another option is to include a vertical or inclined baffle in the vertical vessel. This is most common in situations in which a small volumetric rate of oil is present in a great volume of water. The baffle should extend above the inlet nozzle to ensure that all liquid droplets fall to the interface before passing over the baffle. The baffle should also extend below the light liquid draw, forcing all liquid under the baffle, after which the light phase will rise up on the outlet side of the baffle. A key issue to consider is that the cross-sectional area for determination of superficial velocity is now only a partial circle on the side of the baffle in question. This can be calculated using Eq 13.99 by dividing by the vessel length.

13.7.6 Horizontal Separator Sizing Procedure

Sizing of horizontal separators is basically the same logic as for vertical separators except that the motion of the particles due to gravity is no longer parallel to the bulk motion of the continuous phase. For dilute dispersed-phase systems, we can safely assume that the particles fall vertically as they move horizontally with the continuous phase. We must then determine if a given particle size will fall (or rise) from the inlet nozzle to the interface before the continuous phase reaches its outlet nozzle.

Figure 13.26 shows a simple horizontal vapor-liquid separator and a horizontal vapor-liquid separator with a mesh pad disengagement device at the outlet. The procedure that follows assumes that vapor-liquid separation governs the sizing; alternative cases are discussed briefly afterward.

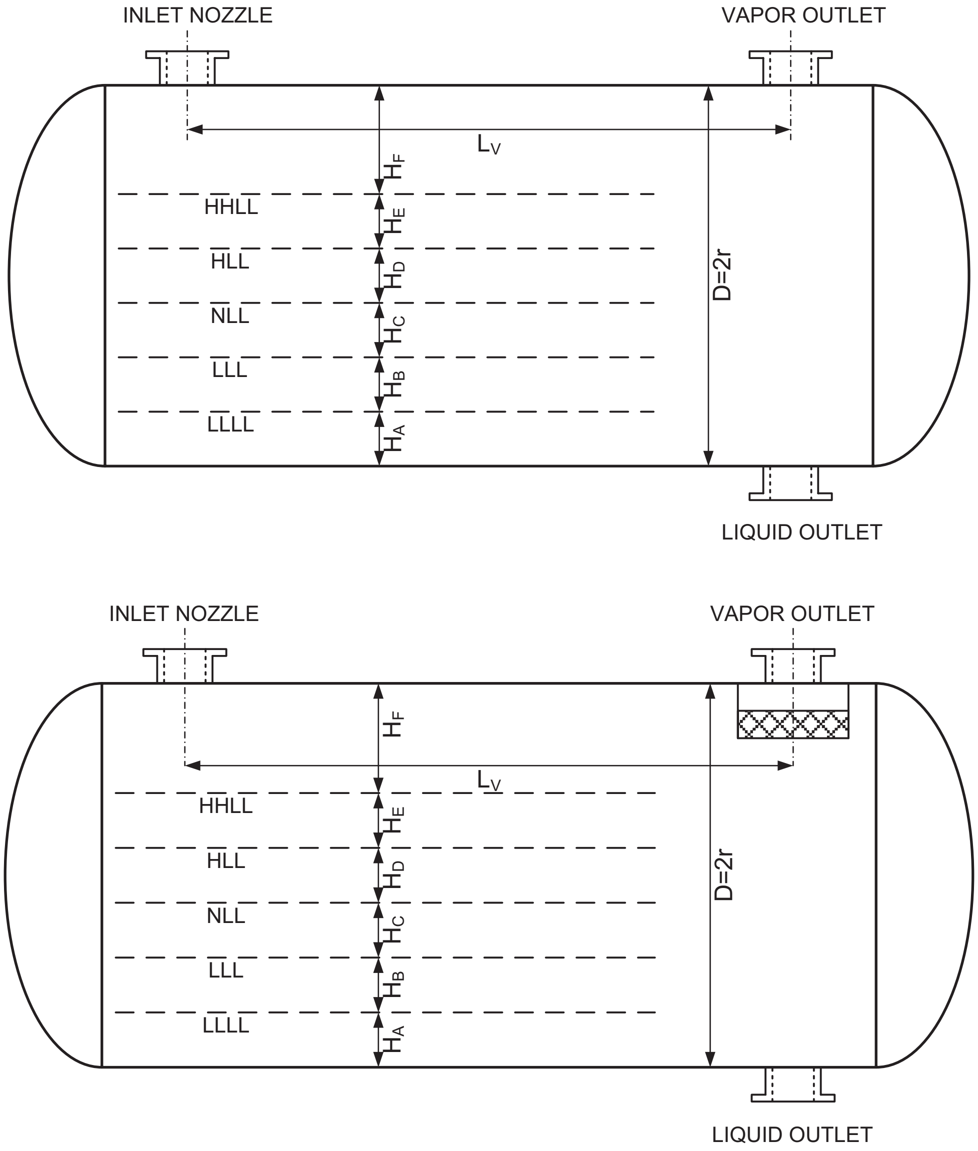


Figure 13.26—Schematics of two-phase horizontal separators.

1. Determine the terminal velocity of a liquid droplet falling through the vapor using Eqs 13.89 through 13.93.
2. Select the desired hold-up and surge times from Table 13.8. Determine the hold-up and surge volumes via

$$\begin{aligned} V_H &= T_H Q_L \\ V_S &= T_S Q_L \end{aligned} \tag{13.100}$$

3. Select an appropriate L/D ratio from Table 13.10.
4. Calculate a preliminary cross-sectional area using the following equation:

$$A_T = \frac{\pi}{4} \cdot \left(\frac{4 \cdot (V_H + V_S)}{0.4 \cdot \pi \cdot \left(\frac{L}{D} \right)} \right)^{2/3} \tag{13.101}$$

5. Determine diameter via simple geometry.
6. Calculate the length of the vessel using the selected L/D ratio. Some engineering and operating companies use the full length of the vessel for separation. The author recommends deducting length to account for the fact that the inlet and outlet nozzles are not located at the tangent line of the vessel and therefore the travel path of the continuous phase is shorter than the tangent-to-tangent length of the vessel. A good assumption for the distance from the tangent line to the inlet and outlet nozzles is half of the diameter of the nozzle plus 150 mm (6 in.) to allow for reinforcing pads and the usual distance from the tangent to the seam weld. This should be checked later once the vessel mechanical drawings are available. The nozzle sizes can be sized based on normal hydraulic criteria for the piping (i.e., pressure drop and velocity).
7. Check that the length of the vessel is sufficient for the liquid hold-up volume. This can be calculated by dividing the hold-up volume by the cross-sectional area

of the liquid phases in the vessel. You may calculate this using Eq 13.99 with the liquid height as h. This should result in a value very close to the L calculated in step 6. If not, use the largest L value.

8. Set the vapor space height (H^F) equal to 0.25D or 450 mm (18 in.), whichever is greater. If the vessel will have a mesh pad or other disengagement device, then you must account for the space occupied by the device. Usually, a mesh pad is approximately 150 mm thick and placed approximately 150 mm from the top of the vessel. Additionally, you must have sufficient clearance under the mesh pad to the liquid level—usually at least 300 mm (18 in.). Therefore, in such a case the dimension H_F must be at least 750 mm (24 in.) to provide sufficient disengagement space.
9. Using Eq 13.99, calculate the cross-sectional area of the vapor space using H_F as h.
10. Calculate the liquid dropout time:

$$\Theta_L = \frac{H_F}{u_T} \tag{13.102}$$

11. Calculate the minimum length of the vessel for vapor-liquid disengagement:

$$L_{\min} = \frac{Q_V \Theta_L}{A_V} \tag{13.103}$$

12. If L_{min} is less than the length calculated in steps 6 and 7, then the vessel is large enough for disengagement. If not, use either a larger diameter or a large L/D ratio and repeat calculations starting at step 5 to check that all of the requirements are met or exceeded with a larger vessel.

13.7.7 Horizontal Three-Phase Separators

A horizontal three-phase separator is usually the most common type of three-phase separator in a refinery or gas processing plant because it offers the best separation of the liquid phases. There are three basic types of separator that are usually used: a weir configuration, a boot configuration, and a bucket and weir configuration. These are shown in Figure 13.27.

13.7.7.1 SEPARATOR WITH WEIR

A weir configuration is commonly used if the volume of the heavy liquid phase is much larger than the light liquid phase and if the separation of the light liquid phase is more difficult that the reverse. This is common of light hydrocarbons and water as well as light hydrocarbons and amine solutions.

The vapor-liquid separation is as described previously and can be calculated the same way. The key difference here is that the length for the hold-up of the heavy liquid is only on the left side of the weir (as shown in the figure), and the hold-up of the light liquid is only on the right side of the weir. The procedure for sizing the liquid sections of the vessel follow.

1. A first guess at the overall diameter of the vessel can be obtained using the method shown above for the simple two-phase separator, combining the hold-up volumes of the two liquids in Eq 13.100. The sizing of the vapor space can also be done as shown above.
2. The first step in the liquid-liquid disengagement is to calculate the rise rate of the light liquid droplets in the heavy liquid. As for the vertical separator, you must select a droplet size that is acceptable to carryover. For low-viscosity continuous phases, 100 μm or less is achievable in a reasonably sized vessel. For high-viscosity systems, droplet sizes of 1000 μm may be required. Stokes' law almost always governs liquid-liquid separations because of low Reynolds number.
3. Calculate the liquid droplet rise time:

$$\Theta_{LL} = \frac{H_A + H_B + H_C + H_D + H_E}{u_T} \tag{13.104}$$

where the dimensions designated H are shown in Figure 13.27a.

4. Calculate the cross-sectional area of the heavy liquid phase ahead of the weir using Eq 13.99. The height h is the numerator of Eq 13.104. In the following equations, this area will be designated by A_{HL}.
5. Calculate the minimum length ahead of the weir of the vessel for liquid-liquid disengagement:

$$L_{\min} = \frac{Q_{HL} \Theta_{LL}}{A_{HL}} \tag{13.105}$$

6. Check the hold-up time volume:

$$V_{HL} = L_{\min} \cdot A_{HL} \tag{13.106}$$

7. If the hold-up volume calculated in step 6 is greater than or equal to that selected in step 1, then the vessel is large enough. If it is not, then the hold-up time governs the sizing. Increase the diameter or length and recalculate to check the separation.
8. You can also check the separation of the heavy liquid droplets from the light liquid. This is done by calculating the cross-sectional area of the light liquid above the high-high interface level (HHIL) and the top of the weir (dimension H_L in Figure 13.27a) using Eq 13.99 twice: once for the HHLL level and once for the HHIL level and subtracting. The HHIL should be approximately 150 mm (6 in.) below the top of the weir to ensure no heavy liquid flows over the top of the weir. Then, calculate the falling time for the heavy liquid droplet to fall across this distance in the length of the vessel upstream of the weir. Usually this is done iteratively to check the droplet size that can be separated.
9. Finally, set the distance after the weight to the tangent line by selecting a series of liquid levels below the weir top and use the hold-up volume of the light liquid.

13.7.7.2 SEPARATOR WITH BUCKET AND WEIR

A separator with a bucket and weir arrangement (see Figure 13.27b) is sized in the same manner as for the weir configuration except that the distance for liquid-separation is only up to the bucket inlet. The bucket is more of a trough across the width of the vessel for a small volume of light liquid to be "skimmed" from the surface of the much larger heavy liquid phase. This is a common configuration for a sour water or rich amine flash drum, in which very small quantities of hydrocarbon are expected.

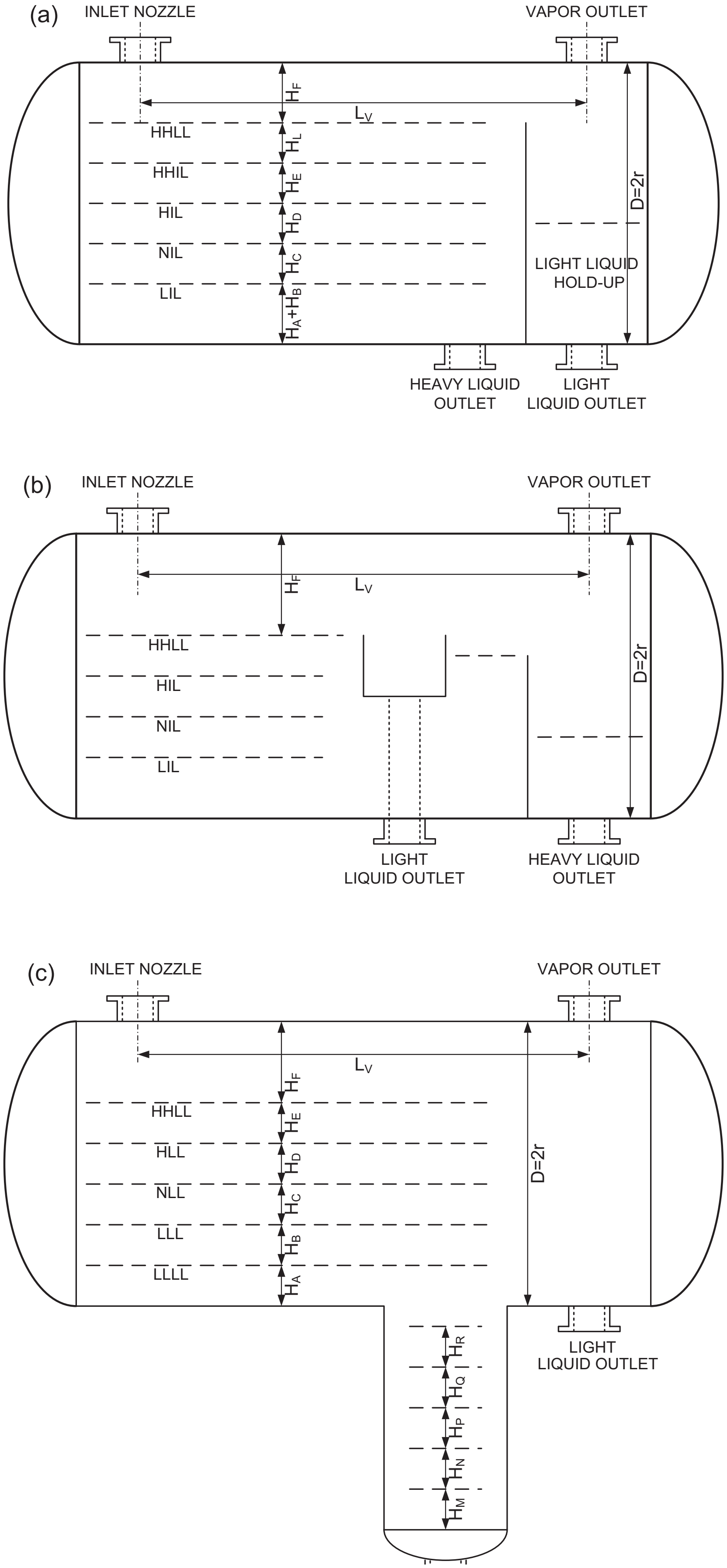


Figure 13.27—Three-phase horizontal separator schematics.

The bucket size is determined using the desired hold-up time of the light liquid assuming level controls 150 mm (6 in.) from the top and bottom of the bucket. Equation 13.99 can be used to determine the cross-sectional area of the bucket. Because there is no possibility of getting heavy liquid out of the bucket, it is not necessary to check for liquid-liquid disengagement therein.

Finally, in a bucket and weir situation the hold-up and surge time of the heavy liquid phase for purposes of protecting downstream equipment (i.e., a pump), one must only consider the volume on the outlet side of the weir. For such vessels, the volume after the weir can be significant such that the weir may be located some distance from the outlet end of the vessel.

13.7.7.3 SEPARATOR WITH BOOT

A separator with a boot is used primarily when the volume of light liquid is significantly larger than the volume of heavy liquid or when the separation of the heavy liquid from the light liquid is more difficult (light liquid is more viscous). The procedure follows.

1. A first guess at the overall diameter of the vessel can be obtained using the method shown above for the simple two-phase separator, combining the hold-up volumes of the two liquids in Eq 13.100. The sizing of the vapor space can also be done as shown above for the two-phase separator.
2. The first step in the liquid-liquid disengagement is to calculate the drop rate of the heavy liquid droplets in the light liquid. As for the vertical separator, you must select a droplet size that is acceptable to carryover. For low-viscosity continuous phases, 100 μm or less is achievable in a reasonably sized vessel. For high-viscosity systems, droplet sizes of 1000 μm may be required. Equations 13.89 through 13.93 are used; Stokes' law almost always governs liquid-liquid separations because of low Reynolds number.
3. Calculate the heavy liquid droplet fall time:

$$\Theta_H = \frac{H_A + H_B + H_C + H_D + H_E}{u_T} \qquad (13.107)$$

   where the dimensions designated H are shown in Figure 13.27c.

4. Calculate the cross-sectional area of the light liquid phase using Eq 13.99. The height h is the numerator of Eq 13.107. In the following equations, this area will be designated by A_{LL}.
5. Calculate the minimum length ahead of the boot of the vessel for liquid-liquid disengagement:

$$L_{\min} = \frac{Q_L \Theta_H}{A_L} \qquad (13.108)$$

6. Next, we must size the boot. The boot diameter must be set such that the superficial velocity of the heavy liquid phase downward is less than the terminal rising velocity of a light liquid droplet. Once again, we must select a droplet size. A reasonable value is 100 μm for most of these services. The methodology is identical to that shown previously for a vertical separator. Boot diameters are usually a minimum of 600 mm (24 in.) for fabrication reasons. If the boot diameter is more than 50 % of the vessel diameter, then consider a weir configuration because the heavy liquid volume is too large for a boot.
7. Once the boot diameter is determined, set the length of the boot using the desired hold-up time of the heavy liquid. If the boot length is greater than $3D_{boot,}$ consider a larger diameter boot. Also, consider that the minimum distance between liquid levels should be 150–300 mm (6–12 in.) because many level instruments only have fidelity to such distances. This means an absolute minimum boot length at 5 × 150 mm or 750 mm (30 in.).
8. Once the boot size is known, we can check the overall length of the vessel. The overall length can be calculate using

$$L_T = L_{\min} + 1.25 \cdot D_{boot} + d_N + 300\ mm\ (12'') \qquad (13.109)$$

   where:
   D_{boot} = boot diameter and
   d_N = light liquid outlet nozzle diameter.

   The 1.25 factor and 300-mm (12 in.) allowances are to ensure enough space is present for reinforcing pads. Another check that should be performed is whether the dimension given by $L_T - L_{min}$ is greater than 2400 mm (96 in.). If so, then a circumferential seam in the vessel may fall inside of the boot connection. This is not desirable. Talk with your mechanical engineer or vessel fabricator about alternatives, such as placing a girth seam between the outlet nozzle and the boot.

9. Check the hold-up volume for the light liquid:

$$V_{LL} = L_T \cdot A_{LL} \qquad (13.110)$$

10. If this is less than the desired hold-up volume, then the vessel should be made longer or the diameter increased.

13.7.7.4 CONCLUSIONS

As can be clearly seen, the sizing of a three-phase separator required significant iteration to ensure that all of the required criteria are met. For an existing separator that you wish to check rate, the equations can simply be solved in an alternative order to determine the particle sizes that can be separated.

13.7.8 Inlet Devices to Assist Separation

As can be seen clearly in Eq 13.89, the force of gravity and droplet size are the primary parameters for separator performance, other than the fluid properties themselves. Therefore, various technologies are available to improve separation by conditioning the inlet flow to a separator to improve the separation.

13.7.8.1 SIMPLE DEFLECTION BOX

The first device is a simple deflection plate at the inlet to a separator. The purpose of a deflection plate is to direct the inlet flow to prevent entrainment or splashing. The key design parameter of an inlet box is that the velocity of the fluid passing through the outlets of the box should be lower than that of the fluid entering the inlet nozzle. This should ensure reduced velocities and minimize small droplet formation.

In a vertical separator, these are usually boxes to direct the flow around the sides of the vessel. The designer should remember to consider the flow area out of each side of the box.

In a horizontal separator, the inlet box usually directs the inlet flow toward the head and away from the vessel outlets. As previously stated, the inlet box should reduce the fluid velocity from the velocity entering via the inlet nozzle. A good rule of thumb is also that the inlet box depth should be half of the distance from the top of the vessel to the HHLL and should allow 450-mm (18 in.) clearance between the HHLL and the box.

13.7.8.2 VANE-TYPE DEVICE

Vane-type inlet devices are proprietary to several suppliers, including Koch-Glitsch, Shell Global Solutions (i.e., Schoepentoeter), and others. These devices are most common in vertical separators and distillation columns. They are designed to evenly distribute the vapor and liquid throughout the vessel, avoiding localized entrainment of liquid droplets in the vapor phase. They are also designed to minimize the formation of very small droplets as well to minimize entrainment.

13.7.8.3 CYCLONE DEVICES

Cyclone devices include single and multiple cyclone devices that can be used in vertical and horizontal separators. There are numerous suppliers of such technology. The idea of a cyclone device is that by accelerating the fluid around a conical tube, the value of g in Eq 13.89 is increased significantly, improving separation. Additionally, liquid droplets are forced to coalesce into larger droplets on the surface of the cyclone. The sizing of these devices is proprietary but can be effective to ensure separation, to reduce vessel sizes, or to debottleneck an existing separator.

13.7.9 Foam

One problem that exhibits itself in some refinery separators is the formation of foam. This is most often found in crude preflash drums/columns, hydrocracker high-pressure separators, and amine flash vessels. Foam can form in any system, but it is more prone to form in systems containing surface-active species, including but not limited to carboxylic and naphthenic acids, phenols, asphaltenes, heat-stable salts, iron-sulfide particles (in amines), or fine mineral particles. The presence of water in the hydrocarbon phase can contribute if there are polar surface-active species that are hydro- and oleophilic in the system.

Shell published an empirical correlation [55] that relates fluid parameters and vessel dimensions to a predicted foam height:

$$H = \frac{1.7\times 10^{12}\cdot \nu_L \cdot u_L^{3.67}}{g^2 \cdot u_i^{0.67}\cdot (1-\varepsilon)^{6.32}}\left(\frac{\rho_L}{\rho_L-\rho_V}\right)^{1.33} \qquad (13.111)$$

where:
H = foam height (m),
ν = kinematic viscosity of the liquid (m²/s),
u_L = superficial downward velocity of liquid (m/s),
u_i = inlet velocity of mixed-phase fluid (m/s),
g = acceleration due to gravity = 9.81 m/s²,
ε = volumetric hold-up vapor fraction in foam (Shell found 0.70 for their experiments of propane boiling out of light crude oil),
ρ_L = density of liquid phase (kg/m³), and
ρ_V = density of vapor phase (kg/m³).

This equation shows that increasing temperature (reducing viscosity) and increased vessel size (reducing superficial velocities) will help reduce foam height if it is prone to form in a system. Additionally, because the height of a foam generated is proportional to the inverse square of the acceleration of gravity, this supports the experience in the industry that cyclone-type inlet devices help prevent foam formation [20–22].

13.8 COMPRESSORS AND PUMPS

The purpose of this chapter is not to provide all of the design details of compressors and pumps, but rather to provide a brief overview with some of the key equations a process engineer may need when evaluating or specifying this equipment.

13.8.1 Compressors

A compressor is a machine that increases the pressure of a compressible fluid. The operating suction pressures can be anywhere from deep vacuum to high positive pressures; discharge pressures can be anything from subatmospheric to hundreds of megapascals. Compressors have been designed to be operated on molecular weights ranging from 2 (hydrogen) to 352 (uranium hexafluoride) [56].

Compressors can be of two basic types: intermittent and continuous. Intermittent compressors operate by taking a volume of fluid and compressing it, releasing the compressed fluid, and then starting again with another volume of fluid; because the volume of fluid admitted is always the same for a given compressor, these are often referred to as constant-volume machines. Continuous compressors can compress the fluid volume without any interruption in the flow at any point; because they are based on accelerating the fluid using some motive force (which is constant), these are often referred to as constant-mass machines.

Intermittent compressors can be subdivided into two basic groups: reciprocating and rotary devices. Reciprocating compressors use a mechanical piston (or series of such pistons) in cylinders to compress the gas. Fluid is admitted through a valve into the cylinder when the piston is retracted, and then the piston moves down the cylinder pushing the fluid against the head of the cylinder. As the piston reaches the end of the cylinder, the discharge valve opens, rejecting the compressed gas into the outlet piping. This is then repeated. Because the volume of gas admitted is fixed by the geometry, the properties of the fluid do not affect the performance of the machine with the exception of the power required. For a given compressor geometry, the volumetric flow and pressure differential will be the same (power and temperatures will of course vary). Reciprocating compressors are common in the hydrocarbon processing industry for smaller flows with high pressure ratio requirements, such as for natural gas transmission and hydrogen makeup to hydrotreaters. For low-molecular-weight gases such as hydrogen, the thermodynamic efficiencies of these machines can approach 100 %.

A rotary compressor can be of various types, including sliding-vane, liquid-ring, helical-lobe, and straight-lobe screw devices. These machines differ from reciprocating machines as the machinery rotates on a shaft and they do not have inlet or outlet valves, but they are intermittent. A volume fluid is admitted into the first chamber as the rotor moves over the inlet port. As the rotor turns, the chamber in which the fluid is trapped becomes smaller because of the geometry of the rotor and casing. Once the chamber reaches the outlet port, the now-higher pressure fluid exits via the outlet port. The direction of travel for the fluid may be radial (sliding-vane, liquid-ring) or axial (screws), but the principle is the same.

Sliding vane and liquid-ring compressors are often used in low-pressure applications and as vacuum pumps. They have capacity ranges from 3 to 27,000 m^3/h (2–16,000 cfm) and generally with a pressure ratio of 3–5 in a single stage.

Screw compressors are used in a wide variety of applications (e.g., instrument air, nitrogen, flare gas recovery, PSA tailgas) and have capacity ranges of 800–60,000 m^3/h (500–35,000 acfm) with pressure ratios in a single stage of approximately 3. Screw compressors can be of either dry or flooded type. The dry type uses timing gears to ensure the perfect meshing of the screws; the flooded uses an oil layer to keep the screws from touching. The flooded type can handle higher compression ratios because the lubricating fluid can be used to remove some of the heat of compression. However, in fluids containing dust, a flooded screw is not reliable because the dust will contaminate the lube oil.

Continuous compressors can be divided into two types: ejectors and dynamic machines. An ejector is a low-efficiency machine that uses Bernoulli's principle that a high-velocity motive fluid can produce a low static pressure and that slowing down the fluid will raise its pressure. Ejectors have no moving parts and are therefore highly reliable and low maintenance (unless the fluids contain solids that erode the ejector). Ejectors are often used in vacuum applications in which very low pressures are required. Motive fluids for ejectors are usually steam or gas, but liquids can also be used. In such services, these may be referred to as jet pumps.

Dynamic compressors impart energy to the fluid using a set of rotating blades. The energy is exhibited as velocity and pressure increase, although much of the pressure increase occurs in the stationary elements. Because these machines use force to accelerate the gas, the density and molecular weight of the gas will affect the performance of the machine. In general, for a given compressor the mass flow will be constant at a given power input, with volumetric flow and pressure varying with varying fluid properties. Dynamic compressors come in three forms: centrifugal, axial, and mixed flow, which combines the features of the first two.

Centrifugal compressors function by admitting fluid into the rotor near the shaft and radially accelerating the fluid toward the edge of the rotor. As the fluid is pushed outward by the blades of the spinning rotor, it moves faster and increases in pressure. The fluid then decelerates in a diffuser that creates more pressure. These have a capacity range of 1700–250,000 m^3/h (1000–150,000 acfm) with a compressor ratio generally limited to approximately 3 for a single stage. They are often built as multistage machines with multiple rotors on one shaft and have been built to operate at pressures up to 68 MPa (10,000 psi). These are some of the most common compressors in the hydrocarbon processing industry and are used for wet gas compressors in FCCs and cokers; recycle compressors in hydroprocessing units; and for larger flow instrument air, fuel gas, or nitrogen compression.

Axial compressors are large-volume machines that are characterized by the fluid moving along the shaft of the machine through a series of unshrouded blades. Each stage of the machine consists of one set of rotating blades, followed by a stationary set of blades. The fluid passes through the rotating blades, where it is accelerated and increased in a pressure. The fluid then slows through the static blades and increases in pressure further. Because each stage is only capable of producing a small pressure increase, these machines are always built as multistage compressors. The blades of an axial compressor are made to exacting tolerances and often of expensive materials, making these expensive, but often more economic for large volume applications. The most common application of the axial compressor is in the turbo-fan (jet) engine used in commercial and military aircraft. Axial compressors for process use can be built from 120,000 to 1.7×10^6 m^3/h (70,000–1,000,000 acfm). Axial compressors in the petroleum industry are generally limited to natural gas pipelines and air compressors for air separation facilities because there are few other applications that require the volumetric capacity.

Mixed-flow compressors offer some of the features of centrifugal and axial machines. The rotors are more like a centrifugal compressor, but the blades are angled along the shaft (in the axial direction). These provide a unique head-capacity offering, which is typically used for gas pipeline booster compressor services.

All compressors, regardless of type, are governed by the same basic equations. All compressible fluids obey the real gas law:

$$PV = nZR_{\circ}T \tag{13.112}$$

It must be noted that the compressibility factor, Z, is dependent on pressure, temperature, and composition. Estimating the Z value for a given fluid can be done using thermodynamic charts or calculated using one of various equations of state. A commercial simulator program is the fastest way to estimate this value.

In theory, compression could be isothermal or adiabatic (or something in between). However, because building an isothermal compressor would be difficult, most operate closer to the adiabatic mode. For adiabatic compression, on the basis of Eq 13.113,

$$PV^{\gamma} = \text{constant} \tag{13.113}$$

where γ is the ratio of the specific heats of the gas,

$$\gamma = \frac{C_p}{C_v} = \frac{C_p}{C_p - R} \tag{13.114}$$

The latter part of this equation is generally used in industry, although it only applies to ideal gases (i.e., low-pressure gases with minimal intermolecular interactions). This is because specific heats were more easily measured at constant pressures, and even calculating C_v rigorously is somewhat involved. However, with modern simulation programs, calculation of a rigorous (and real) specific heat at constant volume is possible. However, you may find that vendor and performance data for compressors are still based on the ideal relationship.

Although it is essentially impossible to build an adiabatic machine (it would be isentropic and completely reversible), the minimal heat losses in a positive displacement machine mean that it operates very close to adiabatically.

The adiabatic head, or ideal enthalpy change, of a compressor is calculated via

$$h_{ad} = \Delta H_{ideal} = Z_{avg} R T_1 \frac{\gamma}{\gamma - 1}\left(\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right) \tag{13.115}$$

The discharge temperature of an adiabatic compressor can then be calculated via

$$T_2' = T_1\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \tag{13.116}$$

This is the theoretical discharge temperature assuming zero heat losses. This is never quite true, but for many reciprocating compressors it will give a reasonably close approximation, particularly for fluids of low molecular weight. If you know the actual adiabatic efficiency, you can calculate the actual discharge temperature via

$$T_2 = T_1 + \frac{(T_2' - T_1)}{\eta_{ad}} \tag{13.117}$$

Dynamic compressors are less thermodynamically efficient than positive displacement machines; therefore, they operate according to the polytropic equation:

$$PV^n = \text{constant} \tag{13.118}$$

where n is the polytropic exponent. This is determined from experiment by measuring the inlet and outlet conditions of the compressor:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} \tag{13.119}$$

The polytropic exponent is related to the ratio of specific heats by the polytropic efficiency:

$$\frac{n-1}{n} = \frac{\gamma - 1}{\gamma \eta_p} \tag{13.120}$$

The polytropic head is determined via an adjusted version of Eq 13.115 where we replace the ratio of specific heats by the polytropic exponent:

$$h_p = Z_{avg} R T_1 \frac{n}{n-1}\left(\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right) \tag{13.121}$$

Similar to adiabatic compression, we can calculate the outlet temperature of the compressor by rearranging Eq 13.119. However, unlike the adiabatic compression process, the temperature we calculate is the actual discharge temperature, assuming no jacket cooling of the compressor.

The shaft power required by an intermittent or dynamic compressor can be calculated from the adiabatic or polytropic head via the following:

$$W_x = \frac{m h_x}{\eta_x} \tag{13.122}$$

where the subscript x indicates either polytropic or adiabatic values. In this equation, m designates mass flow, and you must ensure that you use a consistent set of units to obtain a valid result.

For a multistage compressor, the pressure ratio per stage can be determined by

$$r_S = \sqrt[S]{r} = \sqrt[S]{\frac{P_2}{P_1}} \tag{13.123}$$

The question of how to determine the correct number of stages depends on the inlet temperature of the gas, what is a reasonable interstage cooling temperature, and what type of compressor you are specifying. In most facilities, the interstage cooling temperature that can be obtained is limited by the use of a low-cost cooling medium, such as air or water. This usually limits the suction temperatures of each stage to approximately 30–50°C, depending on location. The discharge temperatures should be limited to 150°C (300°F) for reciprocating compressors (as recommended in reference [57]). Reciprocating compressors in hydrogen service (or any gas mixture with a low molecular weight) should be limited to a discharge temperature of 130°C (266°F) [57]. The maximum recommended discharge temperature should be limited to 260°C (500°F) for centrifugal, axial, and screw compressors. The actual temperature limits of rotary compressors are dependent on the material selection, lubricants, and process gas. Keeping temperatures below 200°C (390°F) is good practice to provide lower maintenance requirements and lower cost materials of construction.

Dynamic compressors are often described by compressor maps, which are similar to pump curves. An example compressor map is shown in Figure 13.28.

In this figure, the surge line is the minimum stable flow of the compressor. At these flows, the compressor blades "stall," much like the wings on an aircraft at low flow. The result is that high-pressure gas flows backward through part of the machine and then reverses back to forward flow. This occurs repeatedly, and if the machine operates for any significant period of time in this mode then machine damage is likely to occur. Because operating to the left of the surge line will damage the machine, most manufacturers recommend setting control alarms above the surge line by a few percent such that warnings occur before surge happening.

The stonewall line is the point at which the compressor reaches choke, or near-sonic flow, usually in the diffuser at the outlet of a stage. Because you cannot accelerate the fluid past the sonic velocity in a dynamic machine, there is no way to push more fluid through the machine. Operating near the

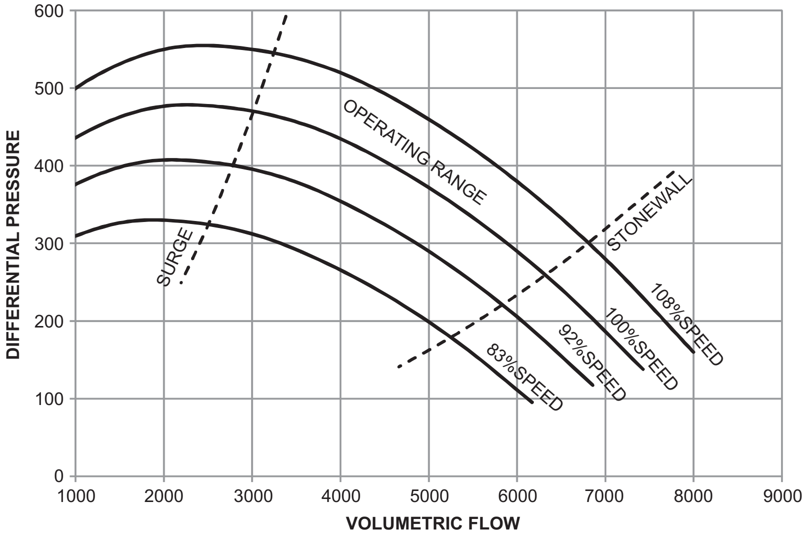


Figure 13.28—Example centrifugal compressor map.

stonewall line will not damage the machine. Dynamic compressors must operate between these two lines.

There are numerous texts that go into much more detail on compressor selection, sizing, and operation [56,58,59]. Additionally, the reader is recommended to review industry standard documentation, specifically API Standards 617 (centrifugal and axial), 618 (reciprocating), and 619 (screw) [57,60,61].

13.8.2 Pumps

Similar to compressors, pumps are for increasing the pressure of a fluid, the difference being that pumps are used for essentially incompressible fluids—liquids and supercritical (dense-phase) fluids. Similar to compressors, there are numerous types of pumps, but generally they fall into two categories: dynamic and positive displacement.

Dynamic pumps are those that increase pressure by accelerating a liquid using the kinetic energy input of an impeller. Most dynamic pumps are centrifugal, although there are some axial pumps. Because the centrifugal pump is the most commonly used pump in the process industries, it will be the focus of this section.

Centrifugal pumps increase the pressure of a liquid primarily through centrifugal force. The pump impeller is spun at high speed, and fluid admitted through the eye of the impeller is accelerated toward the outside of the impeller. The fluid is then slowed in a diffuser or volute, which converts velocity to pressure.

The performance of a centrifugal pump follows a declining head profile with capacity as shown in Figure 13.29, which displays a centrifugal pump curve.

Because the head developed by the pump rises with declining flow, this is a good fit with a control valve for controlling the flow of the pump.

The relationship among the impeller size, pump speed, flow, and head are known as the fan laws because they were first developed for such equipment, although their use is most common for centrifugal pumps:

$$Q_2 = \frac{D_2}{D_1} Q_1 \quad \text{or} \quad Q_2 = \frac{N_2}{N_1} Q_1 \tag{13.124}$$

$$H_2 = \left(\frac{D_2}{D_1}\right)^2 H_1 \quad \text{or} \quad H_2 = \left(\frac{N_2}{N_1}\right)^2 H_1 \tag{13.125}$$

$$W_2 = \left(\frac{D_2}{D_1}\right)^3 W_1 \quad \text{or} \quad W_2 = \left(\frac{N_2}{N_1}\right)^3 W_1 \tag{13.126}$$

One can estimate the performance of a pump with a different impeller size or speed using these relationships.

Centrifugal pumps can suffer decreased performance and even pump damage if cavitation occurs in the pump. Cavitation is the phenomenon by which vapor bubbles form because of a drop in pressure below the vapor pressure of the liquid. As the pressure then rises, the bubbles will collapse back to the liquid phase. Pumping of bubbles is inefficient, and the violent collapse of said bubbles can damage the internal parts of the pump. Preventing cavitation is done by ensuring that the system in which the pump is installed avoids pressures in the pump impeller eye that are below the vapor pressure of the fluid. The parameter that is used for this is called the net positive suction head (NPSH).

The required net positive suction head (NPSHR) of pump, shown in Figure 13.6, can be estimated before a vendor pump curve is available using the relationship between suction-specific speed and NPSHR:

$$NPSHR = \left(\frac{N\sqrt{Q}}{N_{SS}}\right)^{4/3} \tag{13.127}$$

where:
N_{SS} = suction-specific speed,
Q = flow (usgpm), and
N = speed of the pump (rpm).

This equation should be used using U.S. customary units. For preliminary estimates, the suction-specific speed should be assumed to be between 8000 (water) and 11,000 (hydrocarbon). For double suction pumps, use half the flow in Eq 13.127.

The NPSH that is available from the system, or NPSHA, can be calculated using

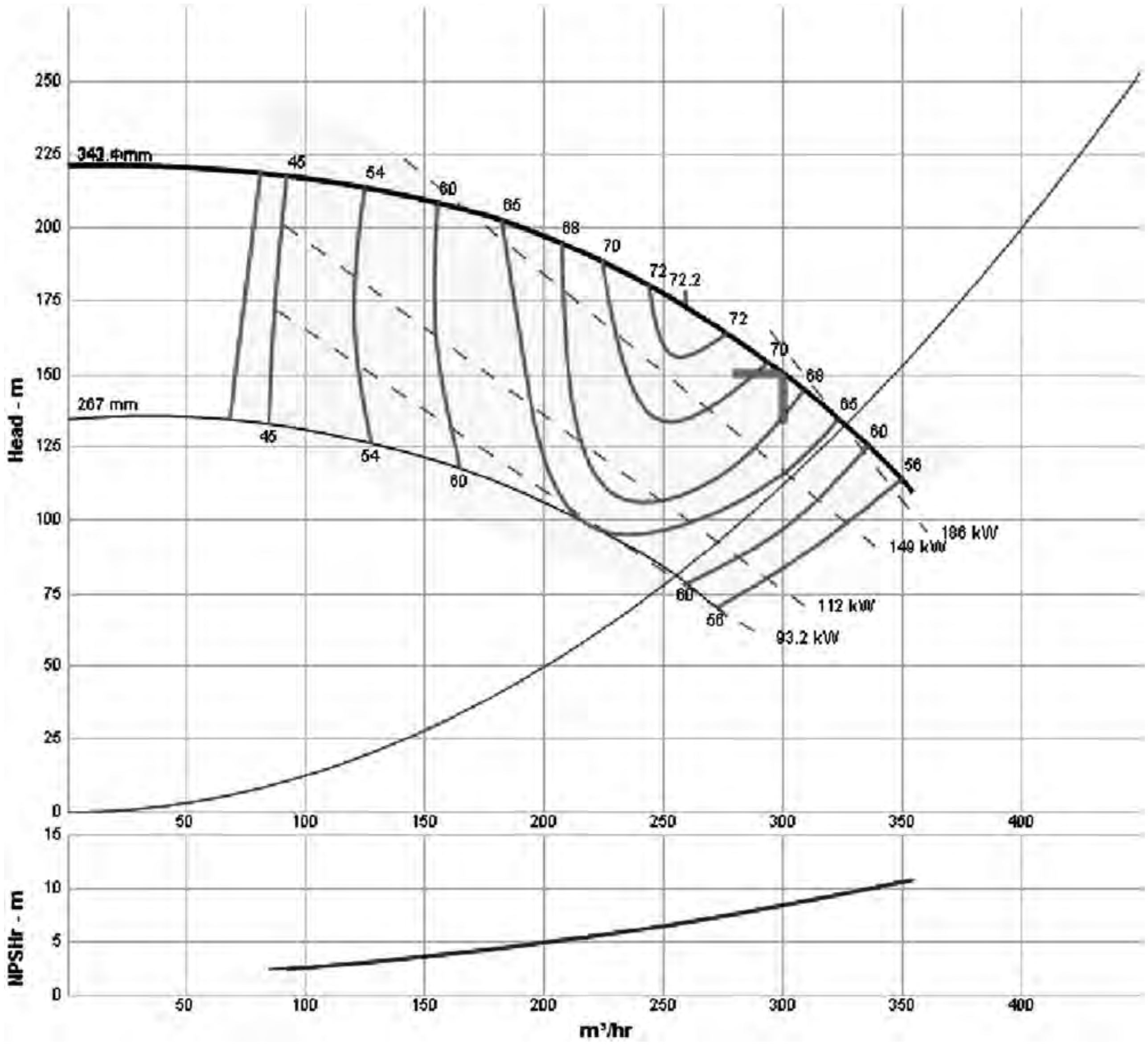


Figure 13.29—Typical pump curve. *Source:* Curve from www.pump-flo.com pump selector, courtesy of Afton Pumps, Inc.

$$NPSHA = \frac{P_{src} - \Delta P_f - P_{vap}}{\rho g} + h_s \qquad (13.128)$$

where:

P_{src} = absolute pressure above the liquid in the source vessel or tank;

ΔP_f = frictional pressure drop between the source and the pump, including fittings, strainers, valves, and inlet losses at the drum;

P_{vap} = vapor pressure of the fluid at the pumping temperature;

ρ = fluid density;

g = acceleration of gravity; and

h_s = elevation difference between the liquid level and the pump.

For a new pump, one should set the NPSHA equal to NPSHR plus a margin (usually 1–2 m) and set the suction vessel elevation by adjusting h_s to balance the equations. For existing installations, it may require selecting a lower speed pump or multiple smaller pumps operating in parallel to obtain a pump with a low enough NPSHR.

For fluids that contain dissolved gases, it is possible to operate a pump with some gas bubbles in the pumped fluid, without significant performance degradation or damage. This is because dissolved gases behave differently than vaporized liquid. In a water pump, if the pressure drops below the vapor pressure of water, then steam bubbles will form. The collapse of these bubbles is a thermodynamic phase change and happens very quickly because there is no other limitation. For water with some dissolved gas, the bubbles can form in the suction piping, but they may not collapse violently in the pump; the process of re-dissolving the gas in the water is limited by mass transfer, not thermodynamics. Because this is orders of magnitude slower, there will be no damage to the pump.

For these pumps, rather than using the vapor pressure of the bulk fluid in Eq 13.128, one can use a pseudovapor pressure [62,63,64]. A few simple rules can be used to help decide how to approach this

- If the dissolved gases are similar to the fluid (i.e., light hydrocarbons in heavy hydrocarbons), then it is generally safest to assume that the fluid is at the bubble point.
- If the dissolved gas is air (in subcooled water), then you can generally assume that the dissolved gas is irrelevant if the pump suction level is above the pump nozzle.
- If the dissolved gas is somewhat soluble in water (i.e., ammonia, H_2S) you should use a pseudovapor pressure method.
- If the dissolved gas is hydrogen in hydrocarbon, then you should use a pseudovapor pressure method.

The pseudovapor pressure method is as follows:

- Simulate the process stream with the expected dissolved gases using a commercial simulator program. Determine the pressure required (at operating temperature) that results in 2.5 vol % vapor (actual volume).
- This can be done for any pump, but as noted above, the pseudovapor pressure for the first case will likely be more than 95 % of the bubble-point vapor pressure whereas for the second it will likely be less than the actual vapor pressure. It is only for the third and fourth cases that it is significant.

This is acceptable because centrifugal pumps can handle 2–3 % vapor in the inlet if this vapor is not going to “condense” in the pump. Methods have been published [57,64] providing a route for this without using a simulator for rigorous thermodynamic prediction of vapor pressure; however, in most instances today, a simulator is the fastest route.

The power requirements of a centrifugal pump are easily calculated via Eq 13.129:

$$W_{shaft} = \frac{Q \cdot \Delta P}{\eta} \qquad (13.129)$$

where the units are consistent (e.g., power in W, flow in m^3/s, differential pressure in Pa). Because most designers do not work in base units, common versions of this equation are shown below for various unit sets:

$$W_{hp} = \frac{Q_{usgpm} \cdot \Delta P_{psi}}{1714 \cdot \eta} \qquad (13.130)$$

$$W_{kW} = \frac{Q_{m^3/h} \cdot \Delta P_{kPa}}{3600 \cdot \eta} \qquad (13.131)$$

Often the pressure rise across a pump is described in terms of total developed head, which is the equivalent static head of fluid. This is done because pumps generate constant “head,” not pressure; therefore a change in fluid specific gravity will result in a change in differential pressure at a given speed. Therefore, Eqs 13.130 and 13.131 are often written in terms of developed head:

$$W_{hp} = \frac{Q_{usgpm} \cdot \Delta H_{ft} \cdot SG}{3960 \cdot \eta} \qquad (13.132)$$

$$W_{kW} = \frac{Q_{m^3/h} \cdot \Delta H_m \cdot \rho_{kg/m^3} \cdot g_{m/s^3}}{3.6 \times 10^6 \cdot \eta} \cong \frac{Q_{m^3/h} \cdot \Delta H_m \cdot SG}{367 \cdot \eta} \qquad (13.133)$$

Positive displacement pumps are those that increase pressure by moving a discrete volume of liquid from the suction to discharge side of the pump. The discharge pressure is defined not by the pump but by the discharge system. The maximum discharge pressure of a positive displacement pump is limited only by the power input and the mechanical integrity of the pump. Positive displacement pumps can be reciprocating or rotary.

Reciprocating pumps utilize a piston or diaphragm to displace the liquid. This piston or diaphragm can be moved by a motive fluid, such as steam or air, or mechanically using a piston rod connected to a crankshaft and thus driven by a turbine, engine, or electric motor. In piston-type reciprocating pumps, the piston can be single or double acting, meaning the piston displaces fluid on one or both ends of each stroke. As the piston moves away from the cylinder head, the chamber becomes larger, and liquid is admitted via a suction check valve; the piston then moves back toward the cylinder head, pushing the fluid out the discharge check valve. A reciprocating pump may be referred to as a simplex, duplex, or triplex pump; this is simply a designation of how many cylinders are mounted in a single base or frame (1, 2, or 3).

Reciprocating pumps have the downside of producing pulsating flow on the suction and discharge sides. This can be somewhat mitigated using a pulsation dampener. A pulsation dampener can be a diaphragm device or a direct pressurization device, with the only difference being whether there is a separation between the gas that provides the “dampening” pressure. The sizing of the pulsation dampener depends on the speed and size of the pump:

$$V = \frac{5 \cdot Q}{60 \cdot n \cdot N_C} + 1.5 \cdot V_D \qquad (13.134)$$

where:
Q = flow of the pump,
n = speed of the pump (rpm), and
N_C = number of acting cylinders (e.g., 1 for single acting simplex pump, 4 for double-acting duplex, etc.).

The second term of the equation is the minimum gas volume behind the diaphragm, which is equal to at least 1.5 times the volume of a single cylinder displacement of a piston. This equation is best for pumps operating below 100 rpm. For speeds above 100 rpm, multiple the volume calculated using Eq 13.134 by the pump speed divided by 100.

One parameter that is critical for all pumps is the NPSH, which in the case of the reciprocating pump must be sufficient to ensure that the pump cylinder fills completely with liquid during the suction stroke. Because reciprocating pumps have a dynamic valve action, the NPSH of such pumps is usually specified in terms of pressure, not head, as is done for centrifugal pumps. For this reason, some pump manufacturers also refer to the NPSH of a reciprocating pump as the net positive inlet pressure (NPIP). The NPSH or NPIP available to a reciprocating pump is defined by

$$NPSH_A = P_{src} + \rho g h_s - \Delta P_f - (P_{vap} + \rho g h_{HI}) - \rho g h_a \qquad (13.135)$$

where:
P_{src} = source pressure,
h_s = liquid static head from the source liquid height to the suction connection on the pump,

ΔP_f = frictional pressure drop in the suction piping,
P_{vap} = vapor pressure of the fluid,
h_{HI} = NPSH margin recommended by the Hydraulic Institute (7 ft/2.13 m), and
h_a = acceleration head.

Unlike centrifugal pumps, the acceleration head of the fluid in a reciprocating pump is not negligible because of the pulsating nature of the machine. It may be determined via

$$h_a = \frac{L u_{avg} n C}{g k} \tag{13.136}$$

where:
L = actual length of the suction piping,
u_{avg} = average velocity in the suction piping,
n = pump speed (rpm),
g = gravitational constant (9.81 m/s², 32.174 ft/s²), and
k = compressibility factor of the liquid (2.5 for LPG or hot oils, 1.4 for water and similar fluids).

The value of C is based on the pump configuration (Table 13.11).

The power requirements of a reciprocating pump are easily determined, although you will require data from a pump vendor with regards to the efficiency of the pump.

$$\begin{aligned} W_{brake} &= \frac{Q \cdot \Delta P}{3600 \cdot \eta_v \eta_h \eta_m} \quad \text{metric (m}^3\text{/h, kPa)} \\ W_{brake} &= \frac{Q \cdot \Delta P}{1714 \cdot \eta_v \eta_h \eta_m} \quad \text{US customary (usgpm, psi)} \end{aligned} \tag{13.137}$$

The efficiency terms are the volumetric, hydraulic, and mechanical efficiencies. For the product of the volumetric and hydraulic efficiencies, it is relatively safe to assume approximately 0.90. For the mechanical losses, it is dependent on the stroke and operating pressure (as a percentage of the maximum the pump can produce):

$$\begin{aligned} \eta_m \cong -4.7831 \cdot \ln (F_{MOP})^2 + 48.638 \\ \cdot \ln (F_{MOP}) - 37.964 \end{aligned} \tag{13.138}$$

where F_{MOP} is the percentage of maximum operating pressure at which the pump is operating. The equation is approximate because it was curve-fitted by the author from a limited dataset and should be used with caution.

Rotary displacement pumps are similar to reciprocating pumps in that they move a discrete volume of fluid from the low-pressure suction to a higher pressure discharge system. However, unlike reciprocating pumps, rotary pumps do not produce pulsating flow and there is therefore no need to consider acceleration head in the NPSHA calculation. However, similar to reciprocating pumps, the NPSH is usually reported in pressure units, not head of liquid (and is called NPIP, not NPSH).

TABLE 13.11—Reciprocating Pump Acceleration Head Constant

Type	C Factor
Simplex, single-acting	0.400
Simplex, dual-acting	0.200
Duplex, single-acting	0.200
Duplex, dual-acting	0.115
Triplex, single- or dual-acting	0.066
Quintuplex, dual-acting	0.040
Septuplex, dual-acting	0.028

13.9 FILTRATION

Filtration is a unit operation in refineries that is often overlooked by those designers with limited experience in operations because the challenges that can be solved by filtration are not easily seen from a heat and material balance. Solid particles in fluid streams can come from several sources, including but not limited to mineral fines (i.e., clay, sand) from the crude oil reservoir, asphaltene precipitates, polymers and gums from unstable products reacting or oxidizing in storage or during processing (e.g., cracked stocks, chemicals used in oil well maintenance), catalyst fines, coke particles, and corrosion products. Such solids can poison or plug catalyst beds; foul heat transfer equipment and column internals; and abrade piping, valves, instruments, and equipment.

Some solids in a refinery can be of significant size, particularly if the facility contains a vacuum tower, coker, visbreaker, or other unit that cracks the product. However, most particles that refineries are concerned with are small (<500 μm). Very large particles (>12 mm / 0.5 in.) will generally settle in tanks, and vessels are only a problem if they are in sufficient quantity to block outlets or reduce storage volumes.

Strainers can be used to prevent large particles, generally those larger than 5 mm that can damage pumps, valves, or plug tower internals. These are usually of a basket or "T" type, allowing for operators to isolate the strainer and remove the material from the strainer when the unit becomes plugged. These are commonly included on pump suctions from tankage in solids-bearing services, but they may also be included on such process streams as coker/FCC main fractionator bottoms, atmospheric and vacuum distillation bottoms products, HVGO pumparound draws, wash oil/slop wax draws, and hydrocracker fractionators bottoms.

These differ from temporary suction strainers (TSS), which are usually of a cone (i.e., witch-hat) type, which are installed in pump suctions for startups of new facilities and after maintenance shutdowns to prevent materials left after construction/maintenance (i.e., bolts, weld slag, gloves) from entering the pump suctions.

13.9.1 Filter Selection

Filters can be of many types, including replaceable cartridge or bag filters, continuous backwashing filters, sand filters, activated carbon beds, and precoat filters. Cartridge filters are significantly less expensive, but they have higher operating costs because you must regularly replace the filter elements. Backwashing filters have lower operating costs, but they will have significant instrumentation that will require maintenance. Sand filters are usually only used for treating water to remove solids. Precoat filters are filters with elements that must be coated with a medium that provides the filtering action. Common precoat materials are diatomaceous earth and wood pulp. The precoat material is disposed of after it has been used. Activated carbon beds are often used to remove insoluble (or partially soluble) materials from a stream where that component has a high affinity for activated carbon. Precoat filters are also often used to remove insoluble liquids from aqueous solutions, such as removing oil from amine or steam condensate.

The selection of which filter is corrected for a given application depends on several factors:

- *Fluid hazard/risk:* If the risk of exposing operations personnel to the process fluid during the task of changing a filter cartridge is deemed to be too high, then a backwashing filter may be preferable. This may be due to the toxicity, temperature, or pressure of the process.
- *Filtering temperature:* For services in which filtration of the process fluid occurs at high temperature because of viscosity concerns (i.e., hydrocracker feeds), it may be desirable to use a backwashing filter because cooling the filter for cartridge replacement may be problematic because of plugging and draining concerns.
- *Solids load:* For services in which the solids load is expected to be high, a backwashing filter may be preferable because changing cartridges every shift or day is very expensive in materials and labor.

Filter media must also be selected to be compatible with the process fluids. Filter media may be constructed from several materials, including natural fibers (e.g., cotton, cellulose), polymers (e.g., polypropylene), metal (e.g., stainless steel, nickel alloys), and sintered metals. The selection of the proper material should be done in consultation with a materials engineer.

Cartridge and backwash filters are often sold with a basis for what size of particles they will allow to pass through the filter. There are two general classes of filter material: those with an absolute rating and those with a nominal rating. An absolute rating indicates that the filter material will allow nothing (OSU-F2 test requirement is 99.98 % retention) to pass through the filter that is larger than specified. Therefore, a fluid containing 10,000 particles/L that are larger than 10 μm would have only 20 particles larger than 10 μm after passing through a 10-μm absolute filter.

A nominal rating indicates that the filter will retain or capture some percentage less than 99.98 % of the particles of the rated size. This is often between 60 % and 85 %. Some filters rated as nominal can actually reach something approaching an absolute rating once a cake of filtered material builds up on the filter media. This is because the cake becomes the filter media and can improve the filtration of smaller particles. When discussing this with filter suppliers, be sure to ask if their filter performance is with a clean filter or after a cake has built up. If the quoted performance is after the cake has accumulated, then the clean performance may be less effective. Additionally, higher pressure drops may be required for these types of installations. Filter selections for some processes as are done typically in a modern refinery are shown in Table 13.12.

TABLE 13.12—Typical Filter Configurations

Service	Type
Hydrotreater feed	
Naphtha/kerosene/ diesel	Cartridge, 10 μm absolute. Backwashing may be desired in coker naphtha service if storage of coker naphtha.
Heavy gas oil/ residues	Backwashing, 10 μm absolute. Especially if upstream units contain coke fine producing processes.
FCC or coker main fractionator, vacuum tower wash oil, HVGO draw	Cartridge, 100+ μm absolute. Larger sizes in cokers, smaller in FCC. Strainers can be used if spray nozzles can handle particles up to 1 mm.
Sour water service	Cartridge/bag, 50 μm absolute.
Amine service	Cartridge/bag, 5–10 μm absolute. Backwashing may be an option if solids load is very high. Rich amine filtration is more effective at keeping process clean.

REFERENCES

[1] Manning, F.S., and Thompson, R.E., *Oilfield Processing of Petroleum, Volume Two: Crude Oil*, PennWell Books, Tulsa, OK, 1995, pp. 145–158.
[2] Biglari, M., Iikhaani, S., Alhajri, I., and Lohi, A., "Process Design, Simulation and Integration of a New Desalter in the Crude Distillation Unit of a Refinery," *Int. J. Oil, Gas & Coal Technol.*, Vol. 3, 2010, pp. 350–361.
[3] Geankoplis, C.J., *Transport Processes and Separation Process Principles*, 4th ed., Prentice Hall, Upper Saddle River, NJ, 2003.
[4] McCabe, W.L., Smith, J.C., and Harriott, P., *Unit Operations of Chemical Engineering*, 7th ed., McGraw-Hill, New York, 2005.
[5] Manning, F.S., and Thompson, R.R., *Oilfield Processing: Crude Oil,* PennWell, Tulsa, OK, 1995.
[6] Perry, R.H., and Green, D.W., *Perry's Chemical Engineers' Handbook*, 7th ed., McGraw Hill, New York, 1997.
[7] Riazi, M.R., *Characterization and Properties of Petroleum Fractions*, ASTM Manual 50, ASTM International, West Conshohocken, PA, 2005.
[8] HYSYS, "Reference Volume 1, Version 1.1," *HYSYS Reference Manual for Computer Software*, HYSYS Conceptual Design, Hyprotech Ltd., Calgary, Alberta, Canada, 1996.
[9] Peters, M.S., and Timmerhaus, K.D., *Plant Design and Economics for Chemical Engineers*, McGraw-Hill, New York, 2003.
[10] Sinnott, R.K., *Coulson & Richardson's Chemical Engineering*, 3rd ed., Vol. 6, R.K. Sinnott, Ed., Butterworth-Heinemann, London, 1999.
[11] Kister, H.Z., "Effects of Design on Tray Efficiency in Commercial Towers," *Chem. Eng. Prog.*, Vol. 42, 2008, pp. 39–47.
[12] Distillation Equipment Company, Staffordshire, United Kingdom, http://www.traysrus.com/ (accessed November 14, 2011).
[13] Euroslot Kdss, http://www.euroslotkdss.com/mtri/tower-internals/distillation-trays.html (accessed January 3, 2011).
[14] Koch Chemical Technology Group, LLC, Wichita, KS, 2009, http://www.koch-glitsch.com/koch/faq/faq.asp.
[15] Kister, H.Z., *Distillation Operations*, McGraw-Hill, New York, 1990.
[16] Binous, H., "Equilibrium-Staged Separations Using MATLAB and MATHEMATICA," *Chem. Eng. Prog.*, Vol. 42, 2008, pp. 69–73.
[17] Kaes, G.L., *Refinery Process Modeling—A Practical Guide to Steady State Modeling of Petroleum Processes*, Athens Printing Company, Athens, GA, 2000.
[18] Hines, A.L., and Maddox, R.N., *Mass Transfer, Fundamentals and Applications*, Prentice Hall, Inc., Upper Saddle River, NJ, 1985, p. 509, Table B-8.
[19] Andersson, E., "Minimising Refinery Costs Using Spiral Heat Exchangers," *Petrol. Technol. Quart.*, Q2, 2008.
[20] Underwood, A.J.V., "Calculation of the Mean Temperature Difference in Multipass Heat Exchangers," *J. Inst. Petrol. Technol.*, Vol. 20, 1934, pp. 145–158.

[21] Bowman, R.A., Mueller, A.C., and Nagle, W.M., "Mean Temperature Difference in Design," *Trans. Am. Soc. Mech. Eng.*, May, 1940, pp. 283–293.

[22] Maxwell, J.B., *Data Book on Hydrocarbons*, Standard Oil Research Company, New York, 1950.

[23] Wales, R.E., "Mean Temperature Difference in Heat Exchangers," *Chem. Eng.*, February 23, 1981, pp. 77–81.

[24] *Standards of the Tubular Exchanger Manufacturers Association*, 9th ed., TEMA, Tarrytown, NY, 2007.

[25] Gulley, D.L., "How to Calculate Weighted MTDs," in *Heat Exchanger Design Book*, Gulf Publishing Company, Houston, TX, 1968, p. 13.

[26] Nesta, J., and Bennett, C.A., "Reduce Fouling in Shell-and-Tube Heat Exchangers," *Hydrocarbon Processing*, July 2004, pp. 77–82.

[27] Brown, R., "Design of Air-Cooled Exchangers—A Procedure for Preliminary Estimates," *Chem. Eng.*, Vol. 85, March 27, 1978, pp. 108–111.

[28] Kumana, J.D., and Kothari, S.P., "Predict Storage-Tank Heat Transfer Precisely," *Chem. Eng.*, March 1982, pp. 127–132.

[29] Churchill, S.W., and Bernstein, M., "A Correlating Equation for Forced Convection from Gases and Liquids to a Circular Cylinder in Crossflow," *J. Heat Trans.*, Vol. 99, 1977, pp. 300–306.

[30] Churchill, S.W., and Chu, H.H.S., "Correlating Equations for Laminar and Turbulent Free Convection from a Horizontal Cylinder," *Int. J. Heat Mass Trans.*, Vol. 18, 1975, pp. 1049–1053.

[31] Chato, J.C., "Laminar Condensation inside Horizontal and Inclined Tubes," *ASHRAE Journal*, Vol. 4, 1962, pp. 52–60.

[32] Dittus, F.W., and Boelter, L.M.K., *Publications on Engineering*, University of California, Berkeley, CA, Vol. 2, 1930, p. 443.

[33] Incropera, F.P., and DeWitt, D.P., *Introduction to Heat Transfer*, 3rd ed., John Wiley and Sons, New York, 1996, p. 413.

[34] Petukhov, B.S., *Advances in Heat Transfer,* T.F. Irvine and J.P. Hartnett, Eds., Vol. 6, Academic Press, New York, 1970.

[35] Gnielinski, V., "New Equations for Heat and Mass Transfer in Turbulent Pipe and Channel Flow," *Int. Chem. Eng.*, Vol. 16, 1976, pp. 359–368.

[36] Barletta, T., "Why Vacuum Unit Fired Heaters Coke," *Petroleum Technology Quarterly*, Autumn 2001.

[37] Smith, J.M., Van Ness, H.C., and Abbott, M.M., *Introduction to Chemical Engineering Thermodynamics*, 7th ed., McGraw-Hill, New York, 2005.

[38] Garg, A., "Good Heater Specifications Pay Off," *Chem. Eng.*, July 1988, pp. 77–80.

[39] Lobo, W.E., and Evans, J.E., "Heat Transfer in the Radiant Section of Petroleum Heaters," *Trans. Am. Inst. Chem. Eng.*, Vol. 35, 1939, pp. 743–778, http://www.heaterdesign.com/LoboEvans1.htm.

[40] Cross, A., "Evaluate Temperature Gradients in Fired Heaters," *Chem. Eng. Prog.*, June 2002, pp. 42–46.

[41] Mekler, L.A., and Fairall, R.S., "Evaluation of Radiant Heat Absorption Rates in Tubular Heaters," *Petroleum Refiner*, June/November/December 1952.

[42] "Introduction to Fired Heater Design," http://www.heaterdesign.com/.

[43] Berman, H.L., "Fired Heaters-I, Finding the Basic Design for Your Application," *Chem. Eng.*, Vol. 85, June 19, 1978, pp. 99–104.

[44] Berman, H.L., "Fired Heaters-II, Construction, Materials, Mechanical Features, Performance Monitoring," *Chem. Eng.*, Vol. 85, July 31, 1978, pp. 87–96.

[45] Berman, H.L., "Fired Heaters-III, How Combustion Conditions Influence Design and Operation," *Chem. Eng.*, Vol. 85, August 14, 1978, pp. 129–140.

[46] Berman, H.L., "Fired Heaters-IV, How to Reduce Your Fuel Bill," *Chem. Eng.*, Vol. 85, September 11, 1978, pp. 166–167.

[47] *Fired Heaters for General Refinery Service*, 4th ed., API Standard 560, American Petroleum Institute, Washington, DC, 2007.

[48] Patel, S., "Simplify Your Thermal Efficiency Calculation," *Hydrocarbon Processing*, July 2005, pp. 63–69.

[49] ZareNezhad, B., "New Correlation Predicts Flue Gas Sulfuric Acid Dewpoints," *Oil & Gas J.*, Vol. 56, September 21, 2009, pp. 60–63.

[50] Pierce, R.R., "Estimating Acid Dewpoints in Stack Gases," *Chem. Eng.*, Vol. 84, Issue 8, 1977, pp. 125–128.

[51] Verhoff, F.H., and Banchero, J.T., "Predicting Dewpoints of Flue Gases," Vol. 70, *Chem. Eng. Prog.*, 1974, pp. 71–72.

[52] Clift, R., Grace, J.R., and Webber, M.E., *Bubbles, Drops and Particles*, Academic Press, New York, 1978.

[53] Grace, J.R., and Weber, M.E., "Hydrodynamics of Drops and Bubbles," in G. Hetsroni, Ed., *Handbook of Multiphase Systems*, McGraw-Hill, New York, 1982, pp. 1–204.

[54] Maude, A.D., and Whitmore, R.L., "A Generalized Theory of Sedimentation," *Br. J. Phys*., Vol. 9, 1958, pp. 477–482.

[55] Barber, A.D., and Wijn, E.F., "Foaming in Crude Distillation Units," *IChemE. Symp. Ser.*, Vol. 56, 1979, pp. 3.1/15–3.1/35.

[56] Brown, R.N., *Compressors: Selection and Sizing*, 3rd ed., Gulf Professional Publishing, Houston, TX, 2005.

[57] *Reciprocating Compressors for Petroleum, Chemical and Gas Industry Services*, 5th ed., API Standard 618, American Petroleum Institute, Washington, DC, 2007.

[58] Hanlon, P., *Compressor Handbook*, McGraw-Hill, New York, 2001.

[59] Bloch, H.P., *A Practical Guide to Compressor Technology*, 2nd ed., John Wiley & Sons, Hoboken, NJ, 2006.

[60] *Axial and Centrifugal Compressors and Expander-compressors for Petroleum, Chemical and Gas Industry Services* (7th ed.), API Standard 617, American Petroleum Institute, Washington, DC, 2002.

[61] *Rotary-Type Positive Displacement Compressors for Petroleum, Petrochemical and Natural Gas Industries*, 4th ed., API Standard 619, American Petroleum Institute, Washington, DC, 2004.

[62] Tsai, M.J., "Accounting for Dissolved Gases in Pump Design," *Chem. Eng.*, Vol. 89, 1982, pp. 65–69.

[63] Chen, C.C., "Cope with Dissolved Gases in Pump Calculations," *Chem. Eng.*, Vol. 100, 1993, pp. 106–112.

[64] Wood, D.W., Hart, R.J., and Marra, E., "Pumping Liquids Loaded with Dissolved Gas," *Chem. Eng.*, Vol. 70, 1998, pp. 110–114.

14

Process Control and Instrumentation

L. Raman[1] and N.S. Murthy[1]

14.1 EVOLUTION OF PROCESS INSTRUMENTATION/MEASUREMENTS

In the last 40 years, the instrumentation field has gone through a tremendous change in every aspect of measurement and control, with the earliest generation including pneumatic devices, next-generation electronic devices, smart devices, and the recent revolution of intelligent devices. In the late 1960s, pneumatic instruments were used for local measurement and control where control loops were closed in the field itself, making it a tedious job for the operator because jobs like changing the setpoint and tuning the pneumatic controllers required manual intervention from the field. Later on, centralized control concepts were developed in which all pneumatic tubes were routed to a control room through a systematically arranged pneumatic control panel with graphics. Further substantial improvements in this field include electronic transmitters, 4- to 20-mA signals for measurement, and electronic-card-based controllers. One remarkable invention was that of Zener barriers and explosion-proof junction boxes, which helped in picking up electronic signals even from/to hazardous areas.

With the advent of microprocessors, all of the electronic controllers have transformed into microprocessor-based smart controllers, with configurations that can be customized for various control needs. This revolution has greatly helped in the centralized control concept, with most of the industries revamping their control systems from pneumatic to electronic because of various advantages such as changes in signal transmission distance, maintenance cost, labor availability, and capital cost. All of the single-loop controllers take I/Os (inputs/outputs) directly from the field through proper marshalling. All of these controllers are monitored through a central supervisory system such as a Digital Virtual Address eXtension (VAX)-based system. However, the control resides with single-loop controllers and operators can change setpoint values from consoles.

The concept of centralized control has led to the advent of distributed control systems (DCS), which helped in the graphical distribution of functionalities. Single-loop controllers have been replaced by card-level controllers in which I/Os are conditioned separately and fed into controllers for various actions on the basis of their configuration. This rendered a greater flexibility in control configuration revamp in a much quicker way as per the plant requirement. DCS vendors provide several control algorithms to suit various applications; however, cabling, routing, and marshalling of signal cables is considered to be the most laborious job in instrument erection, commissioning, and maintenance. Smart transmitters are introduced to make it possible to communicate with transmitters using a HART (highway addressable remote transducer) protocol with which range changes, diagnostics, and calibration are remotely possible without removing the transmitter from its location.

Most of the cabling issues are resolved with field bus technology. Using this technology, all plant signals can be routed to the control room with minimum number of cables. It also brings back the earlier pneumatic concept of local field-level control. Transmitters and final control elements are fitted with an intelligent system that not only does signal conditioning, running control algorithms, sending output to final control elements, and accepting feedback signals, but it also self-diagnoses itself and automatically reports any problem in the device. This leads to a paradigm shift in maintenance of instruments from preventive- to issue-based maintenance. This helps in manpower savings in maintenance and intelligently gives out all necessary information required for maintenance.

Slowly we are seeing that the DCS and programmable logic controller (PLC) elated functionalities are merging with personal computers. Already all major DCS vendors are providing their latest DCS in a Windows platform with "off-the-shelf" hardware. This is a major leap in the control industry, which was earlier dominated by proprietary hardware and software. However, the control hardware still remains proprietary, with operator consoles, graphics, and other user-interface software having been moved to the latest available open technology.

14.2 PROCESS CONTROL—AN OVERVIEW

A refinery can be referred to as a manufacturing unit in which one or more feedstock is processed/distilled for converting it into several useful streams/products depending upon the prevailing market conditions. A manufacturing unit comprises several components such as distillation columns, reactors, vessels, heaters, heat exchangers, pumps, pipelines, isolation valves, control valves, instruments, measurement devices, analyzers, etc. Process control enables harmonious operation of all of these components and helps them to function in unison within the safe limits, producing "high-value" end products at the optimized/least operating cost. However, to have an effective control of process, precise knowledge of the following process variables is very essential.

- *Independent variable*: This is a variable that is used for making changes or manipulating the process for bringing it to a certain specified state. It is used as an input to the process. Examples of an independent variable include control valve opening, speed of a drive, etc., that can be independently changed. It is denoted as "*MV*" in process control language meaning, "manipulated variable."

---

[1] Reliance Industries, Ltd., Gujarat, India

- *Dependent variable:* This is a variable that changes as a result of process manipulation for bringing the process to a certain specific state. It is considered as an output from the process. Examples of such variables include yields, throughput, velocity, heat flux, H_2 consumption, product quality, flooding in columns, energy consumption, vibration, etc.
- *Disturbance variable:* This is a variable that affects the process, but unlike an independent variable it cannot be manipulated. It is also known as a feed-forward variable because it cannot be manipulated despite its significant effect on the process. Examples of these variables include cooling water temperature, ambient air temperature, fouling in heat exchangers, upsets in downstream or upstream units, etc.
- *Controlled variable:* This is a variable that must be regulated to a get a desired product in the process. These are the variables that can be played with to drive the process and can be operated at a fixed setpoint or between ranges of limits. Examples are flow, temperature, pressure, level, speed, heat duty, steam-to-fuel ratio, gas-to-liquid ratio, stream properties, weighted average bed temperature in a reactor, optimum severity, etc.

Typically in a process control environment, a deviation from set value or disturbance induces error. This error between the process value and set value has to occur first for the controller to take action and close the deviation. However, in advanced model-based control, changes are addressed in a feed-forward, predictive manner, and deviations are minimized. Types of process control are discussed in the following section.

14.2.1 Rudimentary Control

These are basic, single-loop, feedback controls that work on the principle of minimizing error/deviation. The controls can simply be proportional + integral + derivative (PID) or any combination thereof depending on the operational requirement. Extremely tight control can at times lead to substantial disturbance in the downstream units. For example, tight control of level of a vessel that is pumping out product will end up passing on upstream disturbance in flow to the vessel to the respective downstream units. In such cases, the buffer level of the vessel is to be utilized to obtain smoothened flow downstream of the vessel so that downstream operations function smoothly.

A few examples of rudimentary controls are

- *Simple ratio controls:* These are used in controlling steam flow to the distillation column depending on product draw-off rate.
- *Cascade control:* Also called “master-slave control,” cascade control is typically used when the primary (master) measurement and control is slower than the secondary (slave) measurement and control. The inner (slave) loop always responds faster and is used to control the outer (master) loop, which is comparatively slower in response. Typical examples include controlling the heater coil outlet temperature (master) by controlling the pressure or flow (slave) of the fuel fired in the heater.
- *Adaptive control:* Typically used in level control of a horizontal cylindrical vessel, where the volume change per unit height varies drastically in the bottom and upper sections of the vessel compared to the middle section of the vessel. Adaptive level control uses different sets of tuning constants for extreme level conditions as well as for normal level conditions. This helps by using buffer capacity available in the vessel without compromising the safety issues related to overflowing or emptying of the vessel.

14.2.1.1 WHAT IS PROCESS CONTROL?

The chemical process industry basically consists of unit operations and processes. Various process parameters such as pressure, level, flow, and temperature are controlled to maintain key profit variables such as product quality, conversion, and yields at the desired levels. Process control helps in reducing the variability of the process, thereby minimizing the deviation from the desired operating conditions and improving the profitability. Process control is also important to ensure that the plant is operating in the safe operating region.

14.2.1.2 ELEMENTS OF A CONTROL LOOP

Most basic process control systems consist of a control loop as shown in Figure 14.1 and have these four main components [1]:

1. Primary measuring element
2. Controller
3. Final control element
4. Process

Primary elements are devices that undergo some changes in their properties with changes in process conditions that in turn are reflected as process measurement. Transducers are used for measuring process parameters. Transmitters/special transducers are normally used for measuring various process parameters such as flow, level, pressure, temperature, etc.

A controller is a device that receives data from a measuring instrument, compares those data against an

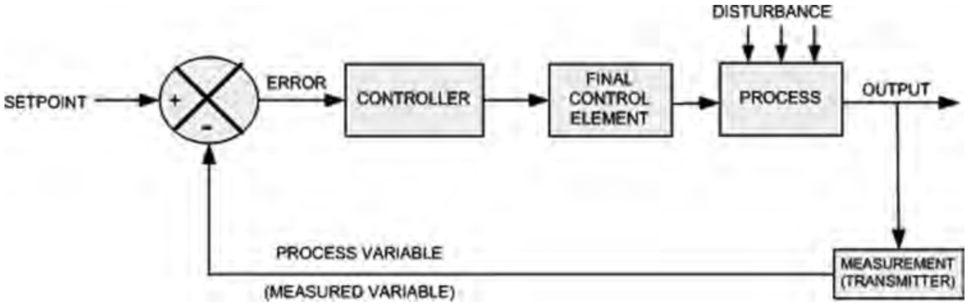


Figure 14.1—Typical process control loop.

operating setpoint, and, if necessary, signals the control element to take corrective action on the basis of the error between setpoint and measurement. In normal feedback controllers, PID algorithms are mostly used for effective control of the process parameters.

Final control elements are used to regulate the process so as to bring the measured process parameter to its setpoint value. In most of the cases, pneumatic (i.e., air-operated) diaphragm control valves, turbine speed, variable frequency drives, fin-fan blade angle, damper openings, etc. are the most common final control elements in process control applications. Final control elements are used to regulate the flow of material or energy into a system.

14.2.1.3 CONTROL VALVES

Control valves are the main final control elements in most of the chemical processing industries' process control loops. Modern day control valves are fitted with smart transducers for tighter control.

Normally control valves are selected based on type of fluids [2]; fluid properties such as temperature, viscosity, specific gravity, and flow capacity; pressures such as inlet, outlet, and pressure drop at normal and shut-off conditions; maximum permissible noise levels; inlet and outlet pipe sizes; flange ratings; body material; speed of response (single acting or double-acting); and failure response such as air failure to close or air fail to open, etc. On the basis of this information, the user and valve manufacturer normally agree on valve size, valve body (butterfly, angle, double-port, etc.), valve plug guiding (cage style, port guided, etc.), valve plug action (push down to close or push down to open), port size (full or restricted), valve trim materials, actuator size, flow action (flow tends to open or close the valve), bonnet style (normal, extended, bellow seal, etc.), corrosion and erosion preventive/resistive design of wetted parts and valve leakage class, based on shut-off requirement.

The most commonly used control valve accessories are supply pressure regulators, analog I/P converters to control the analog signal to pneumatic signal, and pneumatic positioners for better positioning of the stem to have accurate control. Other optional items are solenoid valves, limit switches (to get feedback on the valve open/close conditions), volume booster for faster response on critical and bigger size valves, pneumatic lock-up device, etc.

Positioners are available in all of the three types such as normal, HART-based, and field-bus-based technologies [3]. Field bus technologies enable the traditional PID control at the valve or field transmitter level, thereby increasing product capabilities, and reducing wiring, which enables automatic configuration and setup of the field instruments and valve in a minimum amount of time, leading to the "control by wire" concept. A digital positioner comes with embedded systems that use predefined instrument and valve diagnostics and provides alerts for improper mountings, electronics problems, control valve performance issues like gland tightness, drift in calibration, etc. It can be accessed remotely by a plant instrumentation team to troubleshoot, rectify, and reconfigure valves without much effort, which enables predictive maintenance instead of normal preventive and breakdown maintenance. Partial-stroke and signature tests help in identifying possible valve sticking, pneumatic leaks in the actuator, packing-related problems, etc. This substantially reduces maintenance cost and improves the performance and reliability of the valve. Valve stem travel feedback, actuator pressure sensor, etc., are used to find the control valve performance. Smart transmitters and control valve configurations, performance monitoring, and troubleshooting are bundled as an "Asset Management System" in recent DCS systems.

In a typical refinery system, a wide array of transmitters, analyzers, and control valves are used in various units. Some typical applications are listed in Tables 14.1 and 14.2.

14.2.1.4 BASIC CONTROL SCHEMES

The oldest strategy for control is to use a switch, giving simple on-off control. On-off control is also referred to as two-position control. A typical on-off controller is "on" when the measurement is below the setpoint (SP) and the manipulated variable (MV) is at its maximum value; if the measurement is above the SP, the controller is "off" and the MV is at its minimum. Typical usage of on-off controls in manufacturing plants is for sump level control.

In modulating control, the output of a controller can move through a range of values defined by an upper and lower limit as the operating range. It is a smoother form of control than on-off control.

In open-loop control, the final control element is normally operated manually to get a desired value. However, it needs constant attention to keep the MV at the desired value. In the case of a closed loop, the controller keeps the final control element moving to get the desired value as set in the setpoint. For closed-loop control, proper controller selection and its tuning are important. A typical example of open-loop control is fin-fan outlet temperature control using hand indicator controllers (HICs). In some units, these HICs are converted to temperature indicator controllers (TICs).

In a feedback control loop, the controlled variable is compared to the setpoint, and the difference/deviation/error acted on by the controller is calculated to move the MV in a way to minimize the error.

A feed-forward control system uses measurement of disturbance variables to position the MV and minimize any resulting deviation due to measurable process disturbance. Typical examples are steam reboiler heat-duty controllers, measuring the temperature of the steam flow and process fluid temperature, and adjusting the steam flow for effective, consistent heat energy supply to the distillation column.

In some cases, two or more inputs to the process are used for controlling one process output. The inputs to the process are maintained in a fixed relationship.

- The split range control configuration has only one measurement, such as receiver drum pressure (controlled output), and more than one MV, such as nitrogen supply pressure to pressurize the drum in case of lower pressure than the SP and depressurizing to flare in case there is an excess pressure compared with the SP.
- Normally this kind of control is used in a push-pull type of control, such as heating and cooling, pressurizing and depressurizing, filling and draining, etc.

Ratio control involves a controller that receives input from a flow measurement device on unregulated (wild) flow. The controller performs a ratio calculation and signals the appropriate setpoint to another controller that sets the flow of the second fluid so that the proper proportion of the

TABLE 14.1—Typical Refinery Measuring Instruments and Their Services

Instrument	Instrument Subtype	Units	Equipment	Service
Analyzer	Combustible gas analyzer	Crude, VGO, aromatics	Fired heater	Flue gas
	Conductivity analyzer	Alkylation, clean fuels, utilities	Reactors, headers	BD, feed water, acid, steam
	CO_2 analyzer transmitter	FCC, alkylation, polypropylene	Exchangers, reactors, vessels	Flue gas
	Density analyzer	PRU, clean fuels, utilities, polypropylene, coker, tankfarm	KOD, headers	LPG, additive, fuel gas, diesel
	Dew point analyzer	Clean fuels, utilities	Headers	Instrument air
	Dissolved O_2 analyzer	FCC, CPP	Fired heaters, vessels	Flue gas
	Distillation analyzer	Crude	Pumps, headers	Naphtha, kerosene, diesel, HAGO
	Flashpoint analyzer	Crude, clean fuels, VGO, RTF	Headers, exchangers	Diesel, kerosene, heavy kerosene
	H_2S analyzer	Alkylation, sulfur, Merox, RTF	Absorber, drier, regenerator	LPG, sour water, off gases
	HC analyzer	Clean fuels, utilities	Header	Steam
	Humidity analyzer	FCC	Main column	
	Infrared analyzer	FCC, VGO, aromatics, RTF, utilities	Fired heater, header, exchanger	Flue gases, diesel, alkylate
	Moisture analyzer	PRU, alkylation, PP, RTF, aromatics	Drier, header	Propylene, hydrogen, nitrogen, net gas
	O_2 analyzer	Crude, coker, clean fuels, aromatics, CPP, PP	Fired heater	Flue gas
	Oil in water analyzer	Clean fuels	Header	Cooling water
	pH analyzer	Alkylation, crude, FCC, CPP, utilities	Headers	Storm water
	Pour point analyzer	Crude	Header	
	Reid vapor pressure analyzer	Alkylation	Tank	Alkylate
	Residual Cl_2 analyzer	Utilities	Tank	Potable water
	Sulfur analyzer	Alkylation, clean fuels, ATU, RTF	Tank, drier, header	LCO, diesel
	Thermal conductivity analyzer	Alkylation, VGO, aromatics	Scrubber, compressor, separator	Gas
	Viscosity analyzer	RTF, utilities	Tank, header	Fuel
	Water in oil analyzer	Crude, utilities	Pump	Crude
Level	Capacitance level	Alkylation, aromatics	Boiler	—
	Displacer level	Crude, Merox, FCC, alkylation, utilities	Desalter, KOD, pump	Refrigerant, water oil interface
	Displacer level FF	VGO	Coalescer	Kerosene, diesel
	GWR level	Entire refinery	Vessels, reactors, strippers, separators	HC, amine, fire water
	GWR level FF	Entire refinery	Vessels, reactors, strippers, separators, KOD	HC, amine, fire water
	Magnetic float level	Alkylation, PP	Reactors	Acid, emulsions

TABLE 14.1—Typical Refinery Measuring Instruments and Their Services (Continued)

Instrument	Instrument Subtype	Units	Equipment	Service
	Level	CPP, utilities, coker, Merox, crude	Pump, tank, splitter	Caustic, phosphate, nitrogen
	Level FF	Clean fuels, aromatics	Stripper, KOD	LCO, diesel
	Microwave level	Crude	Desalter	Crude, water
	Nuclear level	Crude, FCC, aromatics, coker, PP	Columns, reactors	Catalysts, slurries-related services
	Nuclear level FF	Coker	—	—
	Radar level FF	PRU, alkylation, clean fuels, utilities	Reactors, columns	Amine, slops, acid
	Radar level	Sulfur, CPP, RTF, utilities, FCC, PRU	Splitter, hopper, tank	Catalyst, amine, fuel oil, diesel, reformate
	Radar level	Crude, RTF, Utilities	Tanks	Gasoline, propane, propylene, naphtha, VR, crude, antioxidant
	Radar level	RTF, ATU, SWS, crude	Tanks, spheres	Diesel, amine, VR, propylene, gas, isobutane
	Sonic level	PP	Pit	Effluent
Flow	Coriolis flow meter	Crude, aromatics, PP, CPP	Pumps, header	Oil, fuel gas, isomar
	Flow transmitter	FCC, PRU, clean fuels, aromatics, utilities, coker	Header, compressor, fired heater, pump	Steam, nitrogen
	Flow transmitter FF	PRU, clean fuels, utilities, VGO, coker	Fractionators, heater, pumps	Water, steam, foam, HC
	Indicating flow transmitter	Coker, aromatics	Fired heater, pump	Steam, water
	Indicating flow transmitter FF	Coker	Fired heater	Steam
	Magnetic flow transmitter FF	Alkylation, CPP, utilities	Reactors, mixers, tanks	Water, acid
	Magnetic flow transmitter	Alkylation, clean fuels, utilities	Tanks, headers	Water
	Rotameter flow transmitter	Alkylation, RTF	Drier, vessel	Gas, inhibitor
	Turbine flow transmitter	Utilities, ATU	—	—
	Ultrasonic flow meter FF	Sulfur, utilities	Header	Fuel oil
	Ultrasonic flow Transmitter	Utilities, RTF, CPP, clean fuels, alkylation	Tanks	Fuel oil, diesel, gas, nitrogen
	Vortex flow meter	Utilities, sulfur	Header	Steam, saturated gas
	Vortex flow meter FF	Alkylation, CPP, RTF, utilities	Reactor, pump, tank, reboiler, ejector	HC
Pressure	DP transmitter	Entire refinery	Mixer, regenerator, compressor, blower	Fuel gas, air, lube oil, steam,
	DP transmitter FF	Entire refinery	Pump, filter, fired heater, expander	Kerosene, HCO, make-up gas, naphtha
	DP transmitter FF flow	Entire refinery	Fired heater, desalter, vessels, columns	HC, nitrogen, fuel gas, pilot gas, nitrogen, amine
	DP transmitter FF level	Entire refinery	Stripper, KOD, separator, tank	Amine, water, caustic, HC
	DP transmitter flow	Entire refinery	Fired heater, compressor, blower, column	HC, comb air, nitrogen

(Continued)

TABLE 14.1—Typical Refinery Measuring Instruments and Their Services (Continued)

Instrument	Instrument Subtype	Units	Equipment	Service
	DP transmitter level	Entire refinery	Reactor, stripper, drier, absorber, filter	Nitrogen, catalyst, HC, lube oil, steam
	DP transmitter weight	PP	Reactor	Catalyst
	Draft pressure transmitter	CPP, utilities	Fired heater, compressor	
	Pressure transmitter	Entire refinery	Fired heater, riser, compressor, turbine, reboiler	Phosphate, refrigerant, steam, HC, BFW
	Pressure transmitter FF	Entire refinery	Pump, separator, column, fired heater	HC, lean gas, wash water, nitrogen, hydrogen
	Pressure transmitter level	Utilities	Sump	Oily water
Temperature	Temperature transmitter	Entire refinery	Fan, compressor, reactor, vessel, column	Air, HC, steam, nitrogen, flue gas, fuel gas
	Temperature transmitter FF	Entire refinery	Fan, compressor, reactor, vessel, column	Air, HC, steam, nitrogen, flue gas, fuel gas
Corrosion	Corrosion transmitter	Alkylation, VGO, ATU, coker, aromatics, utilities	Condenser, stripper, BD drum	—
Current	Current transmitter	Crude, FCC, PP	Vessels, pumps	—
Density	Density transmitter FF	Utilities	—	Fuel gas
Position	Position transmitter	FCC, PRU, clean fuels, CPP, PP	Pumps, header	—
Power	Power transmitter	FCC, aromatics	Compressor	—
Speed	Speed transmitter	Crude, FCC, clean fuels, CPP, VGO, PP	FD fan, ID fan	—
Stack monitor	Stack gas monitor	Clean fuels, VGO	Fired heater	—
Voltage	Voltage transmitter	Crude, PP	Desalter, reactor	—
Weight	Weight transmitter	PP	—	—

ATU, amine treating unit; BD, blow down; BFW, boiler feed water; Cl_2, chlorine; CO_2, carbon dioxide; CPP, captive power plant; FD, forced draft; FF, foundation field bus; HAGO, heavy atmospheric gas oil; HC, hydrocarbon; HCO, heavy coker oil; H_2S, hydrogen sulfide; KOD, knockout drum; LCO, light cycle oil; LPG, liquefied petroleum gas; Merox, mercaptan oxidation; O_2, oxygen; PP, polypropylene; PRU, propylene recovery unit; RTF, refinery tank farm; SWS, sour water stripper; VGO, vacuum gas oil; VR, vacuum residue

TABLE 14.2—Typical Control Valve in Refinery Service

Type of Control Valve	Units	Equipment	Service
Angle control valve	Coker, FCC, PRU, LCO cracker	Pumps, naphtha splitter, stripper	Wash water, naphtha, LCO, diesel
Ball control valve	Crude	Headers, exchangers, splitters, tanks	Crude, isomerate
Butterfly control valve	Crude, acid regenerator	Fired heaters, pumps, KODs	Vapors, hydrocarbon
Control valve	Crude, FCC, PRU, VGOHT, coker	Exchangers, pumps, fired heaters, columns	Crude, caustic, BFW, sour water, DM water, lean amine, hydrocarbon
Damper control valve	Crude, HNHT, LCO cracker, VGO HT	Fired heater	Combustion air, flue gases
FV control valve linear field-bus FF control valve	Platformer, VGO HT, ATU, PRU	—	Lean amine, phenolic water, hydrocarbon
FV control valve linear control valve	FCC, VGO HT	—	Diesel, naphtha, VR, LCGO, wash water

TABLE 14.2—Typical Control Valve in Refinery Service (Continued)

Type of Control Valve	Units	Equipment	Service
FV control valve quarter turn field-bus FF control valve	FCC, ATU	Exchangers, columns	Hydrocarbon
FV control valve quarter turn control valve	TGTU, sulfur, FCC	Exchanger, reboiler, column	Acid gas, lean amine, cycle oil
FV control valve severe service control valve	Alkylation	Pumps, compressors	Hydrocarbon
FV damper valve control valve	—	FD fan	Comb air
Gate control valve	Crude, alkylation, coker, platformer	Condenser	Steam
HV control valve angle control valve	DHDS	Absorber, columns	Sour water, amine
HV control valve angle field-bus FF control valve	DHDS	Stripper	—
HV control valve field-bus FF control valve	Platformer	Header	Gas
HV control valve butterfly control valve	VGO HT	KOD	Flare gas
HV control valve globe control valve	FCC, PP	Headers, vessels	Vents, steam
HV control valve linear field-bus FF control valve	Platformer	Fired heater	Steam
HV control valve linear control valve	—	Scrubber, absorber	Amine
HV control valve severe service field-bus FF control valve	Platformer, FCC	Compressor, reboiler	—
HV control valve severe service control valve	VHO HT	Flash drum	Hydrocarbon
HV damper control valve	Clean fuels	Condenser, fans	Hydrocarbon
HV damper general	Coker	Fired heater	Comb air
HV double acting pneumatic valve control valve	FCC	Separator	—
HV future control valve	CFP	Heater	Oil
HV isolating ball valve control valve	PP	Pump, column	Hydrocarbon
HV manual regulating valve control valve	LCO hydrocracker	Separator	LCO
HV piston-operated valve control valve	Acid regeneration	Nozzles, separator, boilers	Propane, BFW, nitrogen
HV single-acting pneumatic valve control valve	—	Header	BFW
Actuating on/off valve/control valve	PP	Headers, tank, vessels	Nitrogen, gas, slurries
LV control valve ball control valve	—	Vessels	Steam
LV piston-operated valve control valve	FCC	Header	VGO
LV single-acting pneumatic valve control valve	Coker	Vessels	Amine
MOV	—	Compressor, pump, tank	Alkylate, gas, LCO, VGO, steam, LK
TV control valve ball control valve	—	Header	Steam
TV control valve control valve	—	Header	Steam
TV piston-operated valve control valve	FCC	Filter	Catalyst

(Continued)

TABLE 14.2—Typical Control Valve in Refinery Service (Continued)

Type of Control Valve	Units	Equipment	Service
Double-acting pneumatic valve control valve	FCC	Header	Slurry oil
XV actuating on/off valve control valve	Crude, platformer, DHDS, LCO cracker	Fired heater	Fuel gas, fuel oil, pilot gas
XV double-acting pneumatic valve control valve	Coker	Pumps, vessels	Debut feed
XV isolating valve ball control valve	Coker, DHDS	Pumps, headers	Cooling water, flushing oil, off gas
XV isolating valve butterfly control valve	Coker, DHDS	Fired heater, filter, fractionators, pump	Fuel gas, pilot gas, naphtha
XV piston-operated valve control valve	PRU, FCC, VGO HT	Pump, reboiler, reactor, fractionators	Ammonia, wash water, hydrocarbon
XV power actuated valve block control valve	CFP, ATU	Pumps, KOD	Slop oil

CFP, clean fuel project; DHDS, diesel hydrodesulfurization; HT, hydrotreater; TGTU, tail gas treating unit. VGOHT, vacuum gas oil hydrotreating; HNHT, heavy naphtha hydrotreating; LCGO, light coker gas oil; FV, flow control valve; HV, hand valve; FF, field-bus enabled valve; LV, level control valve; TV, temperature control valve; MOV, motor operated valve; XV, shut-off valve

second fluid can be added. In refineries, ratio controls are widely used right from the crude preheating ratio, desalter crude and water ratio, and in the final product blending ratio for making premium-grade fuels with additives for performance boosting.

Cascade control is a control system in which a secondary (slave having fast dynamic response) control loop is set up to control a variable that is a major source of load disturbance for the primary (master having comparatively slow dynamic response) control loop. The controller of the primary loop determines the setpoint of the summing controller in the secondary loop. Cascade control is used when high performance is needed during frequent random disturbances. It allows faster secondary controller to handle disturbances in the secondary loop. Typical examples are distillation column top-tray temperature control using reflux flow and reflux drum-level control using draw-off flow.

Lead-lag control is important in fired heaters, steam boilers, and hydrogen reformers. When heat input to the heater is varied, sufficient air should always be available for complete combustion of fuel fired.

To increase the heater outlet temperature, the main temperature controller increases its output, which in turn increases the air flow to the heater first using a high selector switch (HSS) between temperature controller output and fuel flow controller output before increasing the fuel to the heater. This increase of fuel flow controller output is governed by a low signal selector between temperature controller output and air flow controller output.

Combustion air leads fuel in the case of an increase in firing requirement and lags fuel in the case of a decrease in firing requirement; hence, it is called lead-lag control. It is possible only in the case of balanced draft heaters in which air intake can be finely controlled and measured.

14.2.2 Model Predictive Control

Basic regulatory controls like flow, temperature, pressure and level controls, and advanced regulatory controls like cascade, ratio, lead-lag, etc., work on error between actual plant measurement and operator setpoint. As long as there is an error, these regulatory controllers move the final control element to achieve the setpoint on the basis of the controller mode (PID) and the entered tuning constants.

The next level of advanced control comes into existence through direct digital control (DDC) and supervisory setpoint control (SSC). Both of these are related to an external computer program other than the regulatory PID controllers. DDC has the capability to set the valve output, thus bypassing the regulatory PID loop. SSC has the capability to write the setpoint to underlying PID controller.

Model predictive control (MPC) is one of the advanced process control (APC) variants that has the capability of providing the target for the regulatory controller based on its prediction capability from the underlying plant empirical model derived from the plant step test. Modern-day MPC deals with plant constraints and optimization on the basis of a linear-programming (LP)-based cost optimizer, giving the best operator output on a 24 × 7 basis. MPC knows interactions among all of the "variables" from the output to the input relation model derived from the plant step test, can "predict" the effect of one variable on others (interaction), and takes control actions accordingly. The APC and MPC terms are used interchangeably in the process control domain.

With APC, the unit operations are directly controlled in terms of profit variables such as separation quality, conversion, yield, etc., instead of inferred variables such as pressure, temperature, flow, level, etc. Also, more consistent controls and surety of the respecting constraint observation result in the plant operating much closer to the real plant constraints as compared with the normal regulatory controllers and manual operation by the operator.

14.2.2.1 APC TERMINOLOGIES

There are two major types of variables in a controller. In a given process that is to be controlled, independent variables are input to the process and the dependent variables are output from the process [4].

The dependent variables are also known as controlled variables (CVs). These are the variables for which targets are defined, and the controller tries to maintain these variables to their targeted levels. The dynamic behavior of the CVs can be described totally in terms of specific independent variable changes over time. These might include product stream properties, temperatures, pressures, differential pressures, valve positions, or other outputs from the process.

CVs are normally maintained at a constant value or between high and low limits, which allows the controller more room to optimize the process.

An independent variable is a causal variable for which the value is not affected in any way by any other variable in the process and that, when changed, causes a corresponding change in the process. Independent variables are further classified as MVs and disturbance variables (DVs) or feed-forward variables (FFVs).

MVs

MVs are the independent variables that are moved (i.e., manipulated) by the controller to control the process. Two main criteria for qualifying a variable as an MV are

1. It should affect the CVs.
2. It can be set and manipulated by the controller.

Examples of MVs are SPs to regulatory controllers and valve positions.

FFVs

FFVs are the independent variables that have a significant effect on the process but still cannot be manipulated by the controller. These may include ambient temperature, feed composition, and cooling water supply temperature.

14.2.2.2 STEPS IN DEVELOPING AN APC CONTROLLER

- Functional design study (this includes a detailed study of process and determination of project cost and benefits)
- Preliminary design
    - Review of process objectives
    - Controller scope definition
    - Preliminary process test
    - Control specification report
- Plant step testing
- Detailed design and simulation
    - Develop dynamic models
    - Develop inferential property estimators
    - Offline controller simulation and tuning
    - Controller model review
- Integration and commissioning
    - Closed-loop commissioning
    - Final project documentation
- Develop inferential property estimators
- Postcommissioning sustained performance
    - Controller monitoring
    - Maintain ongoing training efforts

14.2.2.3 FUNCTIONING OF AN APC CONTROLLER

Through the step testing and model identification package, all relationships between the CVs and MVs are obtained in the form of models. Once models are known, the controller can predict the CV values for given changes in the MVs or vice versa. To achieve the desired values of CVs, the MVs are moved such that the net response of changes in the MVs matches with the desired change in the CV values. Thus, more than one MV may be moved to satisfy the CV values. The controller follows certain rules while coming up with the required MV moves.

- Rate of change of MV moves (as defined by the control engineer)
- MV limits (as defined by the control engineer)
- Changes in CV values as a result of MV moves (no constraints are violated)

If all of the above conditions are satisfied, the controller comes up with the best solution. If any of the above is likely to be violated, the controller considers that as an additional constraint and recalculates the MV moves. It tries to maintain all linear CVs to their target values and all constraints within limits. The moment it is not able to come up with the best solution it calculates the next-best solution based on the priorities set by the control engineer.

The controller also retains information of some of the immediate past runs and compares the predictions with the actual responses. On the basis of the differences observed, it generates “bias” factors that in turn are used to fine-tune the next outputs from the controller. This solution may be a MV move away from the ideal resting value (IRV), an offset in the linear CV, or to “give up” on less important constraints. To know the relative importance of constraints, all constants are given ranks that are assigned by the control engineer. Also, all CVs and MVs have a weightage factor assigned to them. This helps the controller in knowing the control hierarchy.

14.2.2.4 BENEFITS OF APC

Some of the benefits of APC are listed below [5].

- The given unit operation/unit process is directly controlled in terms of profit variables such as separation quality, conversion, yield, etc., instead of inferred variables such as temperature, pressure, level, flow, etc.
- Improved and consistent controls and accurate observation of the constraints lead to plant operation being much closer to the real constraints as compared with manual operation. This leads to benefits such as throughput increase. APC considers the effects of changes on all CVs and finds the best overall solution. It reduces variations in process parameters.
- The control action is objective and is an optimal decision for a given change/situation. This is also ensured around the clock. Along with confidence of tighter, timely control, it leads to enhanced profitability in terms of improved/stable conversions, improved yields, reduced energy/utility consumption, etc.
- Smooth and consistent control operation and less manual interference/manpower is required in the normal operation. The operator need not continuously monitor each and every process parameter and take manual action.
- Because the equipment constraints are always observed, it leads to higher equipment service factors. The constraints can be prioritized per operations philosophy and safety considerations.
- Tighter controls reduce the deviation in product quality, thus keeping the product quality parameters at the desired values. Incidents of product off-spec and quality giveaway can be avoided and hence prevent any loss of opportunity.

14.2.3 Benchmark Information

In the hydrocarbon business, the refining sector in particular is challenged with many constraints relating to safety and environment, customer demands on cleaner products, need for sweating the assets to get the best from every drop of oil, spiraling energy costs, varying crude quality, etc. Understanding the crude oil is itself an art with complexities of issues such as compatibility; presence of corrosive species such as naphthenic acids, salts, sulfur, and chlorides; increasing heaviness as seen in drop in API; impediments in transportation in a few cases because of higher viscosity and pour point; and an ingress of undesired elements such as metals, solids, chemicals, additives, etc. Refiners pay immense attention into feedstock management so as to ensure reliability of the processing units while endeavoring to maximize and sustain profitability.

Process control and optimization play a pivotal role in achieving the desired level of performance under such variances faced daily by refining industries. In fact, to get the best from APC/optimization strategies, it is mandatory that basic instrumentation (i.e., measuring elements, control valves, online analyzers, etc.) is well within the operable range with a desired accuracy of measurements. Further, the process automation team, multidisciplinary in nature (drawn from domain experts of operations, process engineering, instrumentation and computing capabilities), has full-time professionals for advanced control/optimizer upkeep. Benchmarking of the process control application facilitates raising the performance bar of a refinery. Some of the elements/key parameters used in the benchmarking of process control are given below. Each refiner can pick up the appropriate element depending on their business environment and work toward excellence.

- Uptime factor of control strategies
- Production plan versus actual closure
- Number of process automation full-time employees per process unit to maintain the strategies
- Benefits from APC/optimizer in cents per barrel of feed to the unit
- Standard deviation of critical controlled process variables (yield, quality, or energy use)
- Sigma average error and time taken to reach steady state from a disturbance
- Tracking of out-of-service controllers on a daily basis
- Mean time to correct controller from off to on
- Time to implement fully functional APC/optimizers in processing unit
- Validation of SP given by APC/optimizer strategies through offline models
- System of embedding "live" business drivers into APC/optimizer strategies
- Bias update frequency in inferential prediction
- Use of adaptive control
- Time to steady state between feed changes in a given unit
- Delta error in inferential prediction with laboratory referee method
- Early event detection capability
- 24 × 7 support to manufacturing onsite or through remote methods
- System of incorporating innovations in control strategies

14.3 QUALITY MEASURING INSTRUMENTS

Maintaining consistent product quality and minimizing the quality giveaway are the main tasks of all manufacturing industries. However, conventional frequent sample collection, analysis of the sample in the laboratory, and then taking corrective actions is not a sufficient way to control the modern-day refining processes that are highly dynamic and economically demanding. Improvements in the sensor technology and availability of digital techniques based on signal processing have led to highly sophisticated, customizable, ready-to-use online process analyzers to overcome the earlier conventional analog-type analyzers. Modern-day analyzers are highly configurable for satisfying various needs because they intelligently diagnose routine samples to minimize maintenance efforts.

Online analyzers are used for continuous monitoring of the feed, intermediate, and final product qualities. These analyzer values are further integrated with the process control systems to give feedback and control the process in real time. Typical applications of the online analyzers are given below.

- Feed/product stream quality monitoring such as sulfur content, density, endpoint, flash point, pour point, humidity, dew point, etc.
- Parameters pertaining to environmental regulations monitoring (i.e., oxygen, carbon monoxide, oxides of nitrogen and sulfur, opacity, etc.) in heater stack flue gas, etc.
- Water quality parameters such as pH, silica, conductivity, dissolved oxygen, chlorine, etc.
- Effluent monitoring parameters such as oil in water, total suspended solids, total organic content, etc.
- Gas chromatographs are widely used for quality monitoring and control of various hydrocarbon streams.

In addition to these online "wet" analyzers, near infrared (NIR)-spectroscopy-based "noncontact"-type analyzers are available for property predictions such as research octane number (RON), cetane number, density, and distillation of petroleum products. It is mainly used in the product blending loop to control various component streams for making a particular blend of product conforming to quality objectives dictated by the blend optimizer.

14.3.1 Introduction to NIR Spectroscopy

Infrared spectroscopy is one of the most important analytical techniques available today. One of the great advantages of infrared spectroscopy is that virtually any sample in any state can be analyzed. Infrared spectrometers have been commercially available since the 1940s. At that time, the instruments relied on prisms to act as dispersive elements, but later diffraction gratings were introduced into dispersive machines. However, the most significant advances in infrared spectroscopy have come about as a result of the introduction of Fourier-transform spectrometers. This type of instrument uses an interferometer and exploits the well-established mathematical process of Fourier transformation. Fourier-transform infrared (FTIR) spectroscopy has dramatically improved the quality of infrared spectra and minimized the time required to obtain data.

Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of vibration of a part of the sample molecule.

The presentation of spectral regions may be in terms of wavelength (λ) as nanometers (1 nm = 10^{-9} m). Another unit that is widely used in infrared spectroscopy is the wave number (ν) in cm^{-1}. This is the number of waves in a length of 1 cm and is given by $\nu = 1/\lambda$. This unit has the advantage of being linear with energy.

The infrared spectrum can be divided into three main regions:

1. Far-infrared (<400 cm^{-1})
2. Mid-infrared (4000–400 cm^{-1})
3. Near-infrared (13,000–4000 cm^{-1})

A typical gasoline NIR spectrum is shown in Figure 14.2.

The x-axis shows the wavelength λ (nm) and the y-axis represents the absorbance in fraction. It is to be noted that the absorbance of the sample if irradiated with NIR varies at different wavelengths. This is because the absorbance of different species (molecules) in the sample gets pronounced at different wavelengths. The figure shows the different species and their active wavelength regimes for a typical gasoline spectrum.

The quantitative analysis method is used to predict the properties of various samples rather than analyzing individual spectra.

14.3.1.1 HOW DOES NIR WORK?

Hydrocarbon molecules contained in refinery streams absorb NIR radiation because of C-H bond "movements." This translates into a product "finger print" that can be recognized by means of chemometric techniques. The absorbance spectra can therefore be translated into performance properties. Those linked to PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics) contents are more likely to be predictable (especially octane number, cetane number, benzene, cloud point, or aromatic content) than those linked with C-H, N-H, or O-H bonds, such as sulfur, which is present in small amounts.

The improvement in computer technology associated with spectroscopy has led to the expansion of quantitative infrared spectroscopy. The application of statistical methods to the analysis of experimental data is known as chemometrics. The most commonly used analytical methods in infrared spectroscopy are partial least-squares (PLS) and principal component regression (PCR). PLS is a least-squares method that involves matrix operations. The PLS method is very useful in investigating very complex mixtures such as petroleum products. This method is used to build a model as a function of the variance in the spectral data set.

14.3.1.2 NIR MODEL IMPLEMENTATION

The implementation of a model occurs in three steps [6]:

1. Model building (i.e., calibration)
2. Model validation
3. Online prediction.

Model building involves

- Calibration set specification to identify the properties and ranges for the model
- Data collection for calibration (laboratory primary analysis and the corresponding NIR spectra for each sample)
- Model building using a multivariate calibration technique
- Preliminary model validation using the same software

It is very important to note that the models are highly specific to refinery, the type of processes used, crude diet, product requirements, etc. Model validation is done by comparing the predicted values with the corresponding

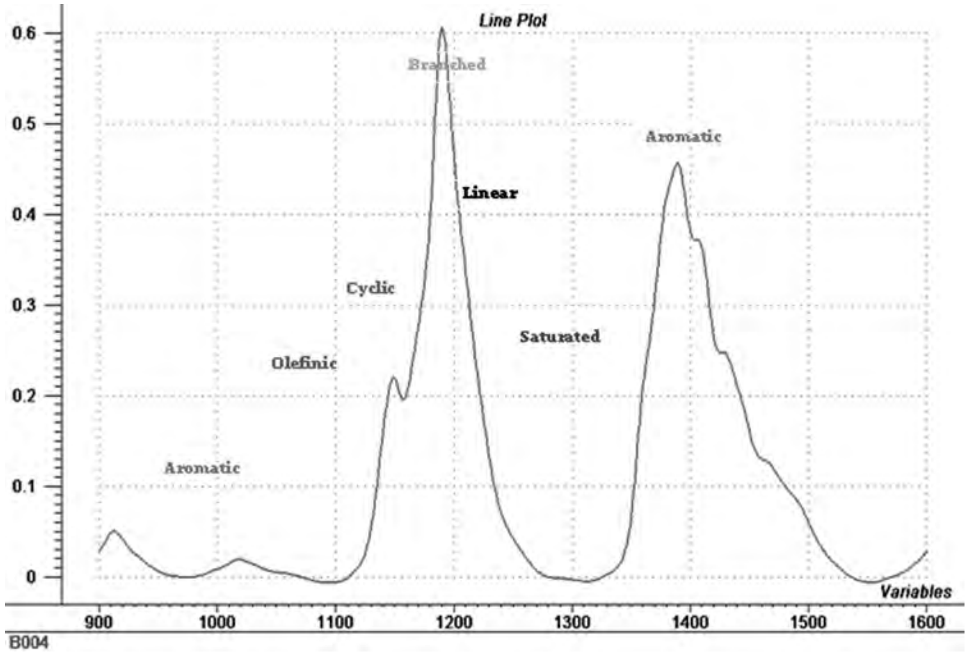


Figure 14.2—Typical gasoline NIR spectra [6].

laboratory primary data. A statistical quality control chart for each property is prepared and validated.

Online model prediction is done by

- Loading the model into an offline laboratory system and online system in the field.
- Configuring the factors, outlier limits, and ranges.
- Online predictions are continuously monitored through a plant historian.
- Periodic laboratory analysis for verification of model performance.

14.3.2 NIR Applications

The typical NIR applications for the refinery include the prediction of the following:

- Gasoline
  - RON
  - Motor octane number (MON)
  - Vapor pressure
  - Distillation
- Diesel
  - Cetane number
  - Cetane index

14.4 ADVANCEMENTS IN INSTRUMENTATION AND PROCESS CONTROLS

14.4.1 Distributed Control System

A distributed control system (DCS) in a modern refinery helps in plant-wide automation. DCS is functionally and geographically distributed with redundant control hardware. The modular nature of the hardware and software provides easy expandability of the various DCS functionalities to new units in a seamless manner.

In a typical refinery, all plant measurements signals are terminated at plant interface buildings (PIBs), which contain all necessary signal conditioning units and control processors for executing more than 100 different software blocks for various functions such as analog and digital inputs, control algorithms, calculations, advanced controls, and analog and digital outputs. All analog and digital output processes from control processors and other similar modules such as emergency shutdown systems are again routed to final control elements in the field. In short, all data acquisition and control functions are done at the PIB level. Signals from PIBs are routed to a refinery control center for monitoring and control through operator consoles.

Other than normal data acquisition and control functions, a DCS also provides a platform for real-time databases such as InfoPlus.21 for collecting periodic plant data for maintaining history as well as performance calculation and monitoring of the units. A DCS also forms the basis for implementation of APC such as multivariable predictive controllers and real-time optimizers.

14.4.2 Process Alarm Management

In today's advanced control systems, one can define various alarms on I/O and various control blocks with different alarm types such as high, low, high-high, low-low, rate of change, deviation, etc. These kinds of messages entirely flood the operator station if not properly configured and are likely to divert the attention of the operators. Recently, most of the control system vendors have come up with alarm management software that can detect the total number of repetitive alarms and the number of I/O bad alarms, alarms per operator, disabled alarms, unacknowledged alarms, nuisance alarms, etc., which allows the operations and instrumentation and control team to prioritize and focus on major problems, thereby reducing the occurrence of the process upset alarms. A domain-specific alarm management system with an expert system to analyze and diagnose the root cause of the problem is the next step toward healthy alarm management. Alarm rationalization exercises are being done in some operating units.

14.5 POOR PROCESS DESIGN LEADING TO CONTROL PROBLEMS

During a recent grass-root start-up of a manufacturing unit, many issues arose because of poor process design, improper instrument selection, which led to different control issues. Some of the major implications were as follows:

- Complete process condition/parameter information not available and/or misunderstood by the design and vendor engineers, during selection of the instruments for various services, leading to failure in the operation of the instrument for that particular service (e.g., dielectic constant of the liquid hydrocarbon is necessary for measurement using radar level transmitters). Also, clean and dirty services are to be mentioned at early stages for proper selection of the instrument.
- Most of the modern control valves are selected with antiflashing/anticavitation trim instead of conventional trim. This kind of selection without necessary study leads to chocking problem in the trim, subsequently calling for more maintenance.
- Only field-proven technologies should be selected for critical services, otherwise any plant emergency/shutdown leading to the failure of the new technology instruments proves costlier.
- All emergency trip signals should be hardwired instead of serial link data communication, which causes a delay in tripping of the equipment and is less reliable.
- Wrong level transmitter tapping during the design, causing improper level measurement in the fractionator pan tray, which causes the level control to be very difficult during a disturbance.
- Inadequate number of trays between two pan trays in the main fractionator leading to jet flooding, which causes a disturbance in the column differential pressure, making it difficult to control the column profile.
- Hydrogen blanketing of the feed surge drum causing more hydrogen solubility in the feed. Because of this, controlling hydrogen flow to the reactor becomes very difficult.

14.6 RELIABILITY ASSURANCE IN PROCESS CONTROL AND INSTRUMENTATION

Reliability-focused culture is catching up in every manufacturing business enterprise. The problems related to poor reliability can range from unplanned interruptions/shutdowns, spurious trips, product becoming off-spec, excessive energy consumption, underutilization of assets, overfill or underfill in dispatches, increased lifecycle cost, or any combination of these factors. Reliability implies availability of the instrument for the intended purpose and precision of the measurement/control thereof close to the desired accuracy. Design for reliability is gaining importance because lessons learned from past incidents/experiences show the need for improvement in equipment selection, ensuring operation within the accepted window and correct manning. While aspects such as personal skill and level of motivation are critical to reliability, they are outside the scope of this chapter. Other issues that enhance/provide assured reliability are dealt with in this section.

Concepts such as quality function deployment (QFD), failure modes and effect analysis (FMEA), 5 Whys, etc., are typically deployed by refiners to improve the reliability factor. Pacesetter refiners are able to achieve a continuous run length of 9 or more years in all major processing areas such as crude distillation, fluid catalytic cracking, coker, platformer, etc. In other words, the process instrumentation and control system in pacesetting organizations must be robust enough with the necessary built-in redundancy to ensure safe and sustained operation.

To elaborate on the above concepts, the process of coker furnace operation is taken as an example. This process involves heating of feed vacuum residue from 600 °F at the coker fractionator bottom to 930 °F at the coker furnace outlet. The furnace heat duty is supplied by coil outlet temperature control, which manipulates the amount of fuel fired. There is a lead-lag system to control fuel fired in the heater and an air preheater for preheating combustion air and balanced draft operation. The furnace outlet temperature is well under control within 1 °C. In other words, the process looks robust; however, the run length of heater coils (i.e., between two decoking operations, which is critical to coker management because it affects refining margin) varies substantially from 120 to 180 days. It shows that a few more operational controls are to be put in place, such as uniformity of heat flux across the length of the furnace, minimizing cracking within the heater coils, feed quality management, etc. With the coker unit increasing the refining margin by approximately $250–400/ton of feed, any downtime of the coker furnace for decoking (by pigging, spalling, or steam/air decoking) will erode the margins. In short, this is a clear case of higher requirements from the customer (business group is considered as an internal customer in this case) demanding additional input variables (vital Xs) to be culled out and controlled.

Understanding each of the business-critical processes in a manufacturing setup and getting deeper into it to improve and sustain profitability are increasingly becoming imperative in today's competitive environment. From the erstwhile pneumatic system supported by audiovisual alarm, the instrumentation has migrated to an intelligent, self-diagnostic, and auto-tuning new-generation system. Digital magic has made immense advancements and possibilities in process control applications. Newer control algorithms such as nonlinear-level control, dead band, and adaptive controls are used, especially when a process is required to operate at different modes, varying regimes, or both for equipment performance curves. Smart controls, which take inputs from past heuristics and expert systems, fuzzy logics, inferential controls, global optimizer, etc., have been made feasible in recent times. Seamless integration of online/real-time applications and unit operations with offline processes (e.g., planning, scheduling, product testing and certification, condition monitoring, and a model-based approach for providing a "best operating window,") is another progression that facilitates a holistic view of the process so that reliability can be enhanced.

Nevertheless, new challenges to process reliability have also cropped up in the form of spurious trips, communication errors, control board component failures, loss of power to the solenoid valve, and so on. For example, in the old pneumatic system, open loops seldom had any alarms and closed-loop alarms were minimal. A typical crude unit used to have approximately 20 audiovisual alarms. With the advent of the DCS, the number of alarms can be three per open loop (including the rate of change of process value as a deviation alarm) and nine per closed loop. In other words, a crude unit with 250 or more open-loop indications and 60 or more closed loops can have as many as 1200 or more alarms, which has made it necessary for reliability, process, control, and operations engineer teams to classify the alarm into "must" and "good-to-have" categories. Modern refineries undertake "alarm rationalization" tasks and optimize the number of alarms for effective monitoring. It is a good practice to review the last 24 h of alarms daily to take appropriate corrective/proactive actions.

On many occasions it is seen that protection of equipment overrides the importance of the whole process in which the specific equipment is just a part. To ensure equipment reliability, the vendor provides several trip logics to prevent it from operating outside of the machine-specific window. However, in reality it is witnessed that such trips have indeed resulted in process upsets/plant shutdown because these have been provided in isolation. For example, it is advisable to operate any pump or compressor within its turndown limits, and to prevent it from being operated below turndown, recycle loops are provided by equipment vendors. Inadvertent/malfunctioning of opening of these spillbacks could result in tripping of heaters or loss of level/pressure in downstream units. Hence, it is imperative that the process is looked at in totality to ensure that cascaded failures do not occur.

There are instances that result in spurious tripping of the plant, especially when single instruments are not backed up for data integrity. To overcome this, the concept of "two-out-of-three" (2oo3) logic was brought in, with three independent field measuring devices to read the process conditions. Only when two of three such instruments read a deviation/error does the process abort and take to a safe shutdown position. Modern programmable logic controllers (operating at an every few millisecond span time) have the ability to display the alarm initially, which helps in failure diagnosis.

Solenoid valve burnout is a common phenomenon in refineries. Normally solenoid valves are energized, and any loss of power would result in activation of shutdown logic, leading to unit operation terminating at a respective safe position. Conversion from "de-energized to trip" to "energized to trip" is one such possibility to minimize/mitigate spurious trips.

Human errors arising from lack of experience/training have been the cause for some of the reliability issues seen in operating units. Use of training simulators to understand the shutdown sequences and process intricacies would help to prevent such failures. In most cases it is even preferred to provide a few seconds delay in tripping if the process/equipment allows such. Attending to boiler drum (three-element controller: steam flow, feed water flow, drum level) level is a classical example for many spurious trips at several manufacturing sites. A systematic study on "instrumented protective function" by a multidisciplinary team (process, operation, and instrument) can also help to eliminate spurious trips by evaluating process dynamics at each phase of operation (i.e., starting, steady state, increasing/reducing throughput, and plant severity, etc.).

In summary, in a complex refinery there are over 110,000 opportunities for defects/failures from a well designed and operated process control and instrumentation system. The refinery management deploys Six Sigma methodology to deliver highly safe and reliable operation. Although the efforts have raised the performance level to a Sigma level of 5.2 in totality, world-class reliability is being relentlessly pursued to attain still higher levels.

All process control and instrumentation is undergoing revamping to include the best of various emerging technologies such as smart sensors, wireless sensors, model-free adaptive control, miniature MPCs, and early event detection systems based on plant operating data.

14.7 ENVISIONING THE REFINERY OF THE FUTURE

There are several ways to visualize the "Refinery of the future," which is gaining importance with hardened crude oil prices coupled with the fear of "oil-peaking." For example, the future refinery will have its own inner ability to evaluate and select the crude within a couple of hours to buy ahead of competition and enjoy the initial market discounts. Refiners are stretching their limits to maximize the profitability (measured as gross/net margins in dollars per barrel) every single day, and yet the mean time between turnarounds must be as maximal as possible (say 9 or more years). There are people-related issues in terms of talent retention, nurturing innovations, cycle time reduction between idea and implementation, etc. However, the refinery of the future relating only to process control and optimization has been taken up further.

Communications technology has matured, and with increased bandwidth over wireless it is possible that the optical fibers and hardcore cables running between the plant and control center could be no longer needed. Process intensification and nanotechnology have made strides into every manufacturing business, and it is feasible that the current system of producing different products from crude will pave the way to choosing/producing any product and converting the entire crude into that singular product. The role of services (process engineering, planning, scheduling, inspection, engineering, etc.) could be consolidated and remote access of plant operation for providing solutions could find roots to manage and provide the "best operating zones" for operation, which could be something similar to the current "global positioning system" that guides travel. In other words, the response time to intervene will reduce to seconds/minutes. "Carbon trading" could go live, and refineries in different parts of a country could increase or decrease their throughputs on the basis of overall greenhouse gas "bubble" margin. With alternate power gaining impetus from most governments, the carbon trading link could also extend to all major industries.

The refinery of the future will be fully automated from crude blending to product blending, with many intelligent sensors and knowledge databases to steer various real-time control applications. Molecular-level analysis, using physical and inferential soft sensors, will dynamically optimize and allocate various plant loads. Refineries will be able to swing their production to operate at various demanding market conditions in a much faster and controlled way.

14.8 PROCESS CONTROL CASE STUDIES

14.8.1 Control of Crude Preheat Exchange Trains

14.8.1.1 INTRODUCTION

Preheat train exchangers form an important part of any crude unit because they are the backbone of heat integration in this unit of a refinery. Total heat requirement in the crude furnace can be offloaded if the preheat is optimum so the unit can be run efficiently with higher margins of throughput. Figure 14.3 depicts a typical crude unit preheat train related control configuration.

The crude received at the battery limit of the crude distiller unit must be preheated from ambient temperature to the temperature required for an efficient desalting operation. This preheating also helps to maximize heat recovery from the crude column outlet streams.

The inlet crude stream is split into two streams with one stream entering on the shell side of the S01 heat exchanger and other stream entering on the shell side of the S02 heat exchanger. The crude is preheated in exchangers S01 and S02 by circulating naphtha, which is drawn from the crude column naphtha accumulator tray through the tube side of S01 and S02. A flow indicator controller (FIC) controls the naphtha flow to exchangers S01 and S02. The naphtha outlet stream from these exchangers is routed back to the crude column top tray. The flow of naphtha through these exchangers is always maximized to enhance heat recovery.

Providing a split range ratio controller governs opening of control valves and ensures equal distribution. One of the control valves will be wide open (of the exchanger train, which exerts more pressure drop) and the other's opening will be adjusted to maintain the same flow as that of the other train.

14.8.1.2 CONTROL SCHEME FOR PUMP AROUND HEAT EXCHANGERS

The controls for the tube side of the S01 and S02 exchanger outlets are obtained by throttling of control valves FV1 and FV2, respectively, by feedback controllers. At the same time, as a process requirement, the return temperature of the naphtha stream to the crude column also must be maintained. The temperature is controlled by TIC, the output of which goes to the control valve TV-1. Depending on the return temperature, the control valve TV-1 opening gets adjusted by directly passing naphtha flows through S01 and S02 to the crude column inlet stream (see Figure 14.3). If the naphtha pump around the return temperature has to be increased, the control valve TV-1 will be wide open, limiting the flow through exchangers S01 and S02 and vice versa.

14.8.2 Fired Heater Control

14.8.2.1 INTRODUCTION

Lead-lag control is the mechanism used in fired heaters for adjusting firing rates while ensuring safety of the

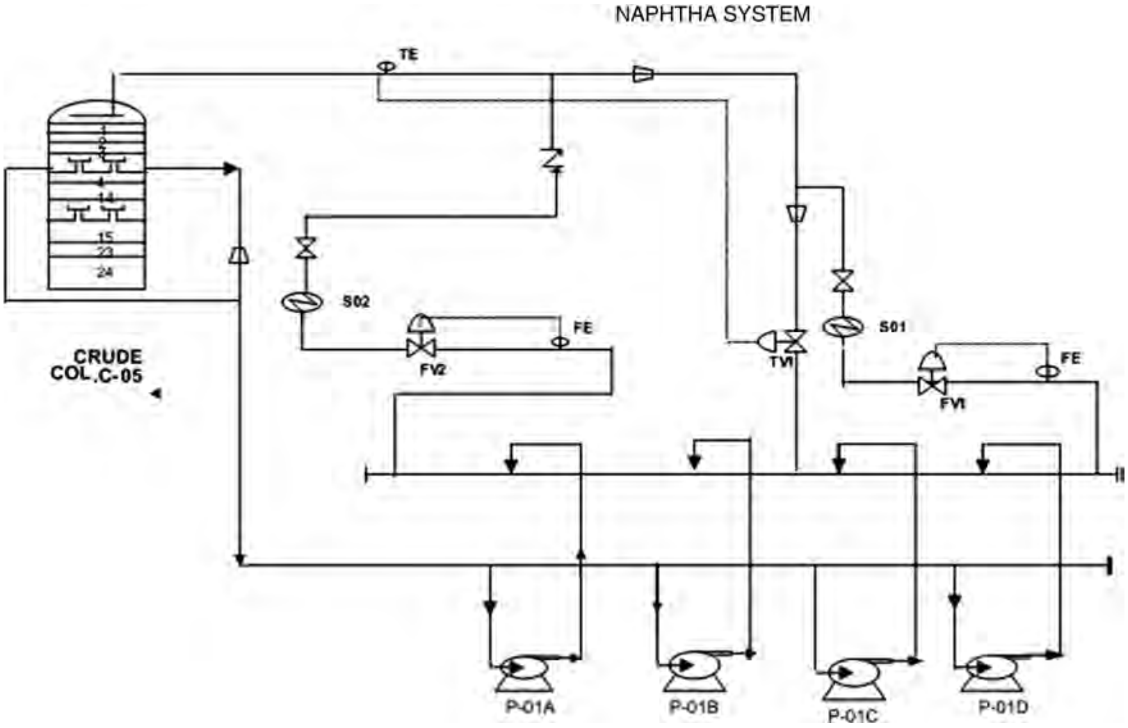


Figure 14.3—Crude preheat train control.

equipment. Complete combustion of fuel in the fired heater is ensured by sending an excess amount of combustion air against the required stoichiometric quantity. A normal air/fuel ratio is between 1.0 and 1.6. Figure 14.4 depicts a typical fired heater lead-lag control configuration.

Incomplete combustion of fuel produces carbon monoxide (CO), which travels along with flue gas from the radiation section to the convection section and to the heater stack via the induced draft (ID) fan. There is ample probability that combustion reactions may occur in the convection section because CO formed is reactive and the energy required for triggering the reaction is available in the form of heat in the flue gases. The combustion reaction being exothermic in nature liberates a lot of heat, thus increasing the chances of tube failure in the convection section.

14.8.2.2 HEATER OPERATION IN A HYDROTREATER

During normal operation, adjusting heater firing is a normal routine for obtaining desired specifications for the products produced. Consider fired heater operation in a hydrotreater. To produce different batches of diesel (different sulfur specifications), the reactor inlet temperature is varied accordingly. This is done by adjusting the firing in the heater, which is upstream of the reactor.

This transition from one firing rate to the other is done by lead-lag control with prewritten logics, which ensures safety and efficiency of fired heater operation. The system ensures that when the fired duty demand increases, the air flow increases first, followed by an increase in fuel supply. Conversely, when demand falls, the total fuel consumption is reduced first, followed by a reduction in combustion air supply. In this manner complete combustion is always ensured with an excess combustion air available all of the time.

Heater operation is an optimal tradeoff between the thermal efficiency and safety of operation. This is done by maintaining an optimum quantity of excess oxygen at all times in the heater box. An analyzer measuring excess oxygen is used for this purpose and acts as an input to the lead-lag controller, which accordingly resets the combustion air flow. Suppose it is decided to maintain an optimum air/fuel ratio of 1.1 (10 % excess air/2 % excess oxygen), and if oxygen analyzer shows a value of 1.5 %, then the combustion air is adjusted accordingly so as to maintain design value.

Case 1: TIC SP is increased and as a result the controller calls for increasing the heat input to the process stream.

This higher signal will be ignored by the low signal selector TY1 but will pass through the high signal selector TY2 to the flow controller (FC) for manipulating the combustion air control valve. The higher signal will open the damper more and increase the combustion air flow, which is measured by flow indicator (FI) available. Now this signal will be sent to the low signal selector TY1 via calculation block. The low signal selector TY1 will pass the lower of TIC and comb air FI. It selects signal from comb air FI.

This signal will be the new setpoint to the fuel FC and cause its output to increase, thereby increasing the fuel gas flow via the fuel gas control valve. The control system will now come to equilibrium according to the new TIC setpoint.

Case 2: TIC setpoint is decreased and as a result this controller calls for decreasing the heat input to the process stream.

This lower signal will be ignored by the high signal selector TY2 but will pass through the low signal selector

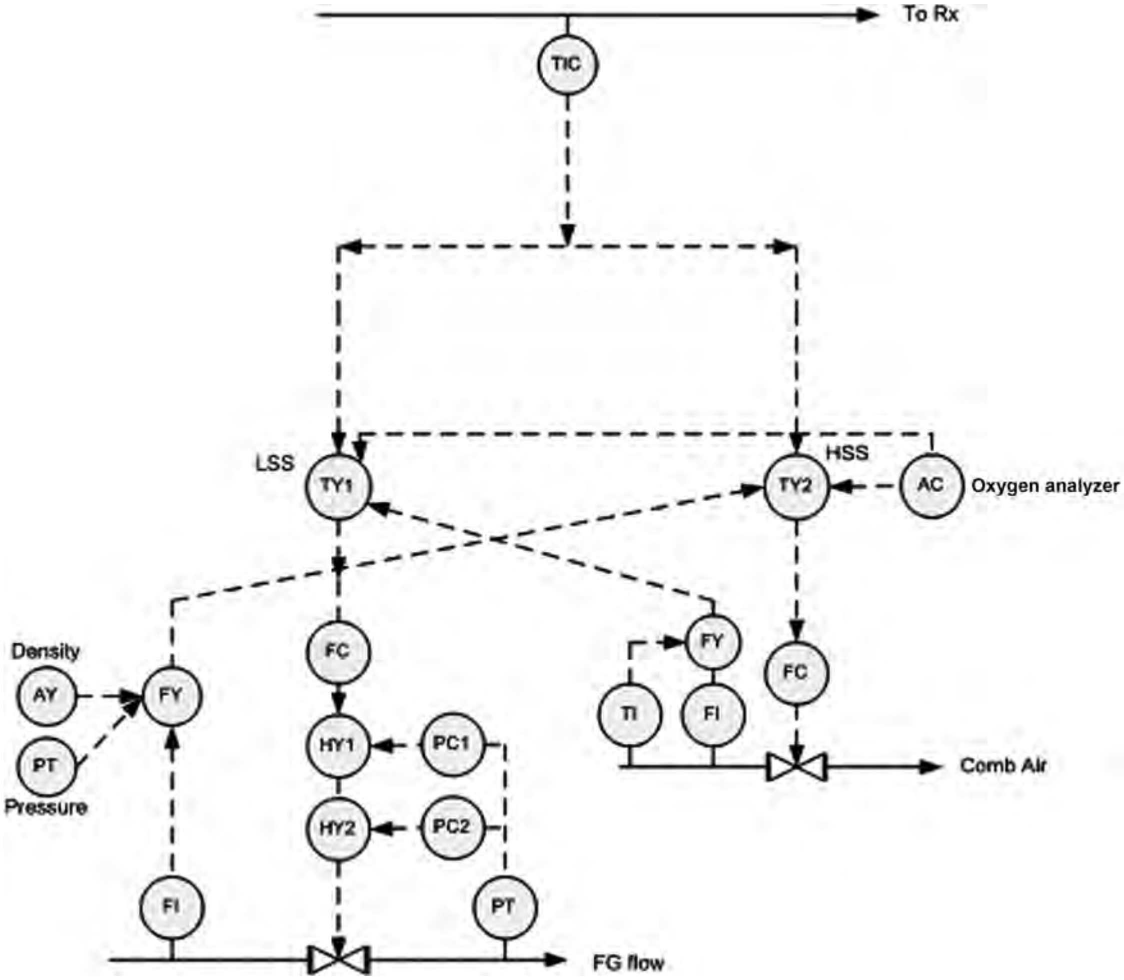


Figure 14.4—Fired heater lead-lag control diagram.

TY1 to the FC for manipulating the fuel gas control valve. The lower signal will close the fuel gas control valve and decrease the fuel gas flow, which is measured by the FI available. Now this signal will be sent to the high signal selector TY2 via calculation block. The high signal selector TY2 will pass the higher of TIC and fuel gas FI. It selects the signal from the fuel gas FI.

This signal will decrease the setpoint to the combustion air FC, which will cause this FC to close the combustion air control valve. The control system will now come to equilibrium according to the new TIC setpoint.

In both of the cases, the heater outlet temperature controller has reset the setpoint to the fuel to control heat input to the heater. The use of the low signal selector and the high signal selector makes it possible for this output signal to adjust the air first in the case of higher heat demand and then to adjust the fuel first in the case of lower heat demand.

Safety of equipment is ensured by using lead-lag control. Transition between two firing rates is done in a smooth manner without compromising on product specifications and safety of the equipment. It reduces the excess consumption of the combustion air/fuel and gas/fuel oil.

14.8.3 Fluidized Catalytic Reactor Control

14.8.3.1 INTRODUCTION

The fluidized catalytic cracking unit is a margin booster unit in the refinery complex. This is meant for cracking the long-chained molecules to comparatively smaller chain molecules having more dollar value. Figure 14.5 depicts a typical FCC reactor-regenerator control configuration. The heavier feed enters the reactor and the cracking reaction takes place in the riser of the reactor with the help of a catalyst in fluidized form. The valuable lighter products leave the reactor for separation in downstream fractionators. The coke gets deposited on the catalyst during the cracking process. Hence, the catalyst is sent to the regenerator where the coke is burnt off using air. The hot regenerated catalyst is circulated back to the reactor for cracking the fresh feed. This is a continuous process and the control systems should be designed in such a way that the integrity of reactor and the regenerator are always taken care of. It is a perfectly heat-balanced system because the heat of combustion is utilized in the reactor for providing the heat required for cracking the feed. The entire heat balance of the system is dependent on the total catalyst circulation through the system and the ratio of catalyst to oil (C/O)/feed being

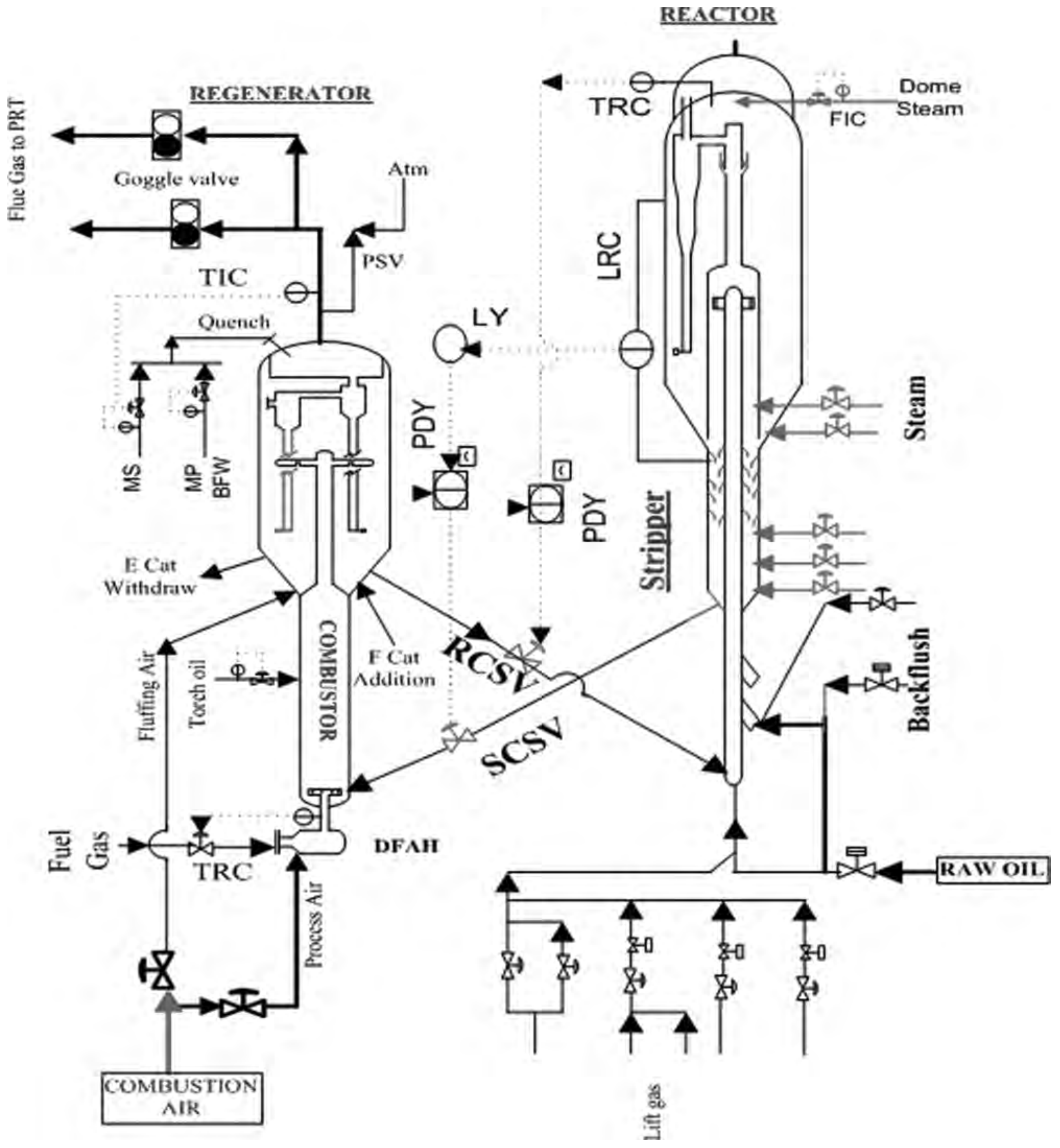


Figure 14.5—FCC reactor-regenerator control diagram.

maintained. (C/O) reactor-regenerator is the weight ratio of the catalyst circulated between the reactor and regenerator to the fresh feed to riser.

$$(C/O)\ \text{reactor-regenerator} = \frac{\text{Weight flow of regenerated catalyst}}{\text{Weight flow of fresh feed}} \qquad (14.1)$$

(C/O) reactor-regenerator is not an independent variable; it will increase with an increase in reactor temperature and decrease with higher regenerator dense bed temperature or combined feed temperatures. When process conditions are changed so that an increase in C/O occurs, an increase in conversion and in coke yield will also be observed.

14.8.3.2 REACTOR

The heart of the fluid catalytic cracker (FCC) unit is the riser where the reaction occurs. Hot regenerated catalyst flows to the riser bottom through the regenerated catalyst standpipe where lift streams (gas/oil) preaccelerate the catalyst and transport it up the riser. The feed to the reactor is sprayed into fine droplets using specially designed nozzles and steam for atomizing it.

The hot catalyst vaporizes the feed and carries the catalyst upward. Cracking reactions take place within 2–3 s, which is the time required for the catalyst and hydrocarbon vapors to reach the top of the riser. Catalyst is quickly separated from hydrocarbons in the reactor vessel to reduce overcracking.

14.8.3.3 REGENERATOR

The regenerator is divided into two sections. The lower section is called the combustor, where the spent catalyst from the spent catalyst standpipe is distributed over the air distributor. Also, the hot catalyst from the upper section of the regenerator is recirculated back to the combustor to provide the necessary heat to start the combustion reaction and for shifting the reaction toward complete combustion. The upper section is called the regenerator, where the combustion reaction is completed and from where the hot regenerated catalyst is sent back to the reactor.

14.8.3.4 IMPORTANT PROCESS PARAMETERS

For economical running of an FCC unit, there are some important process parameters that need to be controlled effectively all of the time. The process parameters of interest are [7]

- Reactor severity (reactor temperature)
- Catalyst level in the reactor
- Delta pressure (DP) across both slide valves opening
- Reactor and regenerator DP

14.8.3.5 REACTOR-REGENERATOR PROCESS CONTROL

The yield of different products from the reactor greatly depends on the reactor temperature, which is controlled via a temperature recorder controller (TRC) located in the upper vapor space of the reactor vessel. Figure 14.6 depicts a typical FCC regenerated catalyst slide valve (RCSV) operation related control logic. The output signal from the reactor TRC controls the opening of the regenerated catalyst slide valve (RCSV), regulating the amount of hot regenerated catalyst flowing to the riser. While adjusting the opening of the RCSV, the DP across it should always be taken care of. Hence, a low selector switch (LSS) is provided to ensure that the DP across the slide valve is always positive.

The reactor catalyst level is controlled with a level recording controller (LRC) located on the reactor vessel. Figure 14.7 depicts a typical FCC spent catalyst slide valve (SCSV) operation related control logic. The output of the LRC resets the spent catalyst slide valve (SCSV) opening, regulating the amount of catalyst flowing from the reactor to the regenerator. Here again, LSS is provided to take care of positive DP across the slide valve.

The reactor-regenerator differential pressure is controlled by varying the regenerator pressure. This is a critical parameter to be maintained because it directly affects the differential pressure across the slide valves. The output from this controller resets the position of the flue gas valves at the expander inlet and bypass lines of the power recovery section to vary the regenerator pressure and maintain the constant reactor-regenerator DP.

The reactor pressure is not directly controlled because it is governed by the speed of the wet gas compressors in the gas concentration section that exert a back pressure on the main fractionator column and thereby the reactor.

The regenerator temperature is not directly controlled and is a function of several other process variables. In simple terms, the regenerator temperature depends on the percent delta coke on the catalyst (i.e., the coke on spent catalyst entering the regenerator minus the coke on the regenerated catalyst leaving the regenerator). Like many other variables in the reactor-regenerator system, this too depends on several factors and is a function of the total catalyst circulation, the amount of coke deposited, and the type of feed being cracked [7].

14.8.4 Extractive Distillation Control Scheme

14.8.4.1 PROCESS DESCRIPTION

Extractive distillation (ED) is used for the separation of substances with low relative volatility that otherwise cannot

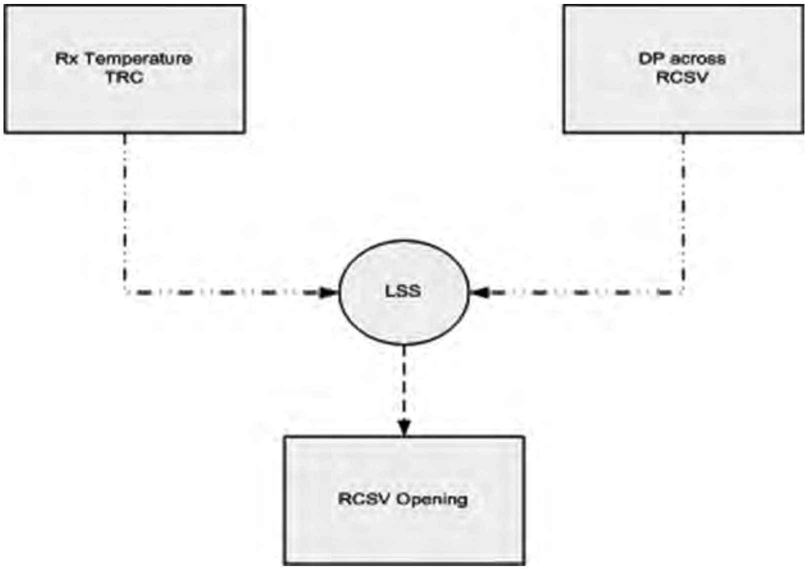


Figure 14.6—FCC RCSV operation control logic diagram.

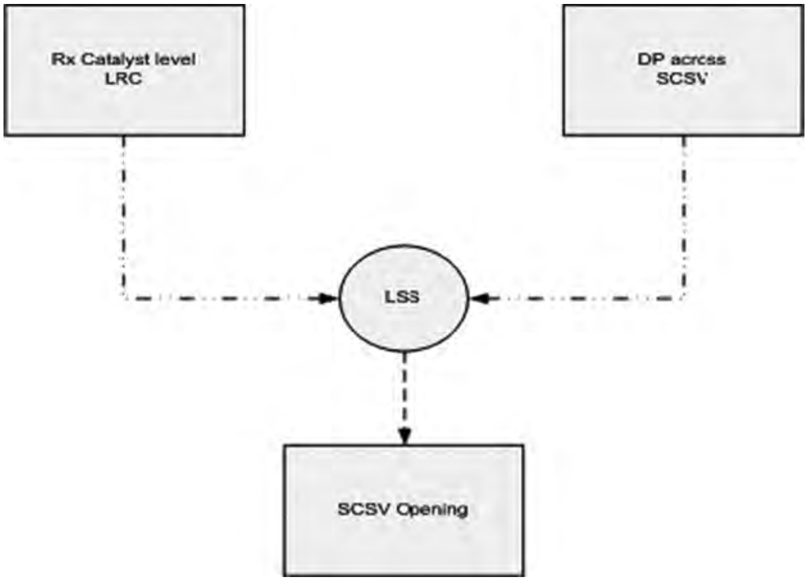


Figure 14.7—FCC SCSV operation control logic diagram.

be separated by normal distillation. A solvent that is relatively nonvolatile and has a high boiling point is used. The component having a lower boiling point is separated out from the top of the distillation column whereas the higher boiling point component along with the solvent that it is extracted into is removed from the bottom. This mixture is quite easily separable in the subsequent distillation column otherwise called a recovery column.

For a typical benzene extraction system, the feed to the column may be a mixture of benzene and nonaromatics. The objective is to separate out benzene from the nonaromatics, maintaining the purity of benzene (in the extract) and at the same time minimizing the losses of benzene along with nonaromatics (i.e., raffinate). The temperature at which the feed and the solvent enter the column is very important for the most effective separation. The feed has to enter at the bubble point, whereas the solvent has to be at a temperature to just vaporize the lighter component (nonaromatics) while extracting the benzene component. The column bottom temperature should never exceed the solvent degradation temperature [8].

The benzene and solvent mixture from the ED column enters the recovery column, where the benzene is removed from the overhead while the lean solvent from the bottom is circulated back to the ED column.

14.8.4.2 PROCESS VARIABLES

The important process variables that need to be controlled are [8]

- Column pressure for column stability
- Feed temperature and lean solvent temperature for effective separation between benzene and nonaromatics
- Benzene in ED raffinate and nonaromatics in extract
- ED column bottom temperature

14.8.4.3 ED PROCESS CONTROL

As indicated in the Figure 14.8 ED schematic diagram, the ED column pressure is controlled by an overhead pressure controller for which output goes to a split range controller. If the pressure is lower than the setpoint (output = 0–50 %), the inert gas valve opens. On the other hand, if the pressure is higher (output = 50–100 %), then the vapors will be routed to the flare to maintain the system pressure.

The temperature controller installed in the feed line takes care of the feed inlet temperature by manipulating the bypass valve of the feed/solvent exchanger. Similarly, the solvent temperature is controlled by adjusting the bypass valve of the solvent cooler.

An APC scheme can be better utilized in an ED system for simultaneously maintaining the benzene product purity and minimizing the losses of benzene. The scheme uses the ED column reboiler duty as a main handle to control the following:

- Tray “p” temperature, which is a good indication of how much benzene is lost in the raffinate.
- Recovery column overhead benzene purity analyzer (ppm of nonaromatics). For a given change in the ED column parameters, there is a significant dead time for the indication of nonaromatics in the recovery column overhead. Hence, the tray “r” temperature of the ED column, which again is a good indication of the amount of nonaromatics escaping along with the solvent, can be effectively controlled.

Both of the temperatures mentioned above are maintained within limits to ensure the optimum performance of the column. The solvent temperature, the solvent flow rate, and the reflux flows are the other handles used in APC.

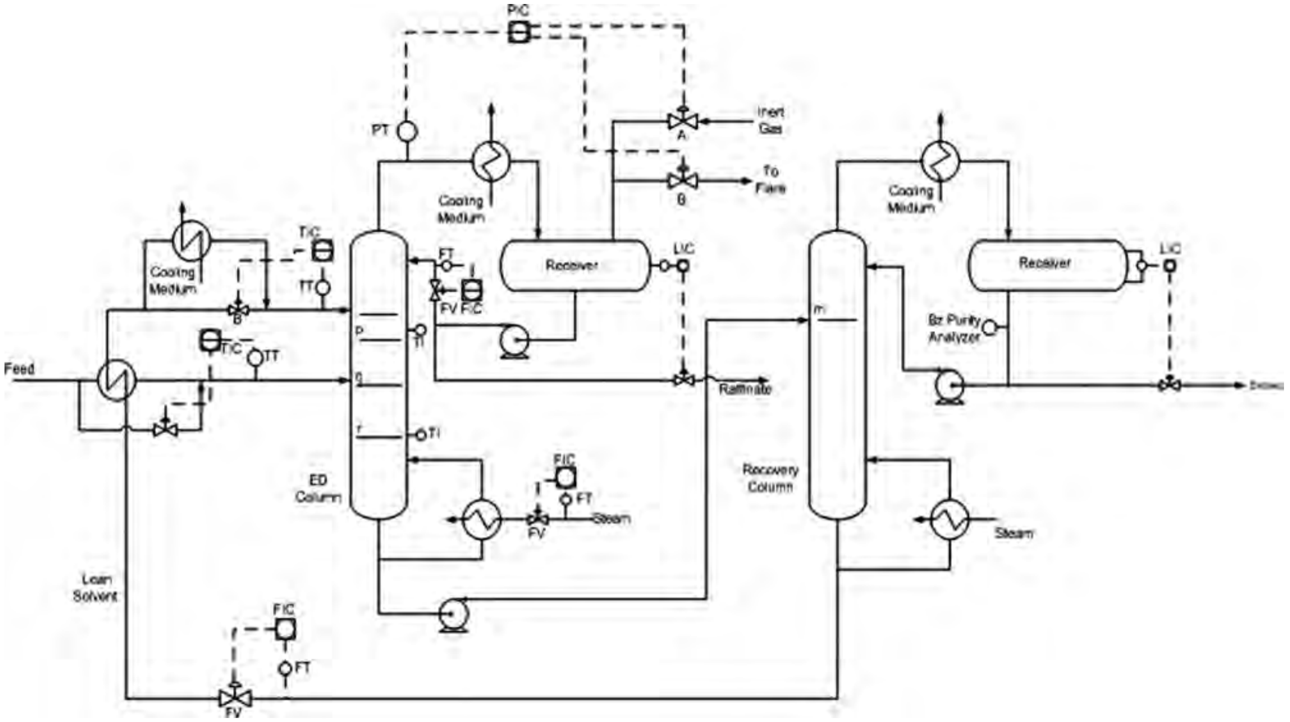


Figure 14.8—ED schematic diagram.

REFERENCES

[1] Altmann, W., *Practical Process Control for Engineers and Technicians*, 1st ed., Newnes, Burlington, MA, 2005.

[2] Emerson Process Management, *Control Valve Handbook*, 4th ed., Fisher Controls International, Marshalltown, IA, 2005.

[3] Venkatapathy, S.R., “Increasing Importance of Smart Valve Positioners,” *Machinist*, April, 2009.

[4] “Introduction to Multivariable Predictive Control with Aspen DMCPlus,” in *AspenTech Customer Education Training Manual*, Course Number MA300.06.08, AspenTech Technology, Burlington, MA, 2007.

[5] “Basics of Advanced Process Control, Training Module,” TES-TS-P-050, Reliance Industries, Patalganga, India, 1998.

[6] Anand, K., and Manav, B., *Best Practices in Building NIR Models for Gasoline and Diesel, Process Automation*, Reliance Industries, Jamnagar, India, 2008.

[7] “UOP Fluid Catalytic Cracking Process,” in *Reliance Jamnagar Refinery Training Course Material*, Reliance Industries, Patalganga, India, 1998.

[8] *UOP Extractive Distillation General Operating Manual*, 2004.

15

Modern Computer Process Control Refining Units

Ravi Jaisinghani[1]

15.1 INTRODUCTION

The period from 1960 to the present may be called the period of modern automatic control. This modern period follows the periods of primitive automatic control (1868 to early 1900s) and classical automatic control (early 1900s to 1960) [1,2]. During this modern control period, there has been an ever-increasing growth of advanced process control (APC) applications such that APC has become a norm for refining and petrochemical units. APC technology has also evolved along the well-known pyramid path [3] of regulatory control to advanced regulatory control (ARC) to conventional APC to multivariable predictive control (MVPC). Further higher in the APC hierarchical level, real-time optimization (RTO) requires a magnitude change in engineering work and cost because it requires first-principle models and large-scale solution of nonlinear equations. Also, at this juncture of MVPC/RTO, other related technologies—advisory/expert systems, neural-networks-based inferential predictions, and fuzzy logic—have been introduced to improve the safety and reliability of the unit operation. The purpose of this chapter is to identify typical APC strategies for common refining processes and develop integrated control solutions for typical refining process units.

15.2 MODERN PROCESS CONTROL

With a historical base of nearly 30 years and with several thousand applications implemented, MVPC technology has not only been well established and proven but has also become the main workhorse of refinery process control and optimization. Despite this long history and a wide base of implementation, MVPC technology still typically takes between 4 and 6 months to implement and can cost several hundred thousand dollars per installation. This is mainly because site- and unit-specific empirical models of the process have to be identified.

Although a powerful technology in itself, MVPC requires a solid base of regulatory proportional integral derivative (PID) controls to work with. And, being reliant on accurate dynamic (empirical) models that are constantly adjusted via biasing to reconcile with actual process data, the service factor of MVPC applications is improved with the availability of online analyzers or inferential predictions (often neural-network based). To design, implement, and commission a unit-wide control scheme for a refining unit requires the understanding of various technologies and their integration to meet the safety, operational, and economic objectives.

15.3 CONTROL TECHNOLOGY—COMPARISON SUMMARY

Table 15.1 and Figure 15.1 summarize the differences between regulatory (PID) control, multivariable control (MVC), and MVPC [4]. In brief, the complexity not only increases in the number of variables being simultaneously controlled and influenced but also in past and predicted future behavior of process variables as the technology progresses from PID to MVC to MVPC.

One of the main differences between MVC and MVPC is that the MVC technology overlooks the transient behavior of dependent variables. Although many refining processes exhibit first-order monotonous-type dynamic response, a few reaction processes have a higher order nonmonotonous response that may be exhibited as an initial inverse response (like in a reactor ΔT control) or as an overshoot-type dynamic response between an input variable and an output variable. As shown in Figure 15.2, if the steady-state gain between these variables is 0.4, then to increase the output by 1 unit, the input will need to be changed by 2.5 units according to MVC control. However, such a large change in the input will cause a transient change of 2.5 units in the output, which may likely cause a quality violation.

To avoid such a transitory upset, the input in this case can initially be changed by a maximum of 0.4 units only on the basis of MVPC control. Then, after the transient response has peaked and the output is steadying out with a change of 0.16 units, the input can be changed by another increment of (1.0 – 0.16)/2.5 = 0.336 units to avoid an overshoot in the output.

Essentially, by implementing time-deferred changes in the input on the basis of the dynamic response curve of Figure 15.2 and the history of changes already made, the MVC scheme is changed to an MVPC scheme as the transient predictive process behavior is also controlled within the desired quality limits.

15.4 MVPC TECHNOLOGY—BRIEF EXPLANATION

It is important to understand the basis of MVPC control because nearly all of the major refinery process units need this technology for process control. Although details of MVPC technology can be found elsewhere [5], in brief, an integrated matrix approach is utilized to simultaneously control all targets (also termed as controlled variables [CVs]) in the steady and transient states by

- Adjusting the manipulated variables (MVs)
- Monitoring and respecting process constraints

---

[1] *Intelligent* Optimization Group, Inc., Houston, TX, USA

TABLE 15.1—Control Technology Comparison Summary

Item	Regulatory (PID) Control	Multivariable Control (MVC)	Multivariable Predictive Control (MVPC)
Number of variables	Single input, single output (SISO)	Multiple input, multiple output (MIMO)	Multiple input, multiple output (MIMO)
Algorithm basis and time behavior consideration	Mainly present error consideration	Present error and steady-state gains (when transient behavior control is not important)	Previous history, present error, future prediction, and steady-state gains
Integration with optimization	Required for nearly all levels of control and optimization as a base control	Can be integrated with simple constraint pushing-type optimization or as an overall optimizer for multiple MVPCs	Can be integrated with simple constraint pushing-type optimization
Implementation platform	DCS	DCS and computer based	Mainly computer based

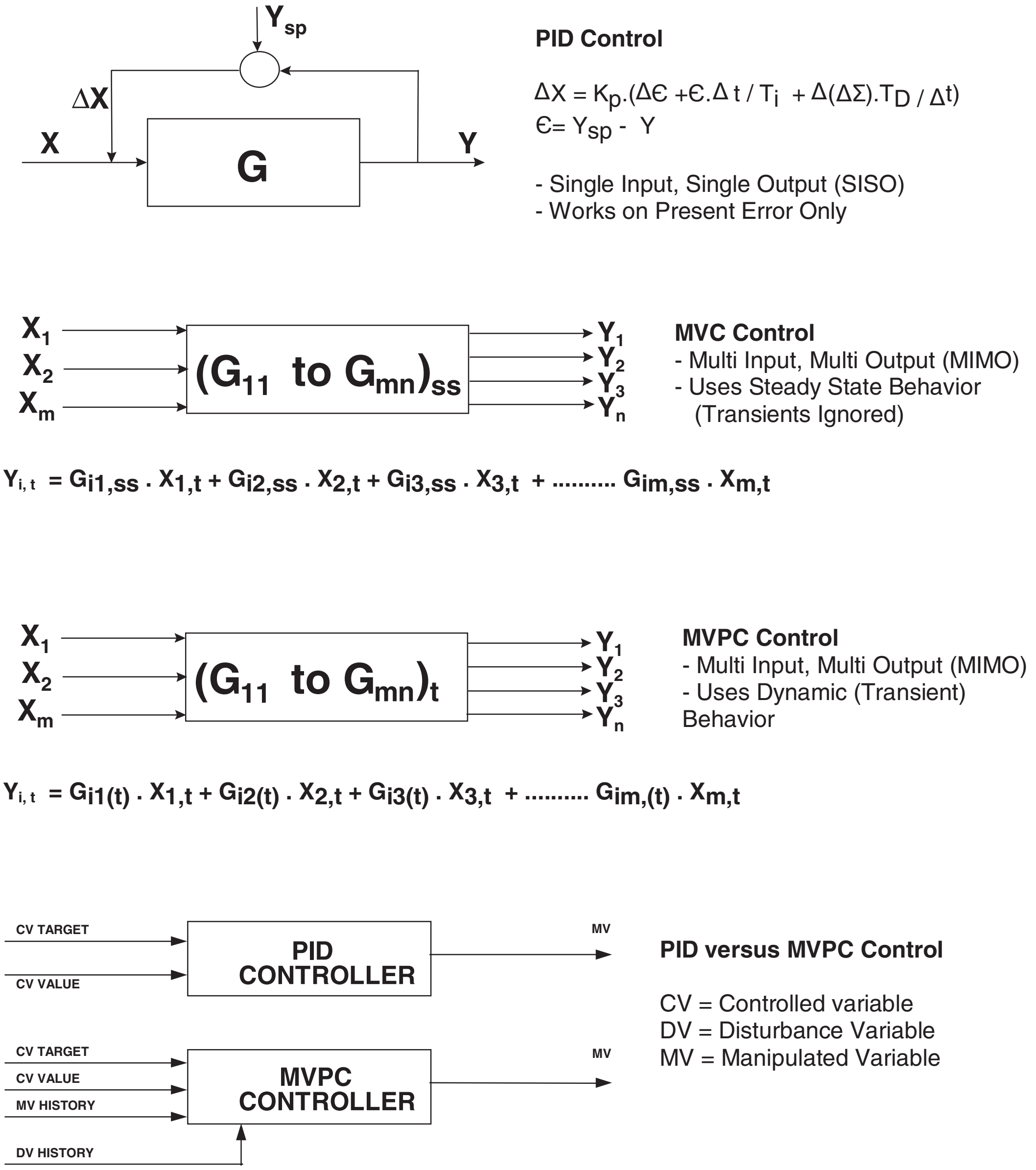


Figure 15.1—PID, MVC, and MVPC comparison.

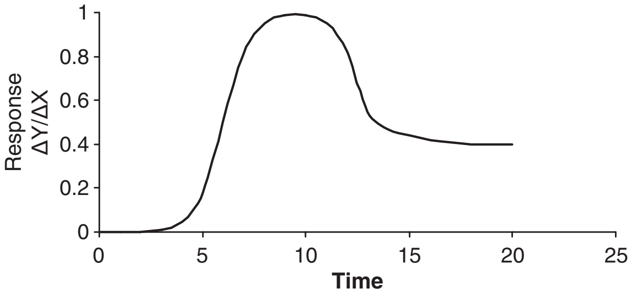


Figure 15.2—Dynamic overshoot process response (MVC vs. MVPC).

- Incorporating the effect of measured process disturbances variables (DVs) [4].

MVPC relies on dynamic response models (see Figure 15.2 for an example) to predict the response of dependent (CVs) variables in terms of independent (MVs and measured DVs) variables. The control moves in the MVs are calculated to minimize the steady-state and transient response of CVs from their targets while observing the high, low, and rate-of-change hard limits in the MVs. The control problem formulation is also conducive to the integration of an optimization formulation, and this often leads to a least-cost solution in terms of MV costs. These concepts are shown in Figure 15.3.

15.4.1 MVPC—Linearity and Superposition

MVPC technology has two basic limitations—linearity and superposition. These limitations may require some adaptive techniques for dynamic models and tuning parameters to make the control implementation robust for a nonlinear process and for changing operating regions (capacity changes, feed-type changes, ramping, etc.).

Linearity Assumption

- For a change in input X of ΔX, the process value Y changes by ΔY irrespective of the operating region.
- For a change in input X of $2(\Delta X)$, the process value Y changes by $2(\Delta Y)$ irrespective of the operating region.
- The common transforms used are log and converting a ratio (Y_1/Y_2) into a difference $(Y_1 - Y_2)$ to make the response appear more linear.

Note: Because most processes may not strictly follow linearity, the MVPC formulation includes a model update step as a part of its control execution cycle.

Superposition Assumption

- The effect of changes in inputs (Xs) are linearly additive in time and magnitude on the outputs (Ys).
- If $\Delta Y(t) = a(t)\cdot\Delta X_1$ when X_2 is constant, and $\Delta Y(t) = b(t)\cdot\Delta X_2$ when X_1 is constant, then by superposition, the effects are additive in time and magnitude:

$$\Delta Y(t) = a(t)\cdot\Delta X_1 + \mathrm{b}(t)\cdot\Delta X_2 \tag{15.1}$$

15.4.2 MVPC—Algorithm Formulation

- Representation of responses between dependent variables (CVs) and independent variables (MVs and DVs) as numeric series until the longest dynamic model time (also known as horizon time or steady-state time).
- Superposition of all effects of changes in independent variables (including most recent ranges in the past steady-state time period) on CVs.
- This calculates the predicted (dynamic) responses of outputs (CVs) on the basis of the present and historical values of inputs.
- Supplementing the above equations with constraint equations that restrict the variables between their limits (for MVs) and targets (for CVs) and allowing tuning based on penalty parameters:

$$Abs(\Delta X_i(t)) <= move\ size_i \tag{15.2}$$

$$Low\ limit_i <= \Sigma(\Delta X_i(t)) <= High\ limit_i \tag{15.3}$$

$$Low\ target_i - Low\ slack_i$$
$$<= Y_i(t) <= High\ target_i + High\ slack_i \tag{15.4}$$

- The MVs have hard limits of the type shown above. However, the CVs, which are dependent on the independent variables, can only have soft limits:

$$High\ slack_i \geq 0 \tag{15.5}$$

$$Low\ slack_i \geq 0 \tag{15.6}$$

15.4.3 MVPC—Internal Calculation Sequence

At every online iteration cycle, the MVPC algorithm goes through a three-step process (there is also an initial identification step offline) as shown in Figure 15.4.

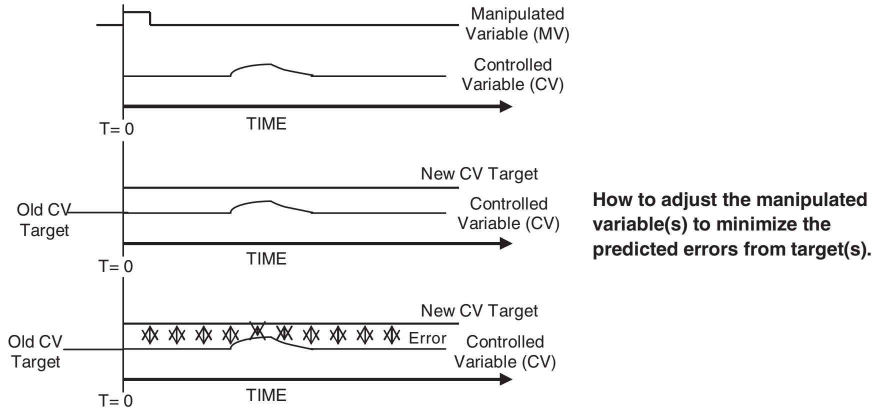


Figure 15.3—MVPC concepts.

Calculation Sequence	Offline/Online	Known	Unknown
Identification	Offline	X, Y	G
Prediction	Online	X, G	Y_{pred}
Model Correction	Online	X, Y, Y_{pred}	G
Control	Online	G, Y	X

Figure 15.4—MVPC calculation sequence.

15.5 REFINING PROCESSES—CONTROL PURPOSE AND OBJECTIVES

The main purposes of APC in the refining processes are

- To improve the profitability and operational stability of the unit by enforcing control objectives subject to equipment and process constraints
- To provide a stable and robust control platform for (future) unit online optimization.

The control objectives include safety, quality, and economic considerations.

- Safety
  - Maintain the process within operating and equipment constraints
  - Assist operators
  - Monitor performance
- Quality
  - Maintain product qualities within specifications
  - Stabilize operations
- Economic (subject to safety and quality priorities)
  - Maximize yield of more valuable products
  - Maximize throughput
  - Minimize energy consumption

15.5.1 APC Development Considerations

Although there are several different refining processes and units, some with chemical conversions and others with physical separation only, the development of integrated control schemes (covering many different physical equipments pieces in one unit) can be simplified by considering the control requirements of each individual process equipment. In this respect, aside from the blending unit, nearly all refining units have a combination of some of the following process equipment:

- Accumulator
- Heat exchanger/condenser (energy source/sink)
- Heater (energy source)
- Compressor
- Fractionator
- Reactor

The individual equipment control schemes can then be combined by integrating them in one large matrix form or by linking them with common variables. Following the principle of *lex parsimoniae* (i.e., Occam's razor)—"All other things being equal, the simplest solution is the best,"—increasing the size of the control matrix does not always result in a better solution in the long term. Ease of maintenance, a ripple effect of tuning changes in a control matrix, and failure of one sensor affecting the whole unit application can sometimes result in a favorable implementation of two or more smaller applications for the unit. For example, in a crude unit control, the heater pass balance and heater outlet temperature controls can be included in the fractionator MVPC matrix. An alternate approach would be to implement heater pass balancing and heater outlet temperature at the distributed control systems (DCS) level and then use the heater outlet temperature as a MV and a high selection for heater tube metal temperature (TMT) as a CV. This can result in a simpler approach without loss of APC benefits. The integration of schemes and the platform for implementation quite often becomes a personal choice.

15.5.2 APC—Property Estimation

A common point in all advanced applications is the availability of analyzers or the development of inferential models for quality predictions. Neural networks (see section 15.8 also) have been used successfully in building these real-time inferential property estimators. In addition, empirical equations based on flow, temperature, and pressure have also been used. Both of these calculations require frequent reconciliation and model updating or model biasing with laboratory updates.

During plant testing for dynamic model identification, laboratory samples are also frequently collected such that dynamic prediction models for product qualities [e.g., 5 % boiling point (BP), 95 % BP, flash point, pour point, and freeze point] can be identified. The MVPC controller uses these models for control, and when online analyzer results or laboratory results become available, the model bias correction inherent in MVPC calculations (see section 15.4.3) is performed. This provides continuity of control even when laboratory analysis is not immediately available or the online analyzer is not continuous.

15.6 REFINING PROCESSES—BASIC CONTROL SCHEMES

Only the basic control schemes for the process equipment listed in section 15.5.1 are listed in Table 15.2 because the control details can be found elsewhere [6,7]. Equations for heater pass balance include the following:

$$F = \Sigma F_i \text{ (material balance)} \tag{15.7}$$

$$T_i = COT \text{ (required for all } i\text{)} \tag{15.8}$$

$$\Sigma \Delta F_i = 0 \text{ (required, for the total flow should remain unchanged)} \tag{15.9}$$

TABLE 15.2—Basic Control Schemes for Refining Process Equipment

Process Equipment	Control Type	Control Schemes
Accumulator	Pressure control	Vent or purge throttling Make-up flow addition rate Gas product draw flow rate
	Level control	Linear or nonlinear control Product draw flow rate Make-up flow addition rate
Condensers	Condensate temperature, or condensing pressure control	Via coolant throttling. If water cooling, limit water velocity to achieve sensitive control and avoid fouling.
		Floating pressure control via valve position control affecting coolant throttling. For partial condensers, floating pressure is achieved via level control (to provide flooding) and pressure control.
		Wetted surface area control. Results in differing degrees of condensate subcooling as a function of residence time and in nonsymmetrical dynamics.
		Incondensable build-up resulting in loss of pressure control.
		Removal of incondensable:
		• Fixed purge rate if economically possible
		• Second pressure controller to modulate purge stream
		High-speed pressure control:
		• Hot gas bypass control
		Vacuum column pressure control
		• Variable load or surge capacity via air or gas bleed
		Large ejector and small ejector combination to reduce steam wastage if load variations can be anticipated
Reboiler	Vapor superheat temperature control or heat duty control	Heat media flow rate
Heat exchanger network	Parallel exchanger balancing	Adjust flow rates on the basis of temperature difference between passes (total flow rate remains same)—see equation 15.10 below
		Adjust dead-band limits on temperature difference between average outlet temperature and individual pass temperature to avoid oscillations.
Heater	Coil outlet temperature (COT) control	Fuel rate feedback control based on outlet temperature Feed rate feed-forward control Feed temperature feed-forward control Fuel heating value (Wobbe index, calorimeter, specific gravity) ratio control
	Excess stack oxygen control (subject to draft pressure constraint)	Excess oxygen target dependent on burner characteristics, fuel type, heater load, etc. Excess oxygen maintained at target via stack damper movement—damper limits based on forced/induced draft type
	Tube pass balance (coking consideration and energy efficiency)	Adjust flow rates on the basis of temperature difference between passes (total flow rate remains same)
		Adjust dead-band limits to avoid oscillations
Compressor	Surge control	See compressor vendors information
	Precise throughput control	Directly manipulate the driver speed (preferable) Suction pressure throttling Discharge pressure throttling
	Simplify start-up and shutdown	Integration of speed and antisurge controllers

Then,

$$\Delta F_i = (T_i - COT) * F_i/COT \qquad (15.10)$$

where:

F = total flow rate
F_i = flow rate through pass i
COT = combined outlet temperature
T_i = outlet temperature of pass i

15.7 REFINING PROCESSES—ADVANCED CONTROL SCHEMES

Following the generic control objectives and the process equipment types listed in sections 15.5 and 15.5.1, and with the common control strategies mentioned in section 15.6, specific control objectives and control schemes for some of the main refining units are discussed below. Quite often, the advanced control strategies are divided, depending on control requirements and equipment integration, between conventional APC and MVPC to handle system constraints and loop interactions.

The need for MVPC technology in most refinery applications is multifold:

- Processes are of multiple-input, multiple-output (MIMO) type and interactive, making it difficult to tune and control with multiple PID loops.
- Dynamic response time is in hours, making it difficult to tune conventional PID loops.
- Nonmonotonous process response (in reactors) requires predictive technology.
- MVPC prediction models supplemented with laboratory analysis can often substitute for online analyzers.
- Control can be combined with cost optimization solution (e.g., side product yield maximization, energy savings, and constraints pushing) in a MVPC matrix.

15.7.1 Crude Unit—Atmospheric and Vacuum

Simplified Description

Crude feed is preheated via heat exchangers and then passes through a heater before the partially vaporized feed is fractionated in the atmospheric tower into wet gas, light or heavy straight run, naphtha, distillates, and atmospheric gas oil (AGO). The atmospheric bottoms (reduced crude) are heated through a vacuum heater and fractionated in the vacuum tower into light vacuum gas oil (LVGO), heavy vacuum gas oil (HVGO), and vacuum residue. For lube units, the vacuum tower feed is split into LVGO, lube stocks, and vacuum residue. Depending on market demands and product price structure, there is an economic incentive to produce more of certain products.

Control Objectives—Atmospheric Tower

- Sidestream quality control (5 % BP, 95 % BP, pour point, freeze point, etc.)
- Maximize feed rate against heater and column constraints
- Maximize pumparound heat recovery subject to product quality
- Maximize yield, or recovery, or both for more valuable products subject to column and product specification constraints

Control Objectives—Vacuum Tower

- Sidestream quality control (5 % BP, 95 % BP)
- Maximize pumparound heat recovery subject to product quality
- Maximize vacuum gas oil recovery subject to column and product specification constraints

The typical product qualities of interest are 90 % BP on gasoline and 95 % BP on naphtha, kerosene diesel, and AGO in addition to jet fuel flash point and diesel pour point. These product specifications and other derived properties are inferred from calculations based on measurements of temperature, pressure, and flow. If analyzers (or neural network models) are available, they can be used to provide feedback trim to the inferential results.

Conventional Control Strategies

- Parallel preheat exchanger balancing
- Crude flow ramp control
- Atmospheric heater pass temperature balancing
- Atmospheric heater stack excess oxygen control
- Atmospheric heater outlet temperature control
- Atmospheric tower nonlinear level control
- Vacuum heater pass temperature balancing
- Vacuum heater stack excess oxygen control
- Vacuum heater outlet temperature control
- Vacuum tower nonlinear level control
- Stripping steam/product ratio flow control (the stripping steam flow rates can also be MVs in the MVPC matrix)

MVPC Schemes

Figures 15.5 and 15.6 summarize the MVPC control schemes for the crude atmospheric and vacuum tower, respectively. Similarly, a list of potential MVPC variables is shown in Tables 15.3 and 15.4.

Crude Feed-Type Change

This can be a major disturbance for the MVPC controller. To reduce the transient time in achieving a new steady state, the MVPC models can be changed based on the crude feed. This requires more plant testing to develop dynamic models for major crude types. In addition, a crude change detector signal is required. Crude feed pump amperage or crude feed viscosity can be used as an indication of crude feed-type change.

Vacuum Tower Feed Cracking

To ensure low-pressure vacuum, the vacuum heater may need to be limited to avoid heater feed cracking. In some cases, the vacuum tower bottoms level may become erratic if feed cracking is taking place.

15.7.2 Fluid Catalytic Cracking Unit

Simplified Description

In this catalytic process, heavy oils (gas oils) are converted into more valuable gasoline and lighter products. Preheated fresh feed and recycle streams enter the unit at the base of the feed riser where they are mixed with the hot regenerated catalyst. The cracking reactions start when the feed contacts the hot catalyst in the riser and continues until the oil vapors are separated from the catalyst in the reactor, with the control of the reaction being maintained by varying the catalyst circulation rate. The cracking process produces coke, which remains on the catalyst particle. To maintain the catalyst activity, the catalyst is regenerated by burning off this coke with air in the regenerator, causing the catalyst to move continuously between the reactor and the regenerator.

Control Objectives

The control objectives for the reactor/regenerator section are designed to increase performance and enhance stability in operations:

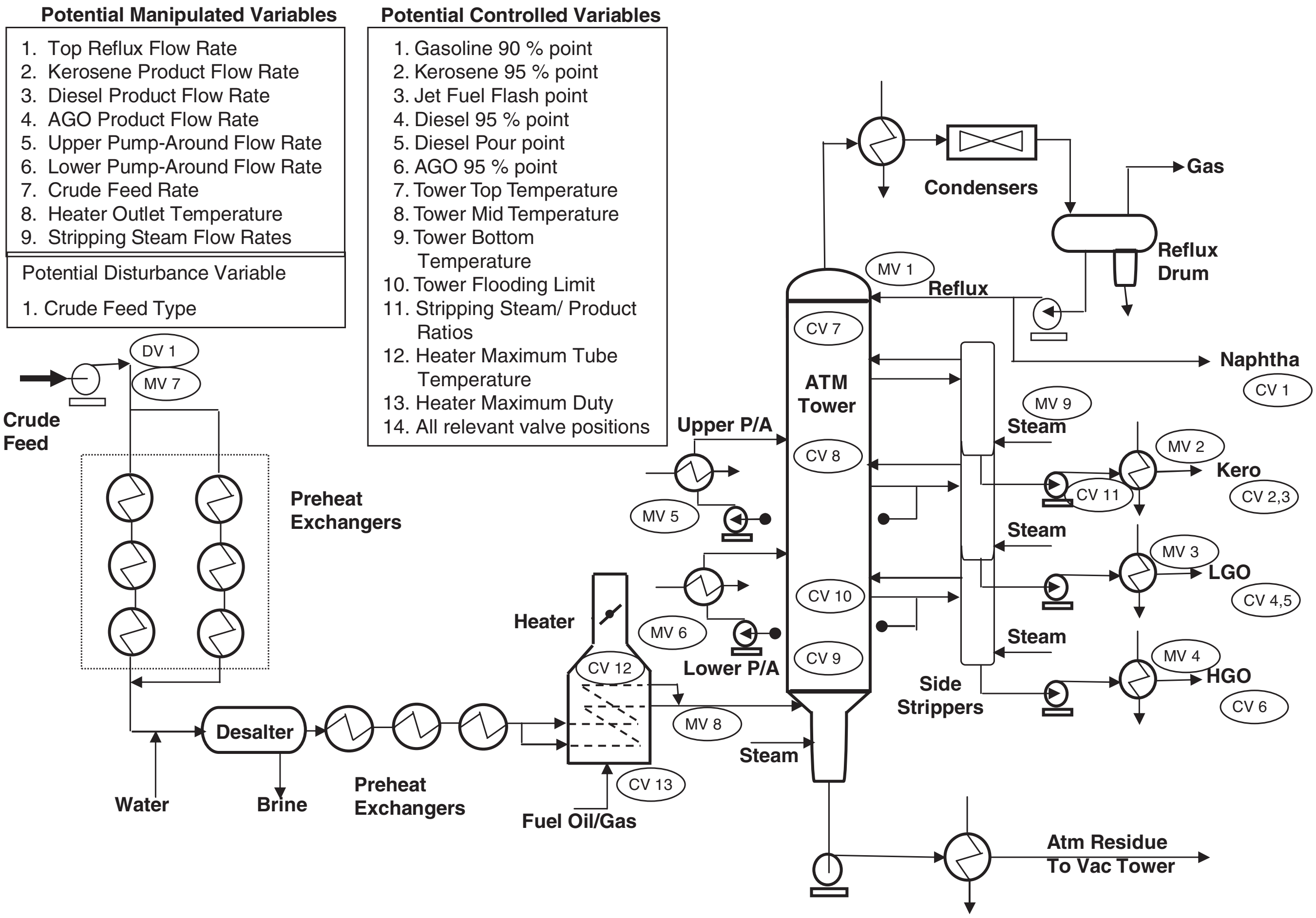


Figure 15.5—Crude atmospheric unit: MVPC control.

TABLE 15.3—Crude Atmospheric Tower: List of MVPC Variables

No.	MVs	CVs	Disturbance Variables
1	Top reflux flow rate	Gasoline 90 % BP	Crude type (assay)
2	Kerosene product flow rate	Kerosene 95 % BP	
3	Diesel product flow rate	Jet fuel flash point	
4	AGO product flow rate	Diesel 95 % BP	
5	Upper pumparound flow rate	Diesel pour point	
6	Lower pumparound flow rate	AGO 95 % BP	
7	Crude feed rate	Tower top temperature	
8	Heater outlet temperature	Tower mid temperature	
9	Stripping steam flow rates	Tower bottom temperature	
10		Tower flooding limit	
11		Stripping steam/product ratios	
12		Heater maximum tube temperature	
13		Heater maximum duty	
14		All relevant valve positions	

Potential Manipulated Variables

1. Overhead Vacuum Pressure
2. Top Reflux Flow Rate
3. LVGO Product Flow Rate
4. HVGO Product Flow Rate
5. Upper Pump-Around Flow Rate
6. Lower Pump-Around Flow Rate
7. Heater Outlet Temperature
8. Bottom Steam Flow Rate

Potential Controlled Variables

1. LVGO/HVGO Cutpoint
2. HVGO/Resid Cutpoint
3. Tower Top Temperature
4. Tower Mid Temperature
5. Tower Bottom Temperature
6. Heater Maximum Tube Temperature
7. Heater Maximum Duty

Potential Disturbance Variable

1. Atm Resid Feed Rate

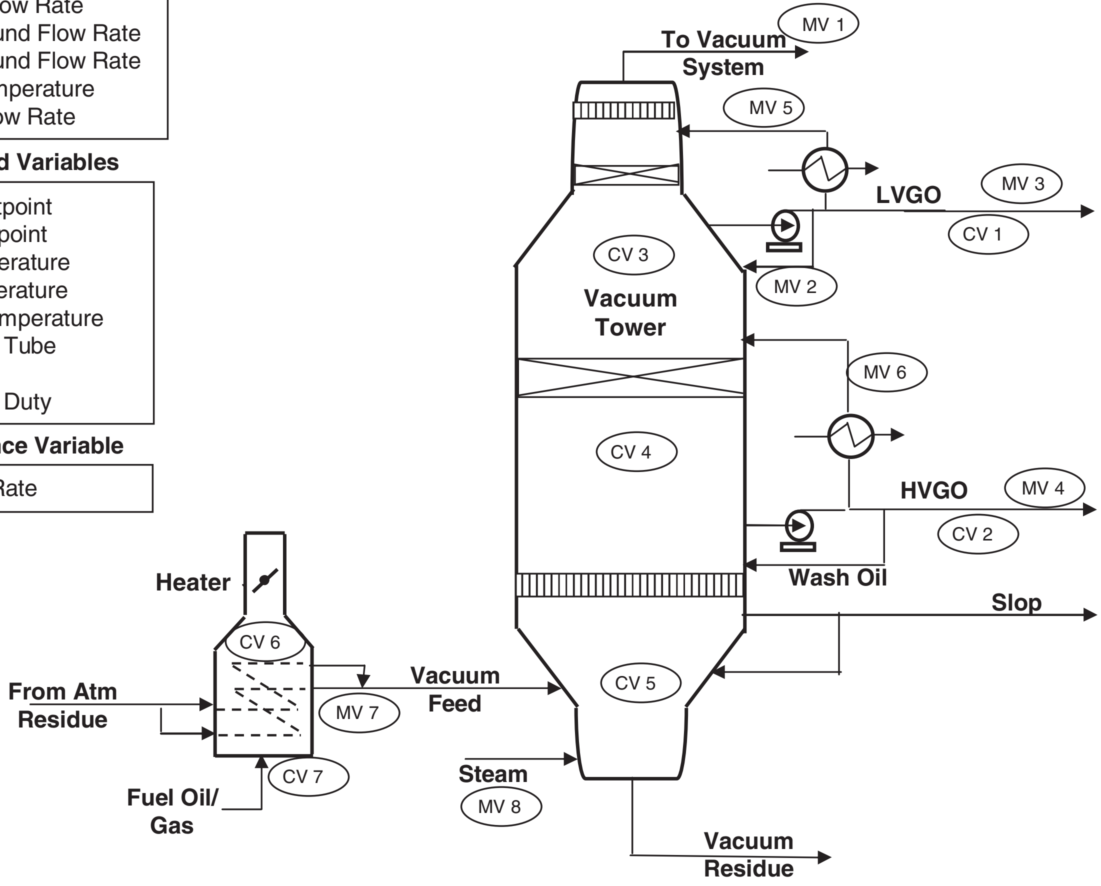


Figure 15.6—Crude vacuum unit: MVPC control.

TABLE 15.4—Crude Vacuum Tower: List of MVPC Variables

No.	MVs	CVs	Disturbance Variables
1	Overhead (vacuum) pressure	LVGO/HVGO cutpoint	Vacuum tower feed rate
2	Top reflux flow rate	HVGO/residual cutpoint	
3	LVGO product flow rate	Tower top temperature	
4	HVGO product flow rate	Tower mid temperature	
5	Upper pumparound flow rate	Tower bottom temperature	
6	Lower pumparound flow rate	Heater maximum tube temperature	
7	Heater outlet temperature	Heater maximum duty	
8	Bottom steam flow rate	All relevant valve positions	
9	100 N product flow rate (lubes tower)	100 N product viscosity (lubes tower)	
10	300 N product flow rate (lubes tower)	300 N product viscosity (lubes tower)	
11	Slop product flow rate (lubes tower)	Slop/residual cutpoint (lubes tower)	

- Maximizing conversion (severity control) consistent with high yields of the valuable products (octane barrels or specific octane number)
- Maximizing charge throughput
- Maintaining process stability and safety through control of process variables such as reactor temperature, regenerator pressure, slide valve positions, etc.
- Minimizing energy consumption

Similarly, the main objectives for the fractionator are maintaining product quality within specifications and maximizing energy recovery subject to product qualities.

This conversion objective is achieved in a complex environment of interacting combustion and severity variables (e.g., reactor temperature, preheat temperature, catalyst/oil ratio, and regenerator temperature) along with equipment and process constraints (e.g., slide valve operating limits, metallurgical limits in the regenerator, combustion air blower capacity, wet gas compressor capacity, and cooling ability in the main fractionator overhead condensers) or column limitations in the gas plant.

Conventional Control Strategies

- Parallel preheat exchanger balancing
- Preheater stack excess oxygen control
- Preheater outlet temperature control
- Stripping steam/catalyst ratio control
- Riser dispersion steam control

MVPC

- Reactor/regenerator severity/combustion control
- Reactor/regenerator pressure balancing control (between wet gas compressor and air blower)
- Throughput maximization
- Fractionator product quality control—Typically, 95 % or endpoint on heavy naphtha, light cycle oil (LCO), and heavy cycle oil (HCO)

Figure 15.7 summaries the MVPC control scheme for a fluid catalytic cracking (FCC) unit and Table 15.5 lists the potential MVPC variables.

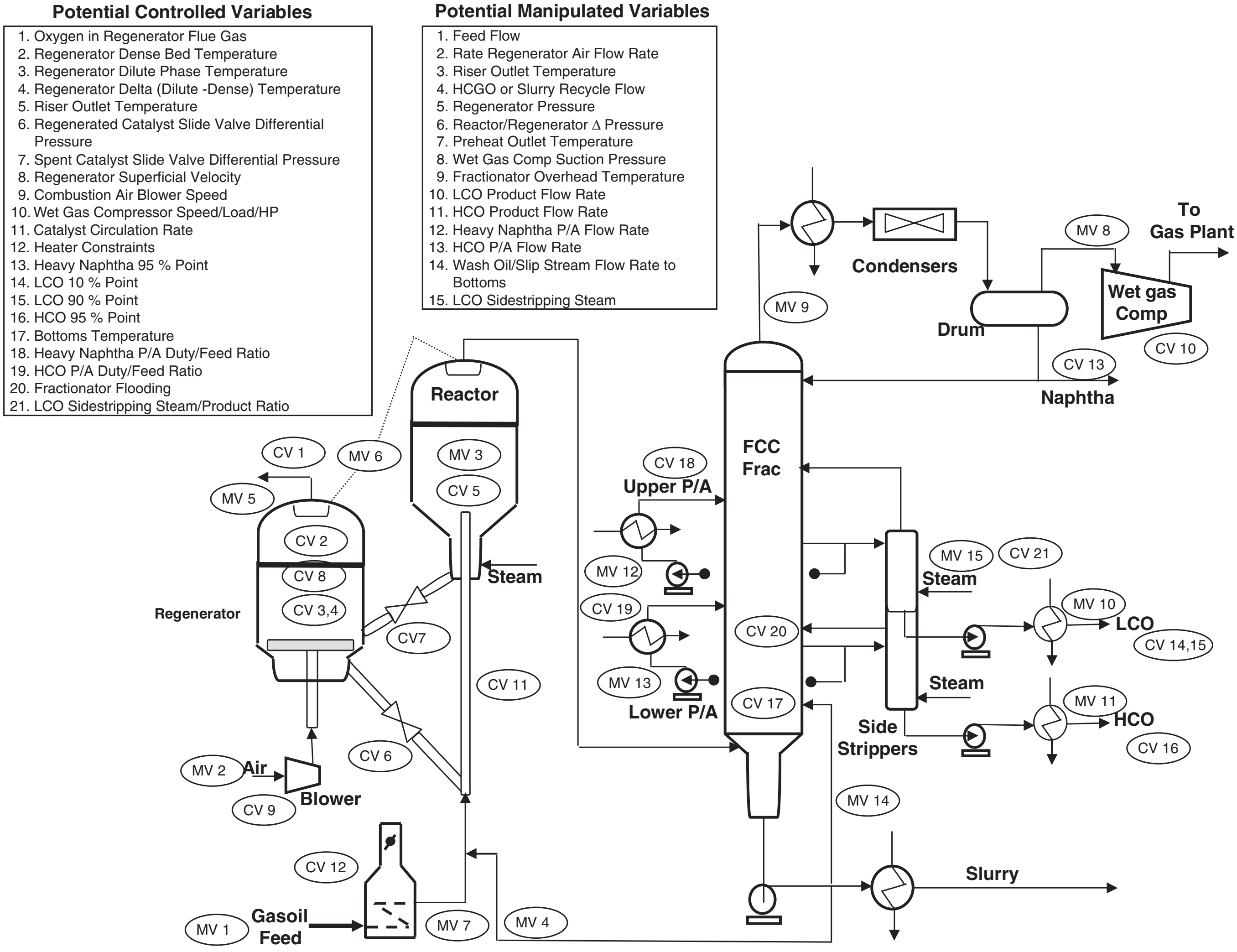
FCC Online Optimization

In this first-principles model-based approach, the profit is maximized based on gas oil feed analysis and octane requirements. The results, in terms of fresh feed rate, riser temperature, etc., are sent to the MVPC controller.

15.7.3 Catalytic Reforming Unit

Simplified Description

In a typical fixed-bed semiregenerative process, low-octane naphtha feed is converted into high-octane reformate for gasoline blending by changing the molecular forms of the feedstock from long-chain naphthenes and paraffins to aromatics, which makes the catalytic



Potential Controlled Variables

1. Oxygen in Regenerator Flue Gas
2. Regenerator Dense Bed Temperature
3. Regenerator Dilute Phase Temperature
4. Regenerator Delta (Dilute -Dense) Temperature
5. Riser Outlet Temperature
6. Regenerated Catalyst Slide Valve Differential Pressure
7. Spent Catalyst Slide Valve Differential Pressure
8. Regenerator Superficial Velocity
9. Combustion Air Blower Speed
10. Wet Gas Compressor Speed/Load/HP
11. Catalyst Circulation Rate
12. Heater Constraints
13. Heavy Naphtha 95 % Point
14. LCO 10 % Point
15. LCO 90 % Point
16. HCO 95 % Point
17. Bottoms Temperature
18. Heavy Naphtha P/A Duty/Feed Ratio
19. HCO P/A Duty/Feed Ratio
20. Fractionator Flooding
21. LCO Sidestripping Steam/Product Ratio

Potential Manipulated Variables

1. Feed Flow
2. Rate Regenerator Air Flow Rate
3. Riser Outlet Temperature
4. HCGO or Slurry Recycle Flow
5. Regenerator Pressure
6. Reactor/Regenerator Δ Pressure
7. Preheat Outlet Temperature
8. Wet Gas Comp Suction Pressure
9. Fractionator Overhead Temperature
10. LCO Product Flow Rate
11. HCO Product Flow Rate
12. Heavy Naphtha P/A Flow Rate
13. HCO P/A Flow Rate
14. Wash Oil/Slip Stream Flow Rate to Bottoms
15. LCO Sidestripping Steam

Figure 15.7—FCC unit: MVPC control.

TABLE 15.5—FCCU: List of MVPC Variables

No.	MVs	CVs	Disturbance Variables
1	Feed flow rate	Percent oxygen in regenerator flue gas	Stripping steam rate
2	Regenerator air flow rate (blower vent or stator vane)	Regenerator dense bed temperature	
3	Riser outlet temperature (or regenerator catalyst slide valve)	Regenerator dilute-phase temperature	
4	HCO or slurry recycle flow rate	Regenerator delta (dilute-dense) temperature	
5	Regenerator pressure	Riser outlet temperature	
6	Reactor/regenerator differential pressure	Regenerated catalyst slide valve differential pressure	
7	Charge preheat outlet temperature	Spent catalyst slide valve differential pressure	
8	Wet gas compressor suction pressure	Regenerator superficial velocity	
9	Fractionator overhead temperature	Combustion air blower speed	
10	LCO product flow rate	Wet gas compressor speed/load/HP	
11	HCO product flow rate	Catalyst circulation rate	
12	Heavy naphtha pumparound flow rate	Heater constraints	
13	HCO pumparound flow rate	Heavy naphtha endpoint or ASTM 95 % BP	
14	Wash oil or slip stream flow rate to bottoms	LCO 10 % BP	
15	LCO sidestripping steam	LCO 90 % BP	
16		HCO 95 % BP	
17		Bottoms temperature	
18		Heavy naphtha pumparound duty/feed ratio	
19		HCO pumparound duty/feed ratio	
20		Fractionator flooding	
21		LCO sidestripping steam/product ratio	
22		All relevant valve limits	

reforming unit (CRU) a net exporter of hydrogen (H_2) gas and a part of refinery H_2 balance. The feed is mixed with the recycled H_2, and the combined stream is brought to reaction temperature in a feed heater before entering into the first reactor. A typical semiregenerative CRU consists of three to four fixed-bed reactors in series and requires a batch-type regeneration procedure on a periodic basis to restore the catalyst to fresh catalyst conditions. In the meantime, the decreased catalyst activity shows up as a loss of reformate yield or high inlet temperature condition. Because of this, the temperature profile across individual beds may be different.

Control Objectives

The control objectives for the reforming reactor section are to

- Maintaining the product octane number target
- Maximizing charge throughput
- Maximizing stabilized reformate yield
- Minimizing energy consumption

Similar to most distillation towers, the objectives for the stabilizer are to

- Maintain reformate Reid vapor pressure (RVP)
- Minimize loss of benzene and pentanes in overhead
- Minimize butanes in the bottoms
- Maintain product composition and tower stability in presence of feed disturbances
- Minimize reboiler energy consumption

Catalytic reforming involves several interactive elements—achieving target octane and maximizing reformate yields in an environment of changing naphtha feed types, feed rate, catalyst activity, recycle H_2 purity, and recycle compressor capacity.

Aside from conventional control schemes and a MVPC scheme, a model-based octane prediction is often included. The inferential scheme calculates research octane number (RON) from reactor temperatures, feed analysis [paraffins, olefins, napthanes, and aromatics (PONA)], liquid hourly space velocity, estimated catalyst activity, etc.

Conventional Control Strategies

- Heater pass temperature balancing controls
- Heater stack excess oxygen controls
- Heater outlet temperature controls

MVPC

- Reactor weight average inlet temperature (WAIT) control, which is based on RON octane model prediction
- Reactor temperature profile control (important for fixed-bed CRU)
- Maximize feed rate subject to process and equipment constraints
- Hydrogen/hydrocarbon (HC) feed ratio control
- Stabilizer bottoms reformate RVP quality control

Figure 15.8 summarizes the MVPC control scheme for a CRU unit and Table 15.6 lists the potential MVPC variables.

Refinery Hydrogen Balance

As refineries have both hydrogen-consuming units (hydrocracker/hydrotreater) and hydrogen-producing units (reformer, H_2 plant), the objective is to minimize net hydrogen production costs. The reformer excess hydrogen production is increased by operating at lower pressure and higher temperature.

15.7.4 Hydrocracker Unit

Simplified Description

In a single-stage unit, fresh feed and recycled hydrogen are preheated in their respective heaters and combined before entering the reactor. The unit may have one or more reactors in series and/or in parallel, depending on unit capacity and desired yield characteristics. To control this exothermic temperature rise, cold hydrogen quenches are injected alongside the reactors. The reactor effluent is separated in a series of flash drums. Part of the vapor flash (hydrogen) is purged, and high-purity makeup hydrogen is added to maintain the desired hydrogen concentration. The liquid stream from the separator is fractionated and some of the liquid bottom product is often recycled back to the reactor.

Control Objectives

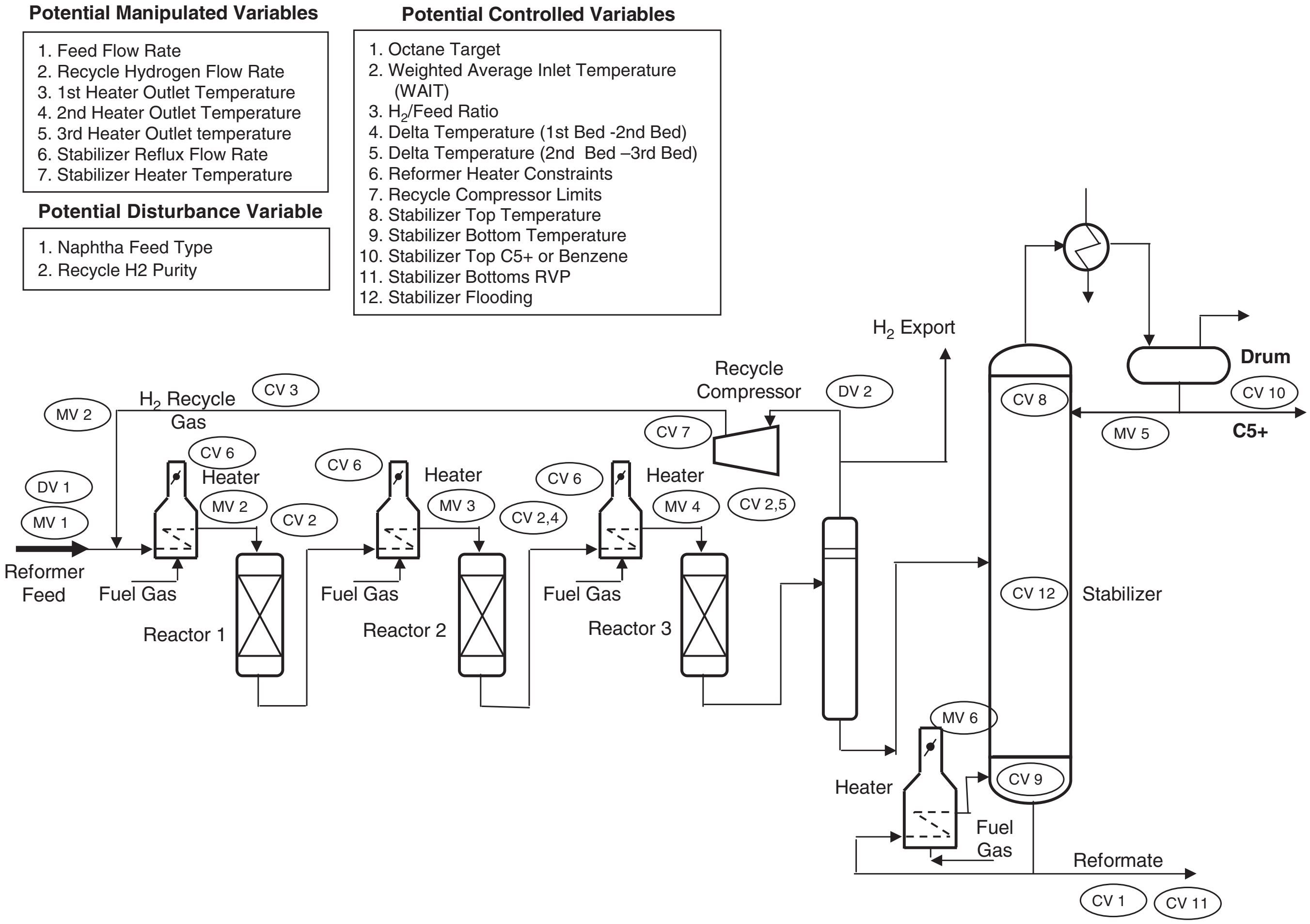
The control objectives for the reactor section are

- Maintaining conversion and severity via weighted average bed temperature (WABT)
- Maximizing throughput
- Minimizing energy consumption

The control objectives for the fractionator are

- Sidestream product purity
- Energy recovery controls

The hydrocracker conversion and severity control is a difficult task because it involves the interaction of several



Potential Manipulated Variables

1. Feed Flow Rate
2. Recycle Hydrogen Flow Rate
3. 1st Heater Outlet Temperature
4. 2nd Heater Outlet Temperature
5. 3rd Heater Outlet temperature
6. Stabilizer Reflux Flow Rate
7. Stabilizer Heater Temperature

Potential Disturbance Variable

1. Naphtha Feed Type
2. Recycle H2 Purity

Potential Controlled Variables

1. Octane Target
2. Weighted Average Inlet Temperature (WAIT)
3. H_2/Feed Ratio
4. Delta Temperature (1st Bed -2nd Bed)
5. Delta Temperature (2nd Bed –3rd Bed)
6. Reformer Heater Constraints
7. Recycle Compressor Limits
8. Stabilizer Top Temperature
9. Stabilizer Bottom Temperature
10. Stabilizer Top C5+ or Benzene
11. Stabilizer Bottoms RVP
12. Stabilizer Flooding

Figure 15.8—Catalyst Reforming Unit: MVPC control.

TABLE 15.6—CRU: List of MVPC Variables

No.	MVs	CVs	Disturbance Variables
1	Feed flow rate	Octane target	Naphtha feed type
2	Recycle hydrogen flow rate	Weighted average inlet temperature (WAIT)	Recycle H_2 purity
3	First heater outlet temperature	H_2/feed ratio	
4	Second heater outlet temperature	Delta temperature (first bed—second bed)	
5	Third heater outlet temperature	Delta temperature (second bed—third bed)	
6	Stabilizer reflux flow rate	Reformer heater constraints	
7	Stabilizer heater temperature	Recycle compressor limits	
8		Stabilizer top temperature	
9		Stabilizer bottom temperature	
10		Stabilizer top C_5+ or benzene	
11		Stabilizer bottoms RVP	
		Stabilizer flooding	
		All relevant valve limits	

process conditions, such as individual bed temperatures, recycled H_2/HC feed ratio, quench rates, heat of reaction, and catalyst activity.

The conversion per pass control sets the ratio of gas oil recycle to fresh feed. Because this can affect the fractionator bottoms level, the severity (WABT) is adjusted to maintain the fractionator bottoms level. If there is no recycle, then only the direct WABT severity setpoint control is implemented.

Conventional Control Strategies

- Heater pass temperature balance
- Heater stack oxygen control
- Heater outlet temperature control
- Recycled H_2 purity control
- Makeup H_2 flow rate control

MVPC

- Severity control via WABT
- Maximize feed rate subject to process and equipment constraints
- Recycled surge drum/fractionator bottoms level control
- Recycled H_2/HC ratio control
- Fractionator product quality control—Typically, 95 % BP or endpoint on heavy naphtha, 95 % BP and freeze on kerosene, 95 % BP and cloud point for diesel

Figure 15.9 summarizes the MVPC control scheme for a hydrocracker unit and Table 15.7 lists the potential MVPC variables.

Refinery Hydrogen Balance

As refineries have both hydrogen-consuming units (hydrocracker/hydrotreater) and hydrogen-producing units (reformer, H_2 plant), the objective is to minimize net hydrogen production costs. Operating at lower temperature, lower pressure, and higher space velocity decreases the hydrocracker hydrogen consumption.

15.7.5 Delayed Coker Unit

Simplified Description

Hot vacuum residue and thermal tar feed or both are fed into the fractionator a few trays above the bottom. The stripped feed and gasoil recycle are pumped from the bottom of the fractionator to the coker heater. The vapor-liquid mixture then enters the coke drum where further cracking takes place as the vapor passes through the drum and the liquid experiences successive cracking and polymerization until it is converted to vapor and coke. The severe thermal cracking produces lighter HC fractions and hydrocracker feed stocks. The unvaporized portion of the heater effluent settles out in the coke drum where the combined effect of temperature and retention time causes the formation of coke; hence, the term “delayed coking.” The coke produced can be used in the steel and aluminum industries or as fuel.

The coke drum overhead vapor enters the base of the fractionator and is separated into gas, naphtha, light coker gas oil (LCGO), and heavy coker gas oil (HCGO), which are withdrawn as products.

Control Objectives

The control objectives for the delayed coker unit are to

- Maximize unit throughput
- Maximize liquid yield of feed
- Maintain product quality
- Minimize energy consumption
- Optimize volatile coke matter (VCM) quality
- Minimize the disturbances during the coker drum switch
- Minimize drum cycle time

Unlike other refining process units in which the process is continuous, the delayed coking process has some batch characteristics when the coke drum gets full and is replaced with a new, empty cold drum. This requires some adaptation in the MVPC control scheme [8]. Also, coker throughput maximization requires adjustment of feed rate

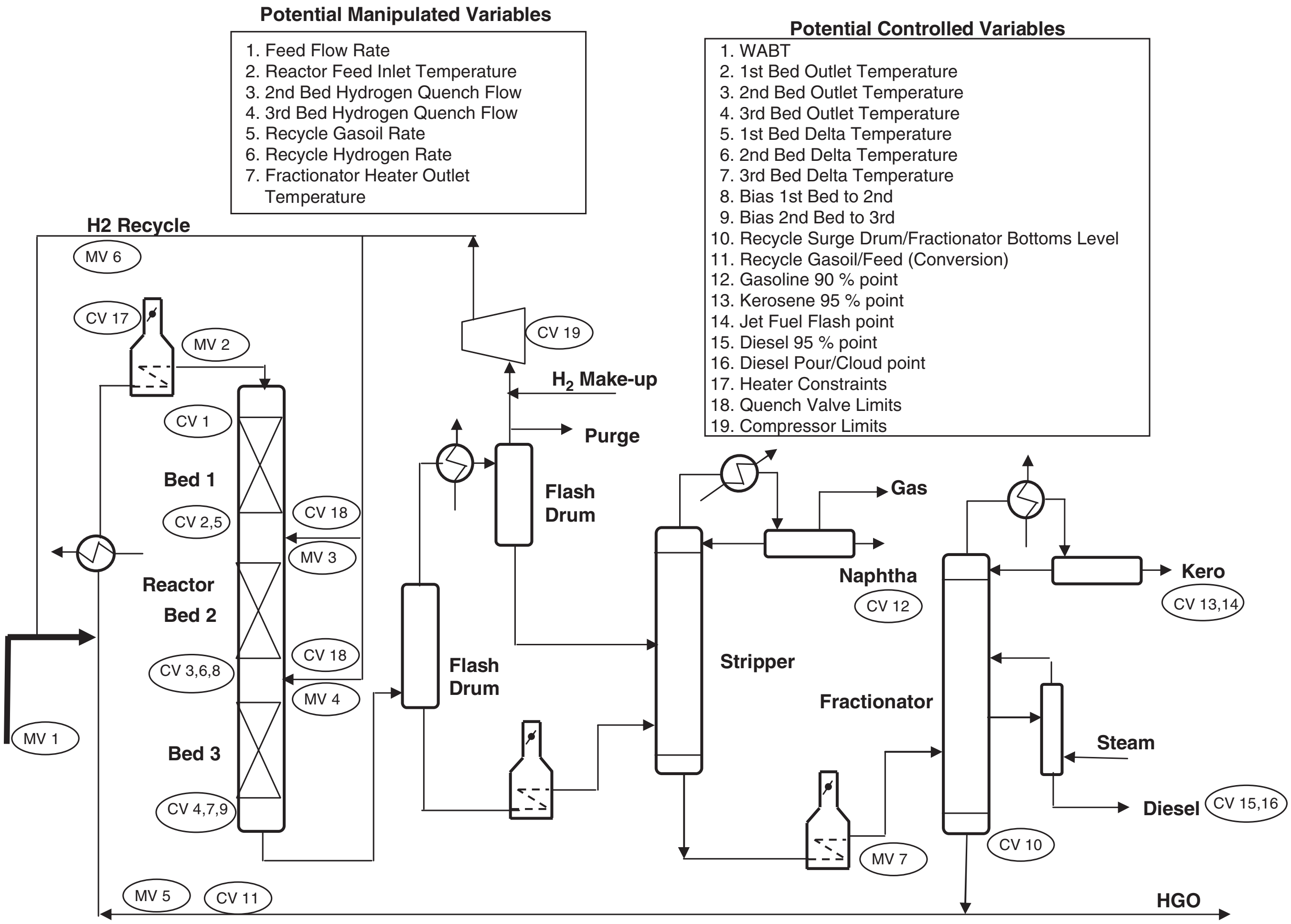


Figure 15.9—Hydrocracker unit: MVPC control.

in the presence of constraints and physical limits such as drum volume and heater TMTs so that the coke drums are full at the end of an operator-entered drum cycle time.

Conventional Control Strategies

- Heater pass temperature balance
- Heater stack oxygen control
- Heater outlet temperature control
- Coke drum cycle time minimization by adjusting steam and cooling water closely for the warming and cooling of the drums
- Nonlinear level control

MVPC

- Coker charge maximization
- Coke quality control
- Recycle minimization
- Pressure minimization
- Product quality control
- Reduction of energy consumption
- Drum switch disturbance minimization

Figure 15.10 summarizes the MVPC control scheme for a delayed coker unit and Table 15.8 lists the potential MVPC variables.

15.7.6 Gas Plant

Simplified Description

Compressed gas feed is fed to an absorber-deethanizer. Lean oil is added in the top section of the absorber to absorb most of the C_3 and heavier HCs. The rich oil is returned for stripping off the absorbed light ends to the column from which it was derived. Sufficient reboil heat is added to the bottom of the stripping section of the absorber-deethanizer to eliminate any absorbed ethane and methane as well as hydrogen sulfide from the bottom liquid product. The deethanized stream then flows to a debutanizer where C_3 and C_4 HCs are fractionated and taken off as overhead product. The bottom product from the debutanizer contains C_5 and heavier HCs. The overhead C_3 and C_4 product from the debutanizer is fed to a depropanizer for separation into propane and butane.

Control Objectives

The control objectives for the gas plant unit are to

- Maximize recovery of valuable C_3, C_4, and C_5+ products from the feed gas stream.
- Produce gas consisting mostly of methane and ethane for use as a fuel gas or as feedstock for hydrogen production.
- Minimize loss of propylene in the deethanizer overhead.
- Maintain the C_2 specifications of the deethanizer bottoms product as limited by the propylene product purity specifications.
- Maintain the debutanizer overhead C_5+ specification as limited by the C_4 product quality specification.
- Maintain the debutanizer bottom C_4 specification as limited by the C_5+ (gasoline) product purity (RVP) requirements.

TABLE 15.7—Hydrocracker: List of MVPC Variables

No.	MVs	CVs	Disturbance Variables
1	Feed flow rate	WABT	Naphtha feed type
2	Reactor feed inlet temperature	First bed outlet temperature	Recycle H_2 purity
3	Second bed hydrogen quench flow	Second bed outlet temperature	
4	Third bed hydrogen quench flow	Third bed outlet temperature	
5	Recycle gas oil rate	First bed delta temperature	
6	Recycle hydrogen rate	Second bed delta temperature	
7	Fractionator heater outlet temperatures	Third bed delta temperature	
8		Bias first bed to second	
9		Bias second bed to third	
10		Recycle surge drum/fractionator bottoms level	
11		Recycle gas oil/feed (conversion)	
12		Gasoline 90 % BP	
13		Kerosene 95 % BP	
14		Jet fuel flash point	
15		Diesel 95 % BP	
16		Diesel pour/cloud point	
17		Heater constraints	
18		Quench valve limits	
19		Compressor limits	

- Maintain the depropanizer overhead C_3 specification with a minimum degree of overpurification.
- Minimize propylene losses in the depropanizer C_4 product.

Conventional Control Strategies

- Deethanizer bottoms nonlinear level control
- Debutanizer reflux drum nonlinear level control
- Debutanizer bottoms nonlinear level control
- Depropanizer reflux drum nonlinear level control
- Depropanizer bottoms nonlinear level control
- Feed drum to gas processing nonlinear level control

MVPC

- Lean oil circulation control
- Tower composition controls
- Energy minimization controls

Figure 15.11 summarizes the MVPC control scheme for a gas plant and Table 15.9 lists the potential MVPC variables.

15.8 NEURAL NETWORKS—INFERENTIAL PREDICTIONS

Artificial neural nets (ANN), also called neural networks, are models based on the parallel architecture of brains for computing. A neural network is essentially a form of nonlinear regression, $Y = f(x)$, which maps an "*n* dimension" input space into an "*m* dimension" output space without the form of $f(x)$ being known in advance. In practice, neural nets are especially useful for classification and function approximation/mapping problems that are tolerant of some imprecision and have lots of training data available.

A neural network topology is the shape of the layered computation structure. It is a combination of neurons, connections, and nodes. For a typical feed-forward (back propagation) neural network, the structure is (see Figure 15.12) [9]:

- An input layer for receiving data.
- One or more hidden layers for computation. The activity of a hidden neuron depends on the activity of the input neurons and the weight of the connection between the input and the hidden neurons.
- An output layer for results (prediction). The behavior of the output neuron depends on the activity of the hidden neurons and the weight of the connection between the hidden and the output neurons.

The advantage of using neural networks for inferential predictions of product qualities is that detailed first-principles-based knowledge of the process is not required and the neural networks can be trained by making them learn from historical sets of data. Training usually requires a large amount of data. Depending on the number of input, hidden, and output units, 30–100 historical points for each output unit would not be uncommon to train the network. So, if flash point is being estimated, and the laboratory analysis is done once daily, then approximately 3 months of historical data would be required. However, once trained, neural networks are very fast in calculating the output from the inputs. As an example, to develop a neural net for predicting the 95 % BP of heavy naphtha,

- The input layer would have approximately nine input units for crude feed rate, crude properties (API and

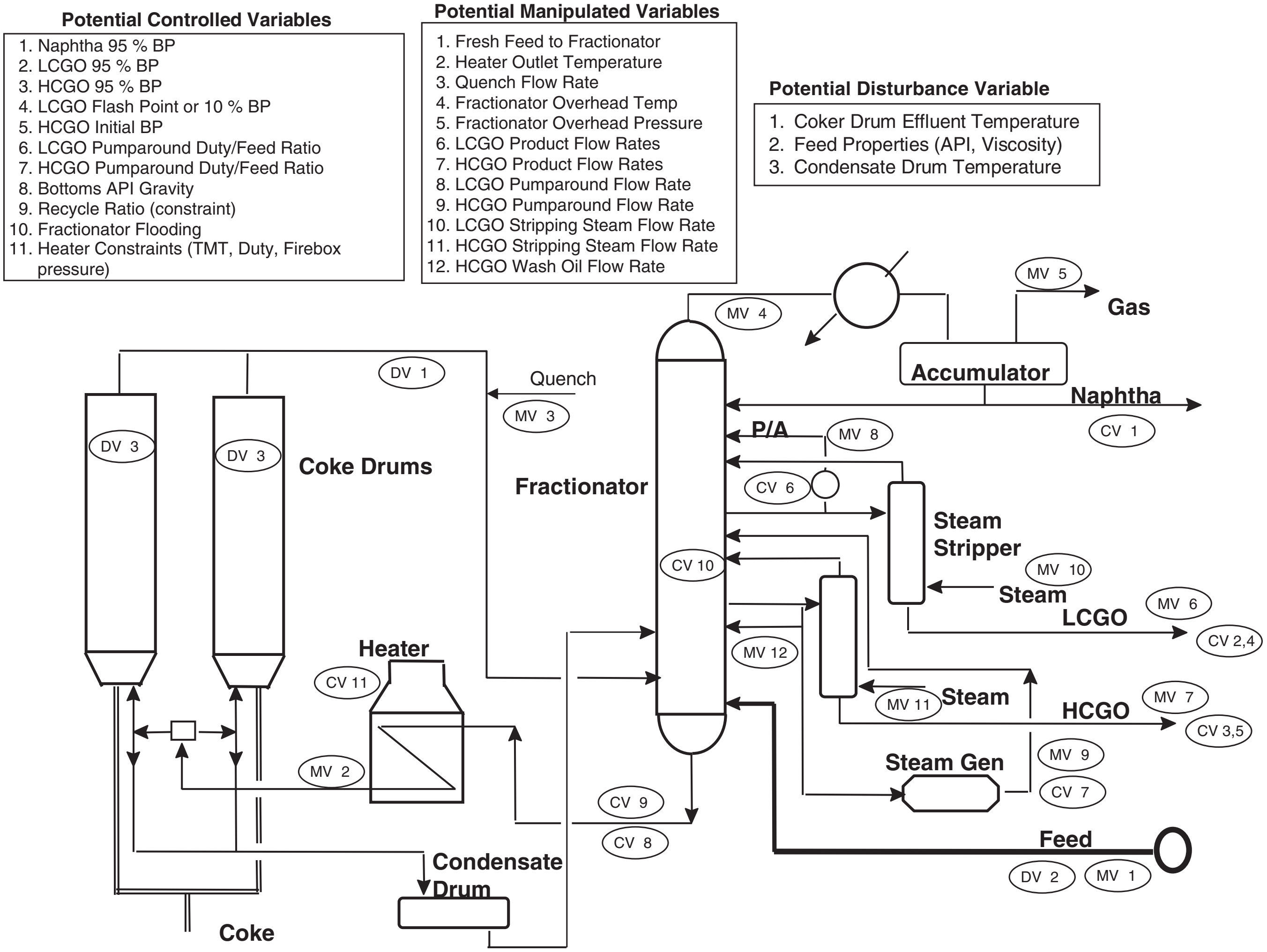


Figure 15.10—Delayed coker unit: MVPC control.

TABLE 15.8—Delayed Coker: List of MVPC Variables			
No.	**MVs**	**CVs**	**Disturbance Variables**
1	Fresh feed to fractionator	Naphtha 95 % BP	Coker drum effluent temperature
2	Heater outlet temperature	LCGO 95 % BP	Feed properties (API, viscosity)
3	Quench flow rate	HCGO 95 % BP	Condensate drum temperature
4	Fractionator top temperature	LCGO flash point or 10 % BP	
5	Fractionator overhead pressure	HCGO initial BP	
6	LCGO product flow rates	LCGO pumparound duty/feed ratio	
7	HCGO product flow rates	HCGO pumparound duty/feed ratio	
8	LCGO pumparound flow rate	Bottoms API gravity	
9	HCGO pumparound flow rate	Recycle ratio (constraint)	
10	LCGO stripping steam flow rate	Fractionator flooding	
11	HCGO stripping steam flow rate	Heater constraints (TMT, duty, firebox pressure)	
12	HCGO wash oil flow rate		

TABLE 15.9—Gas Plant: List of MVPC Variables

No.	MVs	CVs	Disturbance Variables
1	Feed rate to the gas processing unit	Deethanizer top temperature	Lean oil temperature
2	Lean oil flow rate	Deethanizer overhead C_3 composition	Feed rate to the gas processing unit (if not a MV)
3	Deethanizer bottom temperature	Deethanizer bottom C_2 composition	Feed rate to the debutanizer
4	Deethanizer overhead pressure	Deethanizer top delta pressure (flooding)	Feed rate to the depropanizer
5	Debutanizer top temperature	Deethanizer bottom delta pressure (flooding)	Feed composition to the gas unit
6	Debutanizer overhead pressure	Debutanizer overhead C_5 composition	
7	Debutanizer bottom temperature	Debutanizer bottom C_4 composition (RVP)	
8	Depropanizer top temperature	Debutanizer delta pressure (flooding)	
9	Depropanizer overhead pressure	Depropanizer overhead C_5 composition	
10	Depropanizer bottom temperature	Depropanizer bottom C_4 composition	
11		Depropanizer top delta pressure (flooding)	
12		All relevant valve positions	

Potential Manipulated Variables

1. Feed Rate to the Gas Processing Unit
2. Lean Oil Flow Rate
3. Deethanizer Bottom Temperature
4. Deethanizer Overhead Pressure
5. Debutanizer Top Temperature
6. Debutanizer Overhead Pressure
7. Debutanizer Bottom Temperature
8. Depropanizer Top Temperature
9. Depropanizer Overhead Pressure
10. Depropanizer Bottom Temperature

Potential Controlled Variables

1. Deethanizer Top Temperature
2. Deethanizer Overhead C3 Composition
3. Deethanizer Bottom C2 Composition
4. Deethanizer Top Delta Pressure (Flooding)
5. Deethanizer Bottom Delta Pressure (Flooding)
6. Debutanizer Overhead C5 Composition
7. Debutanizer Bottom C4 Composition (RVP)
8. Debutanizer Delta Pressure (Flooding)
9. Depropanizer Overhead C5 Composition
10. Depropanizer Bottom C4 Composition
11. Depropanizer Delta Pressure (Flooding)
12. All Relevant Valve Positions

Potential Disturbance Variable

1. Lean Oil Temperature
2. Feed Rate to the Gas Processing Unit (if not a MV)
3. Feed Rate to the Debutanizer
4. Feed Rate to the Depropanizer
5. Feed Composition to the Gas Unit

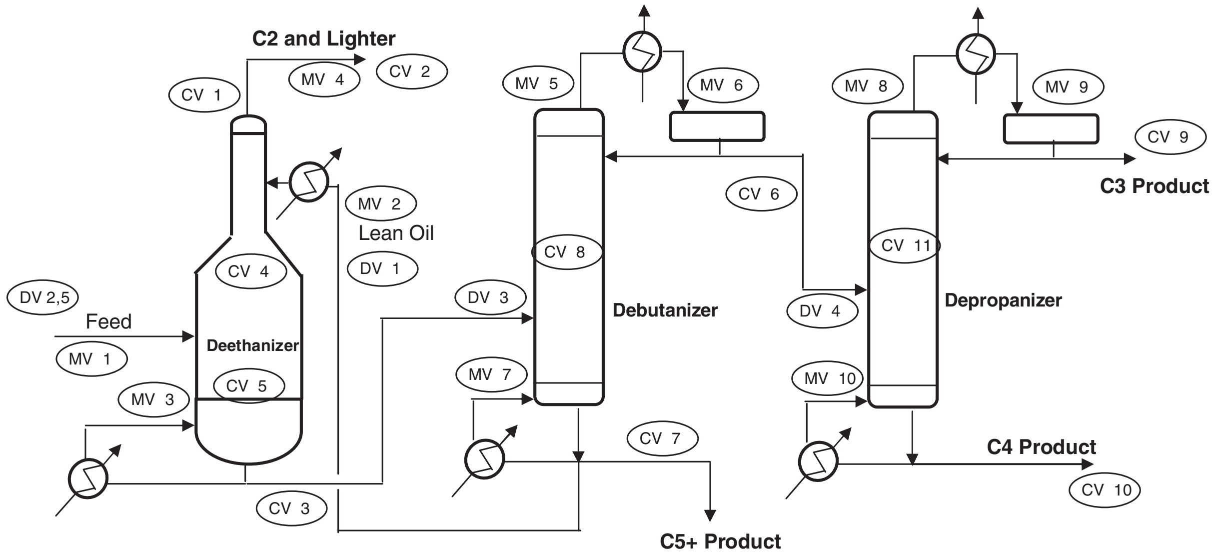


Figure 15.11—Gas plant: MVPC control.

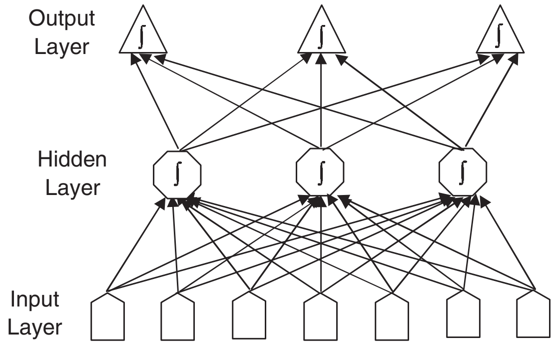


Figure 15.12—Neural network architecture.

viscosity), crude feed temperature (heater outlet temperature), column overhead temperature, column draw tray temperature, overhead reflux, top pumparound flow rate (or duty), and heavy naphtha draw rate.

Literature [9–12] mentions attempts at using neural networks for estimating the following properties:

- Preflash tower
    - Heavy naphtha end BP
- Atmospheric tower
    - Light naphtha end BP
    - Kerosene initial BP
    - Kerosene end BP
    - Kerosene crystallization point
    - Atmospheric diesel 50 % BP
    - Atmospheric diesel 95 % BP
- Vacuum tower
    - Low-viscosity vacuum gas oil (VGO) 95 % BP
    - Medium-viscosity VGO flash point
    - Medium-viscosity VGO viscosity
    - High-viscosity VGO viscosity
    - High-viscosity VGO color
    - Vacuum diesel 95 % BP
    - Residue viscosity

15.9 ADVISORY SYSTEMS

In addition to a strict mathematical approach for the control of refining and petrochemical units, advisory/expert systems offer a supporting way to improve the profitability of process unit by [13]

- Assisting operators and engineers in normal, start-up, shutdown, and emergency situations
- Smart alarm management
- Enhancing APC/MVPC

Advisory systems are a repository of knowledge and experience in many areas (operations, engineering, maintenance, laboratory analysis, planning, and management) collected via interviews, historical logs, incident reports, process manuals, seasonal events/sales, etc., and stored in knowledge base(s) as heuristics (rules of thumb) and event-based procedures.

Because of the uniqueness of the operation of each process unit in terms of operating variables (flow, pressure, temperature, etc.), the advisory systems superimpose unit-specific knowledge on generic knowledge as shown in Figure 15.13.

15.10 FUZZY LOGIC

Fuzzy logic is widely used in machine control, but its application to chemical process control has been quite limited. However, there are processes and conditions (e.g., binary distillation columns, batch reactors, etc.) that can be conducive to the success of fuzzy logic applications without incurring the cost of engineering-extensive MVPC controllers.

- For processes in which mathematical models may not be known but in which rules that adequately describe control actions under various operating conditions are readily available via experience.
- Mathematical conventional control often assumes linear process, time-invariant behavior, and measurement frequency being faster than control frequency. Fuzzy logic control is not limited by these constraints.

A fuzzy logic controller typically consists of four components:

1. *Fuzzifier:* The process behavior is modeled as a matter of degree (in membership functions—see Figure 15.14) rather than in precise discrete measurement. For example,
   99°C = 0.3 (cold), 0.8 (normal), 0.0 (hot)
   100°C = 0.0 (cold), 1.0 (normal), 0.0 (hot)
2. *Rules:* These are based on simple operating heuristics and engineering principles. For example:

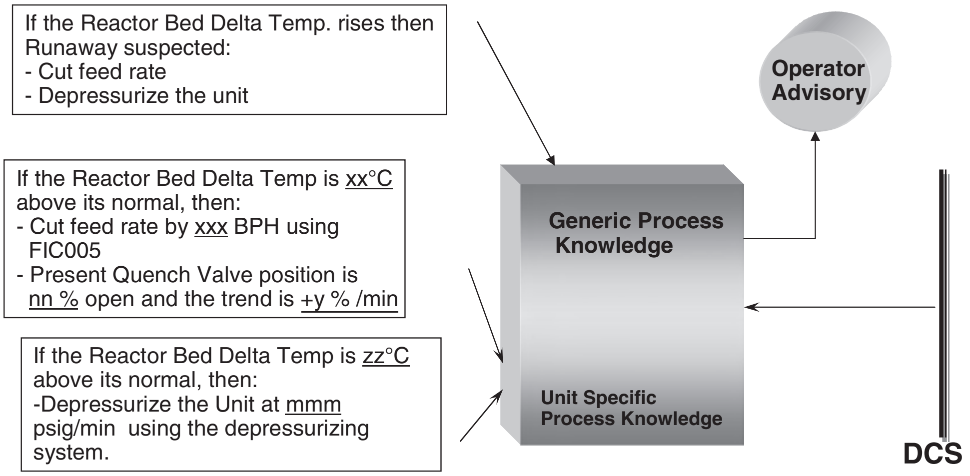


Figure 15.13—Advisory system sample configuration.

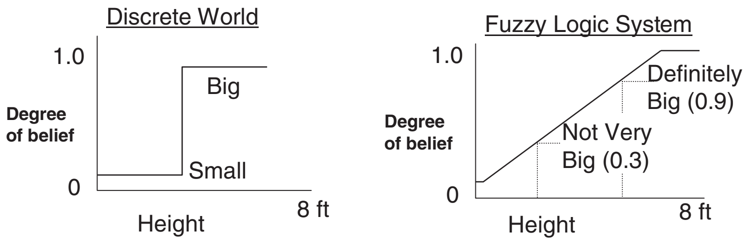


Figure 15.14—Fuzzy logic: Classification.

  - If tray is cold, then decrease reflux by a small amount.
  - If tray is very cold, then decrease reflux by a medium amount.

Here the small amount and large amount are quantified separately via membership functions.

3. *Inference engine:*
   - On the basis of the values of the inputs (e.g. multiple tray temperatures), the fuzzy logic controller checks all of the rules and activates the subconditions to be made in the outputs (e.g. reflux flow, reboiler steam flow).
   - The output aggregation allows for a combination of multiple inferences (of a single rule) via aggregation operators (e.g., MIN, MAX, and PRODUCT) of active subconditions.
4. *Defuzzifier:* Similar, but opposite of fuzzification, the output membership function is converted into a practical number that can be implemented by a PID controller.

Fuzzy logic can also be used to imitate the behavior of a PID controller (In fact, it has been shown that a classic PID controller can be matched exactly using specially selected fuzzy representations and methods [14]) in its simple implementation form. Then, by adding more rules and fuzzification, the desired nonlinear control action can be enforced in routine and ad hoc conditions.

REFERENCES

[1] Friedland, B., *Control System Design: An Introduction to State-Space Methods*, McGraw-Hill, New York, 1986.

[2] Lewis, F.L., *Applied Optimal Control and Estimation,* Prentice-Hall, Upper Saddle River, NJ, 1992.

[3] Yucai, Z., *Multivariable System Identification for Process Control*, Elsevier, Cambridge, MA, 2001.

[4] Jaisinghani, R., GMAXC, "Multivariable Predictive Control Training Course," Intelligent Optimization Group, 2008.

[5] Deshpande, P.B., *Multivariable Process Control*, Instrument Society of America, Research Triangle Park, NC, 1989.

[6] Lipták, B.G., *Process Control—Instrument Engineers' Handbook*, 3rd ed., CRC Press, Boca Raton, FL, 1995.

[7] Lipták, B.G., *Optimization of Unit Operations*, Bela G. Lipták, Radnor, PA, 1987.

[8] Jaisinghani, R., Minter, B., Tica, A., Puglesi, A., and Ojeda, R., "Delayed Coker Fractionator Advanced Control," *Hydrocarbon Process*., Vol. 72, 1993, pp. 173–178.

[9] Ramakumar, K.R., "Predicting Important Parameters Using Artificial Neural Networks," *Hydrocarbon Process*., Vol. 87, 2008, pp. 81–83.

[10] Yang H., Briker, Y., Szynkarczuk, R., and Ring, Z., "Prediction of Density and Cetane Number of Diesel Fuel from GC-FIMS and PIONA Hydrocarbon Composition by Neural Networks," *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*., Vol. 49, 2004, pp. 81–84.

[11] Kataev, P., Slobodkin, W., Slavnov, A., and Heavner, L., "Crude Gets Smart," ISA InTech, March 1, 2007.

[12] Bonavita,, N., and Ruggeri, G., "Neural Net-Based Inferential Quality Control on a Crude Unit," http://www05.abb.com/global/scot/scot267.nsf/veritydisplay/2fcb0cf334d97bea85256f9b005c407d/$file/nnoncruidunit_glasgow_final.pdf (accessed 2011).

[13] Anderson, R.E., Barnett, M., and Jaisinghani, R., "Rule Driven Optimization Boosts Plant Performance," *Hydrocarbon Process*, Vol. 84, 2005, 59–62.

[14] "Tuning of Fuzzy PID Controllers," Technical University of Denmark, Report 98-H 871, September 30, 1998.

16

Refinery Inspection and Maintenance

A.L. Kosta[1] and Keshav Kishore[2]

16.1 INTRODUCTION

Inspection of plant and machinery along with the associated facilities plays a pivotal role in reliable and safe refinery operations. Maintenance is the backbone of refinery operations because wear and tear in the components by way of mechanical rubbing, heat generation, fatigue, degradation of material quality, etc., is inevitable during operations, and we need to maintain the equipment/system in original health to the level of Ex-factory conditions by performing the necessary corrective actions from time to time. Any equipment operating continuously or intermittently requires maintenance to achieve its design life. At the same time, it is essential that the equipment should not undergo over-maintenance, which may result in increased maintenance costs and a change in the original settings and clearances (factory settings). This aspect is much more relevant in the case of mechanical and electrical equipment.

For maintenance, the equipment needs to be opened/or dismantled for inspection, and repairs are performed based on visual and other examinations. Wherever required, equipment or its components are made ready for inspection by cleaning the surface by brushing, filing, grinding, etc. In certain cases suitable access is also provided using ladders, scaffolds, or hydraulic platforms. Inspection or observations are made either while the equipment is in operation or, if required, it should be stopped for inspection. In certain cases if there is a need to enter the equipment, such as with towers, vessels, or furnaces, the equipment needs to be made free of any foreign material, gases, etc., and brought to atmospheric conditions.

There are four basic areas under which separate maintenance activities are performed in the refinery: mechanical, electrical, instrumentation, and civil.

16.1.1 Maintenance Parameters

- *Man*: Require proper education and training to maintenance and inspection personnel.
- *Machine*: Establishment of strong facilities to cater to the maintenance demand.
- *Management*: Timely cooperation among concerned sections to meet the maintenance requirement. Strong facility management system-standards, manuals, diagnostic survey facilities, etc.

16.1.2 Need for Maintenance

Refinery operations process varieties of crude oils at different total acid numbers (TANs) with several chemicals/catalysts as per operational and product demand. Hence, in-service exposure of equipment and facilities causes deterioration because of corrosion and environmental factors. Also, there is a normal process of wear and tear in the components by way of mechanical rubbing, heat generation, fatigue, degradation of material quality, etc. The combined effect of all of these factors is a lowering of equipment health and so equipment life, which results in low reliability. In the case that care is not taken at a predefined schedule, the poor equipment can result in unscheduled breakdowns, which causes a loss of production and increased maintenance costs. Maintenance is also essential to keep the machineries and workplace clean and tidy to avoid any mishaps or accidents. Untidy workplace or machinery conditions are often the cause of fire or other accidents due to slippages, etc.

16.2 MAINTENANCE

Oil refineries generally consist of two types of mechanical equipment: static and rotary. In addition, piping of various metallurgies and other utility systems such as boilers are also maintained by mechanical maintenance.

Maintenance activities are broadly classified into the following categories:

- Breakdown maintenance
- Preventive maintenance
- Predictive maintenance
- Shutdown maintenance.

16.2.1 Breakdown Maintenance

Per this practice, the equipment is allowed to run until it fails. This type of maintenance causes longer downtime of equipment as well as higher maintenance and inventory costs. The production schedule is disturbed because of unscheduled outage of equipment, which leads to significant loss to industry. This practice does not presently exist.

16.2.2 Preventive Maintenance

Preventive maintenance is an age-old practice to maintain equipment or facilities and is much more relevant to rotary equipment. The schedule is derived from the recommendation made by the original equipment manufacturer (OEM) as well as experience gained during operation. Generally the preventive maintenance schedule is timed as monthly, quarterly, half-yearly, or yearly. On the basis of the equipment characteristics, each refinery decides their own schedule of maintenance. Sample checklists for preventive maintenance can be found in Appendixes 1 and 2 at the end of this chapter.

Although preventive maintenance is generally one of the most acceptable norms in the industry, at times it can also lead to overmaintenance. The schedule is thereafter modified to avoid further overmaintenance for such equipment.

---

[1] Indian Oil Corp. Ltd., New Delhi, India
[2] Indian Oil Corp. Ltd., Panipat, India

16.2.3 *Predictive Maintenance*

Predictive maintenance was brought into practice in the late 1970s when gadgets and vibration monitoring tools were put into use. Predictive maintenance is a scientific method of knowing the health of equipment in advance. Measuring vibration, noise, lubricating oil condition, etc., of the equipment has helped to diagnose problems well in advance, thus strengthening predictive maintenance. Use of simple tools such as screwdrivers or iron rods (noise probe) to listen to the noise that develops within equipment can detect problems in bearings components early. Once damage such as this increases in size, it can cause generation of heat, which can be felt during a routine check, and may also result in paint peeling off of the body of the bearing housing.

Predictive maintenance helps in assessing the health of equipment without stopping or dismantling. Signals/indications received during vibration monitoring provide indication on likely causes of abnormality and in assessment of the remaining operational life of the equipment. Predictive maintenance is basically online detection of a problem and is the most acceptable maintenance practice in any industry today.

16.2.3.1 BENEFITS OF PREDICTIVE MAINTENANCE

- Maintenance can be scheduled at a convenient time.
- Resources such as man-material can be arranged beforehand.
- Extensive damage to equipment due to forced failure/breakdown can be avoided.
- Production schedule can be changed as required.
- Time to repair can be optimized, because there will not be any waiting time.
- Because predictive maintenance analysis is able to actually pinpoint the cause of problems, the trial and error method is avoided
- Maximal life can be achieved from the equipment because the equipment can continue to run until there is no sign of further deterioration.

Predictive maintenance comprises the following checks and analyses to investigate the cause of failure so that specific corrective actions can be planned and taken in time:

- Vibration monitoring and trending
  - Amplitude demodulation
  - Peak value analysis
  - Real-time analysis
  - Phase angle analysis
  - Time waveform analysis
- Lubrication oil monitoring and its analysis
  - Wear particle analysis
  - Ferrography
  - Blot testing
- Bearing spike energy monitoring and its analysis
- Infrared thermography
- Ultrasonic analysis
- Online monitoring of process parameters
- Motor current monitoring
- Casing/housing cooling water outlet temperature monitoring and trending in hot pumps/compressors.

16.2.3.2 VIBRATION MONITORING AND TRENDING

Vibration in equipment is either caused by loosening/damage of some part or the presence of an imbalance in the equipment. Whenever such phenomena take place, vibration is induced in the equipment. Three different parameters can be recorded for measuring vibrations: displacement, velocity, and frequency. As a rule of thumb, it is said that if the machine is less than 600 r/min, displacement is measured. If the machine is between 600 and 60,000 r/min, velocity is measured, and if it is more than 60,000 r/min, frequency of the equipment is measured. On any rotary equipment, vibration is measured in three different directions—horizontal, vertical, and axial—at each of the equipment support locations (i.e., at bearings). For velocity, limits provided in Appendix 3 are used for their acceptance or rejection.

Vibrations are measured periodically at fixed intervals and plotted against location and direction, which over a period of time indicate the trend. If the trend is found to be increasing and approaching limits beyond acceptance, the equipment is subjected to vibration analysis. In such cases, advanced vibration analyzers are used and the probable cause of vibration is established. Reference charts and tables in Appendixes 4, 5, and 6 are used to decide what type of measurement is required and whether equipment is operating within acceptable vibration limits.

16.2.4 *Lubricating Oil Monitoring and Its Analysis*

The condition of lubricating oil in a bearing is yet another way of health assessment. On regular monitoring, when traces of metal particles are noticed in the lubricating oil with or without change in the color of lubricating oil, wear and tear in the bearing components are suspected. This indicates that the bearing needs replacement in the near future. This gives prior notice to plan for stoppage of equipment and arrange for requisite spares in the meantime. Sometimes a problem related to the oil itself may contribute to wear. To locate the source of wear particles in the lubricating oil, see the general guidelines in Table 16.1.

TABLE 16.1—Examples of Wear Metals and Their Origin

Wear Metal	Possible Origin
Aluminum	Bearings, blocks, blowers, bushings, clutches, pastors, pumps, rotors, washers
Chromium	Bearings, pumps, rings, rods
Copper	Bearings, bushings, clutches, pistons, pumps, washers
Iron	Bearings, blocks, crankshafts, cylinders, discs, gears, pistons, pumps, shafts
Lead	Bearings (sleeve)
Nickel	Bearings, shafts, valves
Silver	Bearings, bushings, solder
Tin	Bearings, bushings, pistons

The following are some of the laboratory tests that help to identify wear:

- Spectrometric analysis
- Particle counting
- Direct reading ferrography
- Analytical ferrography.

The following physical and chemical tests are generally performed to ascertain the condition of lubricating oil and its future usability:

- Viscosity—TAN
- Moisture content—total bas number (TBN)
- Dispersion—flash point

In addition, any other tests recommended by the OEM may be performed.

16.2.5 Monitoring of Spike Energy of Antifriction Bearings

Apart from various parameters that are measured/observed during a predictive maintenance program, it is also advisable to monitor the condition of antifriction bearings, which are prone to develop defects under adverse conditions and deteriorate fast.

The shock pulse monitoring technique is suitable for analyzing various defects of antifriction bearings. This technique provides early information about impending malfunctions. The shock pulse method monitors metal impacts and rolling noise such as those found in rolling element bearings and gears. When two pieces of metal in motion contact each other, two inter-related yet distinct processes occur. On the initial impact, a shock or pressure wave develops and quickly propagates through the metal. This shock pulse is in the ultrasonic frequency band and typically occurs around a center frequency of 36 kHz.

As the signal travels from its point of origin, it is dissipated by carbon and other impurities in the metal. This shock or pressure wave is measured using the shock pulse method. After getting compressed, the metal regains its shape once the impact load is released. This phase of collision is vibration and the frequency depends on shape, mass, stiffness, and dampening of the metal. These shock pulse waves are measured using shock pulse meters. Shock pulse actually has two readings: carpet value and the maximum value.

Metal impacting metal always occurs in a rolling element bearing. When there is no damage to the bearing, the metal-to-metal contact creates a background noise of shock pulse, which is referred to as the carpet value. When the lubrication begins to break down, there is more metal-to-metal contact and the carpet value increases. The most likely cause of increased carpet value is a decrease in the protective properties of bearing lubrication, which indicates poor lubricating conditions.

When there is a defect in a bearing element, it is hit by another element in the bearing. For example, if there is a defect in the outer raceway of the bearing, the rolling element will hit each time it passes over the defective raceway. This impact creates a high-amplitude burst of shock pulse that is distinct from the carpet value. Thus, the shock pulse method helps in identifying the defects developed in an antifriction bearing. A similar philosophy is also true in the case of damage in a gear train.

16.2.6 Infrared Thermography

Infrared (IR) thermography is the process of generating thermal images of the object. Objects of different materials and colors absorb and reflect electromagnetic radiation in the visible light spectrum (0.4–0.7 μm). Any object at a temperature greater than absolute zero emits IR energy (radiation) proportionate to its temperature. By using an IR thermometer, a two-dimensional visual image reflective of the IR radiance from the surface of an object can be generated. Like other predictive maintenance technologies, IR tries to detect abnormality in the equipment in the form of generation of heat. For example, a loose or corroded electrical connection results in the generation of heat due to increased electrical resistance. Similarly, damaged refractory material on the casing of a furnace will lead to an increase in temperature, which if monitored regularly will help in the early detection and repair of damaged components.

16.2.7 Ultrasonic Analysis

Ultrasounds are the sound waves that have a frequency level above 20 kHz. Sound waves in this frequency spectrum are higher than what can normally be heard by humans. Noncontact ultrasonic detectors detect airborne ultrasounds. The frequency spectrums of these ultrasounds fall in the range of 20–100 kHz. In contrast to IR emissions, ultrasounds travel in straight lines and will not penetrate solid surfaces. Most of the rotating equipment and many fluid system conditions emit sound patterns in the ultrasonic frequency spectrum. Changes in these ultrasonic wave emissions are reflective of equipment conditions. Ultrasonic detectors help in identifying problems related to component wear as well as fluid leaks, vacuum leaks, and steam trap failures. In addition, these ultrasounds also help in detecting sounds from abnormally working equipment.

16.2.8 Online Monitoring of Process Parameters

16.2.8.1 TEMPERATURE

The temperature of equipment, especially at bearing locations, can also indicate the health of equipment. When the temperature of bearing housing remains stable, it indicates that the equipment is running without any mechanical abnormality. On the other hand, a gradual increase in temperature is an indication of a developing problem in the equipment and is a hint to perform a detailed equipment check.

16.2.8.2 PRESSURE AND FLOW

In the case of rotating equipment (e.g., centrifugal pumps, compressors, etc.), the discharge pressure must be monitored regularly. A fall in the pressure indicates an abnormality in the equipment, such as a loose impeller, broken shaft, etc., which can also cause a sharp reduction in amperage of a motor. There is also a probability of increase in internal clearances leading to internal circulation of fluid. Blockage of suction strainers causes reduction in flow and discharge pressure and results in starvation and abnormal noise.

16.2.8.3 NOISE

Noise is another parameter that can indicate the health of any equipment. In normal circumstances, there is an acceptable level of noise in the equipment that is defined when the equipment is purchased. When the equipment remains in operation, generally noise remains more or less at the same level, but in the case of an abnormality, the noise gradually increases and goes to a level that is unacceptable. This is an indication that the equipment requires a thorough check. Generally 80 db of noise 1 m from the center of the equipment is acceptable unless stated otherwise.

16.2.9 Motor Current Monitoring

Regular monitoring of motor current is another tool that helps in detecting mechanical and electrical problems in motors or motor-driven equipment. The motor (acting as transducer) senses mechanical load variation and converts it into electrical current variation. The variation in current is reflective of machine condition. Analysis of these variations can provide an early warning of machine deterioration.

16.2.10 Need for Reliability

Reliability in equipment is envisaged and built right from the time it is conceived, designed, manufactured, operated, and maintained. Needless to say, even the best operation and maintenance practices cannot bring in reliability if there is a basic flaw in the design. Therefore, it is essential that all efforts must be put in place at each stage so that less effort is required during day-to-day activities and attention can be paid to further development and improvement in the equipment.

All equipment in a plant is generally divided into four categories: (1) supercritical, (2) critical, (3) semicritical, and (4) noncritical. Supercritical equipment is defined as that for which an outage will lead to a stoppage of the plant, thus affecting operation of a particular plant as well as other plants on the upstream and downstream side. Such equipment is very costly and does not have standby such as turbogenerator sets, centrifugal compressors, etc.

Critical equipment is that for which failure affects the production of the plant in terms of throughput and quality of output. This equipment is essential for plant operation and should not be allowed to go down unscheduled. Outage of critical equipment brings undue pressure on the maintenance and operation teams, resulting in urgency and higher cost of maintenance. Hence, it is important that critical equipment receives special attention when planning predictive or preventive maintenance as well as daily vigil regarding its health. The required spares should be neatly maintained for easy accessibility.

Semicritical equipment is that for which breakdown does not directly affect plant operations, quality of production, or jeopardize safety of man and machine. This class of equipment just needs care, and its frequency of vibration measurement is slightly less than that of critical equipment.

Noncritical equipment is equipment that does not affect plant operations, quality of product, or safety of man and machine. This type of equipment requires the least attention.

16.2.11 Factors and Methods of Improving Equipment Reliability

The basic objective of maintenance function is to improve the reliability of a plant at minimal cost. Reliability can be improved by various means, but the major contributors to improve reliability are

- The use of trained personal that have an extensive knowledge of the equipment,
- The proper design and selection of equipment depending on its intended use,
- Operating equipment within its designed parameters, and
- Regular and effective maintenance of equipment considering all aspects as recommended by the manufacturers.

It is highly desirable for the people who operate and maintain the equipment to be fully educated and trained for all of its features such as design details and limitation of equipment. While the equipment is in operation, regular checks must be performed and constant vigil must be maintained for any abnormality. The level and condition of lubricant, sound level, operating parameters, etc., should be checked and recorded. Reasons must be established for any abnormality and, if required, equipment should be stopped for checking and corrective action taken. No effort should be made to alter the basic design features of the equipment without consulting the manufacturer.

The performance of equipment greatly depends on whether the right equipment has been selected for the intended use and whether the conditions prevalent during operation have been considered while designing the equipment. To understand the problem, let us consider a case. Suppose a centrifugal pump is required for the pumping of sewage, which generally has a lot of foreign material. If a conventional centrifugal pump with closed impeller is selected for this service, it may not function as designed. Because the liquid to be handled contains foreign material, which is likely to choke or clog the pump, an open or semiopen type of impeller should be selected that will not cause chokage of the impeller. Similarly, if a very hot or very cold liquid needs to be handled, the metallurgy of the equipment should be selected accordingly.

There are ample reasons for nonperformance of equipment, which is generally caused by an incorrect selection of equipment. In many cases there is change in the specification from when the equipment was purchased and actually put into service. Hence, whenever the equipment fails to operate as desired, one must check the design parameters vis-à-vis the operating parameters before initiating any corrective action.

It is also essential to keep the equipment as close to the original condition as possible by way of regular maintenance, including replacement of worn-out parts. The recommended maintenance schedule and procedure should be strictly followed to get the optimal performance and life of the equipment. It has been found that there is generally a tendency to postpone scheduled maintenance if the equipment is functioning normally. This can lead to gradual deterioration and breakdown of the equipment.

16.2.12 Failure Analysis Techniques

To minimize failures, it is very essential to diagnose the root cause of failure and take corrective actions to eliminate the same. Breakdowns are generally caused by the combined effects of several so-called minor defects. Some of the statistical tools that are used to perform detailed failure analysis are why-why analysis, a fish-bone diagram, Pareto charts, and failure mode effects analysis (FMEA) charts. Of these four statistical tools, the first three are the basic methods to identify and eliminate the root cause of failure and do not need explanation. However, FMEA is a comparatively newer technique and is explained as follows.

FMEA and failure mode effects and critical analysis (FMECA) are methodologies designed to identify potential failure modes for a product or a process to assess the risks associated with those failure modes to rank the issues in terms of their importance and to identify and perform corrective actions to address the most serious concerns. The function of an asset or equipment is described as the level of performance expected out of it as designed by its designer. In general, FMEA/FMECA requires identification of the following basic information:

- Environment integrity
- Safety/structural integrity
- Control/containment/comfort
- Appearance

- Protection
- Economy/efficiency
- Superfluous functions.

There are different modes when a failure may occur in equipment or an asset. Some of the common failure modes in rotating equipment are

- Bearing seizure
- Suction line chokage
- Lube oil leak
- Excess load
- Low discharge flow
- Low discharge pressure
- Worn-out wear rings
- Broken spring
- Bad insulation
- Sheared coupling
- Impeller jam
- Motor burnt

The failure effects describe the result of failure. The following steps may be recorded while describing the effect of a failure to establish a proactive maintenance strategy:

- Evidence that failure has occurred
- The threat it poses to safety and environment
- The way it affects the operation and quality of products
- Physical damage caused by failure
- The impact of failure on the overall operating cost in addition to direct repair cost
- The secondary damage, if any, caused by the failure
- Action plan to repair the failure.

16.2.13 Maintenance Performance Indicators

Maintenance performance indicators evaluate the performance of a plant in managing the maintenance systems. The following are the criteria to measure the performance of equipment:

- Mean time between failure (MTBF)—reliability
- Mean time to repair (MTTR)—maintainability
- Overall process effectiveness (OPE)—multiplication of availability, equipment performance efficiency, and operational efficiency.

Equipment performance measures are defined as

- *Reliability (MTBF):* Reliability is the measure of the frequency of downtime or the mean time between failures

$$MTBF = \frac{Total\ operation\ time}{Number\ of\ failures} \tag{16.1}$$

Maintainability: Maintainability is the measure of the ability to make equipment available after its failure, or the average time taken for its repair. It is determined by dividing the total downtime by the number of failures of a particular equipment.

$$MTBF = \frac{Total\ downtime\ of\ failure}{Number\ of\ failures} \tag{16.2}$$

- *Overall process effectiveness (OPE):* OPE is the multiplication of availability, equipment performance efficiency, and operational efficiency. The three factors mentioned herein are defined as

1. *Availability:* A measure of uptime as well as the duration of downtime:

$$Availability = \frac{Schedule\ time - all\ planned\ delays}{Schedule\ time} \tag{16.3}$$

2. *Equipment performance efficiency:* A measure of equipment condition to deliver the designed output:

$$EPE = \frac{Maximum\ available\ capacity}{Design\ capacity} \tag{16.4}$$

3. *Operational efficiency (OE):* A measure of the utilization of equipment:

$$OE = \frac{Actual\ capacity}{Maximum\ available\ capacity} \tag{16.5}$$

Maintenance effectiveness measures are

- Compliance of PM/PDM schedule
- Planning efficiency (*Planned jobs/Total jobs*)
- Compliance of work orders generated (*Completed orders/Notification generated*)
- Maintenance quality performance measures [(*Total jobs – Repeat jobs*)/*Total jobs*]
- Maintenance cost measures such as actual maintenance cost vis-à-vis benchmark cost.

16.2.14 Rotating Equipment Alignment

In a hydrocarbon industry in which there is extensive deployment of rotating equipment such as pumps, compressors, fans, blowers, etc., it is very important to have the best possible alignment of two rotating pieces of equipment such as a pump and motor assembly. Shaft alignment is the positioning of rotational centers of two or more shafts such that they are in one line when the equipment is in operation. Proper shaft alignment is indicated by proper centers of rotation of the shaft-supporting members, such as bearings.

There are generally two basic types of misalignment: offset and angular. In the case of offset misalignment, shafts of two machines are parallel to each other but their shaft center is not in the same line. In angular misalignment, the shaft center lines of both machines are not parallel to each other but form an angle. Misalignment primarily causes vibration in the machine, which may lead to failure of the machine, but there are other associated disadvantages of misalignment such as

- Increased energy loss.
- Increased load on bearings, seals, and other mechanical components
- Reduced productivity
- Reduced product quality
- Undesirable noise
- Unsafe operating conditions
- Reduced equipment life.

Misalignment is the most common cause of rotary equipment failure, and it may be present when the machine is installed or it may develop during operation. Vibration analysis of rotary equipment helps to provide an initial indication if the misalignment has developed in the rotary equipment. To minimize such phenomena, it is essential to check and correct misalignment when the equipment is planned for preventive maintenance.

16.2.14.1 ALIGNMENT PROCEDURES

There are many ways of performing alignment of equipment, which primarily depends on the criticality of equipment and the comfort level of equipment users. The following are the methods generally followed for aligning equipment:

- Straight-edge method
- Rim and face method
- Reverse dial method
- Laser beam method.

The plane where the prime mover meets the equipment to be moved is important. This is the plane, also known as the power plane, where the equipment should be checked for misalignment. Because the equipment such as pumps/compressors are the fixed assembly, correction is generally made at the feet of the motor, which do not have rigid connections. The positions at the feet must be calculated to be able to make correct movements. This is the most important factor, as well as the skill of the person involved in performing the alignment to achieve the desired result in the shortest possible time. In all of the methods readings are taken at shafts or couplings and corrections are made at the machine feet.

16.2.14.2 STRAIGHT-EDGE METHOD

In the straight-edge method, the offset is measured using a straight edge and a set of feeler gages (Figure 16.1).

First, the offset is measured as depicted in Figure 16.1. Angular misalignment is measured by using a feeler gage, taper gage, calipers, etc. The gap difference between two points 180° apart (Figure 16.2) is used to determine the direction and amount of relative slope between the shafts.

However, this method is no longer in use because of a lack of precision and because it is more dependent on the skill of the person involved in alignment.

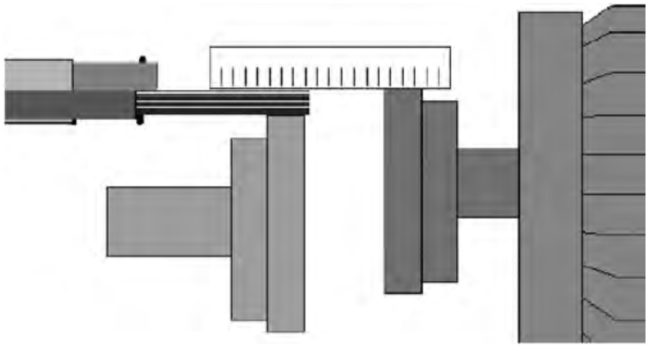


Figure 16.1—Measure offset misalignment.

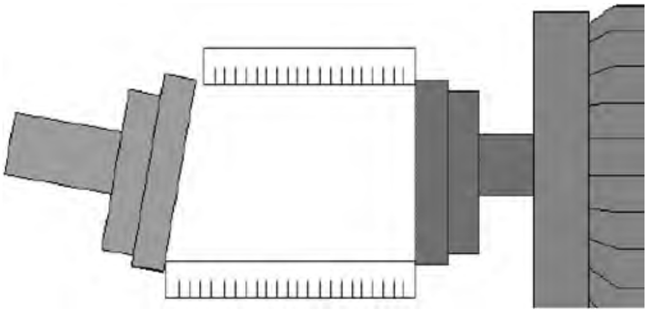


Figure 16.2—Measure angular misalignment.

16.2.14.3 RIM AND FACE METHOD

The rim and face method is an improvement over the straight-edge method and is able to measure more accurately. This method has been in use for quite some time. In this method, one reading is taken on the rim of the coupling and the other reading is taken on the face of the coupling (Figure 16.3). Both dial gages are fixed on the shaft of the fixed machine (i.e., a pump) and readings of dial gages are taken on the movable machine (i.e., a motor). Shafts of both machines are rotated together and readings are observed on both the dial gages after rotating the shafts simultaneously by 90°, 180°, 270° and 360°. Metal shims of suitable thickness are provided to achieve acceptable readings on dial gages in all four positions.

The main limitations of these methods are

- The sag of the bar limit distance over which the techniques can be applied.
- The construction of coupling sometimes prevents access to the face.
- Correction is a multistage process, i.e., first eliminating parallelism error and then rectifying concentricity.
- Re-measuring is required at each stage to see the effects of the corrections made.
- Axial movements of the shafts directly affect the result.

16.2.14.4 REVERSE RIM METHOD

In this method, two measurements are taken on the rims of the coupling to determine the shaft offset at two points (Figure 16.4). The two shafts are rotated simultaneously or,

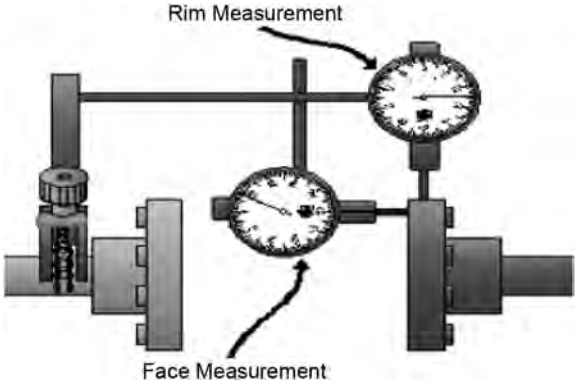


Figure 16.3—Rim and face alignment method.

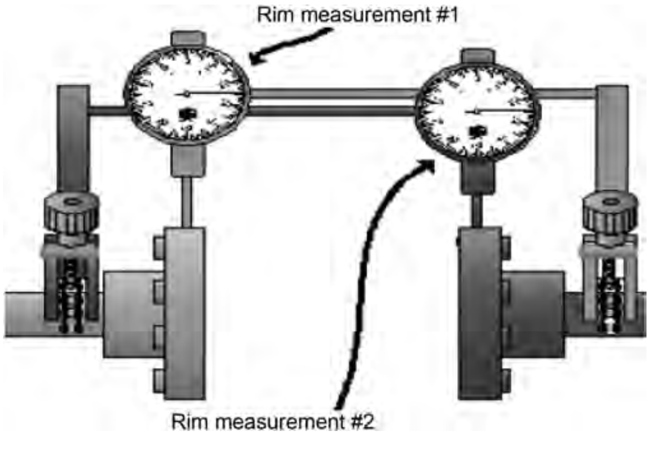


Figure 16.4—Reverse rim alignment method.

Source (Figures 16.1–16.7): Maurya, S.L., Ghosh, A., Paranjape, D.B., and Kacker R., "Indian Oil's Reliability Improvement Report (Refineries Division)," Indian Oil Corporation Ltd., New Delhi, India, 2005.

in some cases, the measurement is done in two stages with measurement taken from one clock but switching positions. Shaft angularity is the slope between the two offset measurement points.

The main advantages are that it gives both offset and angle at the same time and provides for easy calculation and plotting of alignment and corrections. Increasing the distance between measuring points can increase the resolution of the angle. However, this may not be practical with clock gages because the sag of the bar requires compensation.

16.2.14.5 LASER BEAM METHOD

Instead of steel bars and dial gages, this method uses laser beams and electronic defectors. Major advantages of this method are that there is no loss in measurement accuracy due to bar sag. The system includes a laser transmitter, a detector, and a computer that performs alignment calculations.

There are two common types of laser alignment systems available: (1) the single laser with a single target and (2) the twin laser using the reverse indicator technique. The single laser with a single or double target uses autocollimation to measure offset and angle with reflective prism (Figure 16.5). The target simultaneously measures vertical and horizontal components together with the angle.

This method is accurate in angular measurement over a short distance, but it is less easy to use for rough alignment. It cannot distinguish a side-to-side movement by itself or the independent rotation of each shaft. To overcome this limitation, a way to couple the shaft to rotate in unison is required.

The twin laser reverse indication technique has the major benefits of the reverse indicator method. Two measurement systems are used with a laser and detector in each unit (Figure 16.6 and 16.7). This technique is used to display real-time alignment and continually updated corrections as the machine is moved.

The flexibility of the system comes in handy especially in rough alignment when aligning over long-distance cardan shafts or cooling tower fan drives.

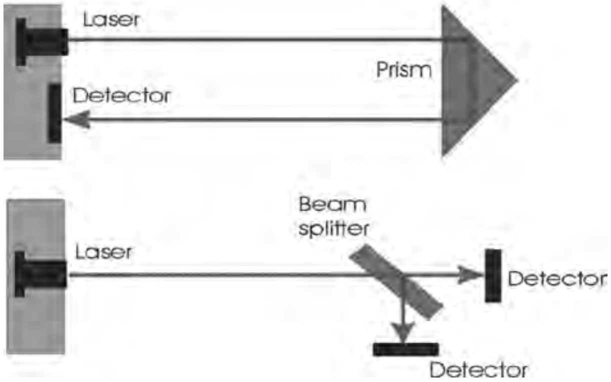


Figure 16.5—Laser beam alignment.

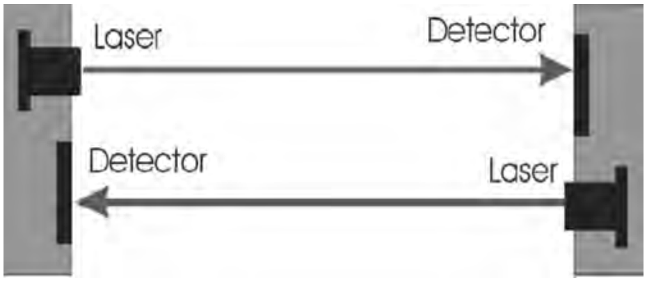


Figure 16.6—Twin laser reverse indication method.

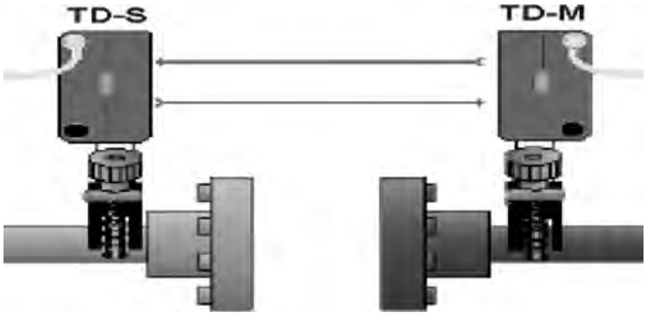


Figure 16.7—Twin laser using the reverse indictor technique.

16.2.15 Important Tools Used in Refineries

With the developments in the field of mechanical engineering and the continuous requirement of high-quality maintenance work, several tools and gadgets have been brought up by various companies that provide safety and quality in the field of maintenance. Some of the important gadgets that are essential and used in day-to-day work are as follows.

- *Flange spreaders:* This tool provides a simple solution for separating matching flanges whenever there is a need to provide a spade or replacing the gaskets in a flange joint. This tool is a hydraulic device and uniformly spreads the flange without use of any impacting device, which may be a source of spark and fire. The movement of the flange spreader is controlled by application of the input force. The device avoids any kind of damage that is sometimes caused to the gasket seating face.
- *Hydraulic torque wrenches:* Hydraulic torque wrenches and console represent the most advanced technology available for bolting purposes. This technique imparts uniform and measured torque on each bolt. The pressure from the hydraulic console powers the hydraulic torque wrench to ratchet with a push of the power console button, thus loosening or tightening the nut faster. Depending on the size of the nut and the pressure it requires to contain pressure, suitable torque is applied to each bolt of the joint.
- *Bolt tensioners:* Application of hydraulics has allowed us to design both loading systems instead of relying on the inherent hit or miss inclined plane and layer (elongation and torque) system. Designed bolt loads can be achieved by using these modern solutions. By applying a predetermined hydraulic pressure to the load cell of the bolt tensioners, the bolt will get stretched along its axis. Bolt tensioners are generally used in a high-pressure system in which precise torque application is essential for making leak-proof joints.
- *Hydraulic nut splitter:* Sometimes old flange joints must be opened after many years of operation, when the nut has seized because of application of higher torque or

because antiseize compounds have not been applied: therefore the nuts become difficult to open and pose a hazard if forcefully opened. Hydraulic nut splitters are a handy tool on such occasions. The device cuts through the larger sizes of seized nuts with no risk of injury or accident. The heads of the splitter along with a cutting tool is placed on the nut, and hydraulic pressure is applied to drive the wedge into the flat side of the nut and cut it.

16.2.16 Tools and Pullers for Mounting/Dismounting of Bearing/Couplings

Premature bearing failures can result because of improper mounting. Such failure can typically result in

- Damage caused during the fitting procedure
- Incorrect size of shafts and housing (i.e., too tight or too loose)
- Retainer lock nuts loosening during operation
- Burred and damaged shaft and housing seals
- Incorrectly mounted bearing.

Tools and pullers designed for mounting/dismounting of bearing/couplings include

- *Induction heaters:* The force required to mount a bearing increases with bearing size. Also, the fits required for mounting of a bearing on a shaft or into housing prevent easy installation. Therefore, the bearings or couplings need to be heated uniformly. Induction heater or electric plates are used for this purpose. Sometimes using hot oil baths also fulfills this objective.
- *Mechanical or hydraulic pullers:* A wide range of pullers for mechanical dismounting of bearings and couplings are available. These pullers facilitate easy dismounting without much effort and without any damage to main equipment.
- *Bearing fitting tool kit:* Bearing fitting tool kits are available and are designed for quick and precise mounting of bearings, which minimizes the risk of bearing damage. The right combination of impact ring and sleeve allows for effective transmission of mounting force to the bearing ring without damaging the bearing raceways or rolling elements. The kit contains various sizes of impact rings, impact sleeves, and a lead-blow hammer.

16.2.17 Shutdown Maintenance

In the refinery, it is not possible to monitor the health of all equipment while the plant is in operation. Although various techniques have been developed to monitor the external health of equipment, assessment of internal equipment conditions requires stoppage. Small- to medium-sized rotary equipment that has a standby can be inspected while the plant is in operation, but major equipment such as furnaces, tanks, columns, vessels, centrifugal compressors and turbines, etc., requires shutting down of the plant at a defined schedule. The shutdown facilitates access to all such equipment for inspection and repair purposes.

16.2.17.1 SHUTDOWN FREQUENCY

Shutdown frequencies of a plant are decided based on the following aspects:

- Statutory requirements
- Repair/replacement of the equipment/piping requiring plant shutdown
- Health assessment of the equipment for remaining life assessment, which cannot be done during operations
- Plant reliability-related issues/operational modifications/catalyst changes, etc.

To minimize the duration of shutdown, several preparatory actions such as procurement, fabrication, arrangement of resources, etc., are taken well in advance. All activities related to shutdown maintenance can be divided into preshutdown activities, shutdown activities, and postshutdown activities.

16.2.17.1.1 Preshutdown Actions

Shutdowns are planned well in advance so that all preparatory actions are initiated and resources are arranged. The shutdown calendar is prepared for all of the units on the basis of their frequencies, and the schedule is updated on a yearly basis. At least 1 year in advance the shutdown job list is prepared by taking feedback from all departments. The list comprises

- Inspection recommendations
- Maintenance (mechanical/electrical/instrumentation/civil) related activities
- Operation/production requirements
- Process modifications for improvements in operations and safety
- Projects and modifications activities
- Materials and infrastructure required for timely and safe completions of shutdown
- Other miscellaneous activities

On the basis of requirements and the time required for arrangement of all such materials/infrastructure/agency line-up/chemicals and catalyst procurement, etc., necessary actions are taken to facilitate all requirements at the site of activities of the unit. Prior to shutdown, meetings with all concerned departments are also arranged from time to time to avoid any lapses in preparatory activities.

Maintenance planning plays a major role for the fulfillment of all shutdown requirements and timely completion of the shutdown. In certain cases there is requirement of generating “end of run” data at various places in the unit. The same data are recorded before shutdown to compare them with postshutdown operating conditions. It is important to have a shutdown organogram showing detailed responsibilities for each person. All of the heavy and safety equipment should be tested and tagged before use. This is done before shutdown.

Maintenance planning prepares a detailed plan with a break-up of each activity along with estimated time and resources during the shutdown. This helps in identifying activities and resources required on a particular day and helps in minimizing idling of resources or overlapping of activities. Primavera or Microsoft project software are generally used for scheduling of activities and allocation of resources.

16.2.17.1.2 Shutdown

Unit shutdown is taken under close coordination with the operations, maintenance (civil/mechanical/electrical/instrumentations), and safety and process departments. When various activities related to shutdown are undertaken, maintenance support is kept informed to avoid any time loss. Once the plant is safely shut down, all of the equipment and piping circuits are flushed and made free of hydrocarbons. Clearances/work permits are issued to maintenance support functions. Once the gas/hydrocarbon-free equipment is handed over to maintenance, the following activities are performed:

- Isolation of the equipment by providing spades at the nearest flange joint.
- Opening the manhole covers to check for the presence of hydrocarbons/gas. If found so, allow it to be gas-free/cooled down.
- Providing safe lights for work inside of the equipment, along with access, if required.
- Cleaning the equipment of all foreign material and its removal wherever required.
- Offering the equipment for inspection.
- Performing inspection/detailed investigation of the equipment.
- Recommendations by inspection for any repairs to be undertaken.
- Performing repairs as recommended and getting certified from inspection authorities.
- Performing hydraulic or pneumatic test of equipment, if required.
- Taking clearance from operating department before closing of the manhole.
- Removal of spades from the flange joints provided for isolation after obtaining clearance from the operating department.

During shutdown, progress is reviewed regularly (preferably twice in a day—one with management and another with working supervisors in the shutdown), which helps in redeploying resources, if required, as well as identifying areas of concern. Safety is always assigned top priority. Independent safety officers continuously look for any unsafe activities and report instantly to authorities for corrective measures. A daily progress report is prepared to keep key personnel updated. Spares and material are made available on short notice on an around-the-clock basis. Efforts are made to maintain the schedule by working around the clock for critical jobs and at least 14–16 h of work for less critical activities. All personnel involved in shutdown are briefed about safety in advance so that the lapses do not occur. Use of safety appliances and gadgets should be used by all personal entering a "hard-hat" area.

The following are some tools/gadgets used during shutdown to reduce duration of shutdown as well as to obtain quality output (see Figures 16.8–16.10 in Appendix 18):

- Bolt tensioners
- Torque wrenches
- Nut splitters
- Flange spreaders
- Portable lift for high-rise towers
- Scissor lift to access overhead piping, etc.
- Gamma ray scanners
- Dehumidifiers
- High-pressure hydro jet clearing machine
- Tube extractors
- Plasma cutting machine
- Diamond cutting tools
- Kit of hydrokinetic technology (for clearing of heavily fouled heater, heat exchange tubes)
- Kit for DDT (decoking decaling technology) for mechanical cleaning of furnace tubes.

16.2.17.1.3 Postshutdown Actions

After the shutdown of a plant is completed and the unit is commissioned satisfactorily, a review and analysis on the activities performed during shutdown is made to find the scope of further improvement. The activities that were planned but could not be performed and the activities that were not planned but needed to be completed are analyzed and planned for corrective actions. The leftover jobs in the shutdown are also reviewed and planned for early compliance. This list is also known as the "zero-hour jobs list." On the basis of this job list, if any long-term actions are required, actions are initiated to ensure availability of the required materials in time.

16.3 ELECTRICAL SYSTEMS

The electrical power system is the lifeline of any industrial plant. Good design, proper installation, quality assurance, and sound operating and maintenance practices provide the basic foundation for reliable and safe operation of electrical power systems. The expected reliable and safe performance of an electrical power system is dependent on the following fundamental elements:

- Reliability and safety considerations in system design, including maintenance, operation, and safety aspects
- Maintenance and operation strategy to ensure long-term reliability and safety
  - Development of recordkeeping and documentation systems
  - Development and implementation of testing and inspection methods
  - Development of procedures to ensure personnel safety
  - Development of procedures of auditing maintenance and operation performance
- The recommended practices provide constructive guidance on the requirements considered essential for assessing the integrity of an electrical system/equipment.

16.3.1 Essential Reliability Requirements in Electrical System for Reliability

To establish a highly reliable electrical system, the design of the system should ensure that a single failure will not cause interruption. Various factors of reliability are related to man, machine, and management as follows:

- *Man:* Education and training
- *Machine:*
  - Establishment of strong facilities for zero interruption
  - Well-designed and constructed facilities to avoid failures
  - Individual facility reliability
- *Management:*
  - Cooperation of sections
  - Facility management system (i.e., standards, manuals, diagnosis, etc.)

16.3.2 Inspection and Maintenance Practices for Electrical Equipment System

In view of the large variety of electrical equipment in the refinery electrical system, the practices considered and indicated are those that are essential for assessing equipment and systems integrity from which more specific requirements are to be developed by the site engineers.

16.3.2.1 GENERAL PRACTICES/REQUIREMENTS

- All fixed installations and temporarily fixed installations should be clearly and permanently identified.
- A register should be compiled of all equipment requiring regular test and inspection. Each item should be uniquely identified (tagged).
- A register of distribution system "fault levels," including calculations, should be maintained.
- For each plant, a dossier containing all relevant data for equipment should be compiled.
- For each circuit and component part, test and inspection programs, which include procedures, outlining the extent and frequency should be prepared.
- Safety rules and "permit to work" systems should be applied before any work is undertaken on electrical equipment.
- A permanent record should be established for all items/circuits to be regularly tested/inspected. The system should contain a permanent operational history including details of faults, repairs, modifications, and the results of tests and inspections performed.

16.3.2.2 INSPECTION PRACTICES/REQUIREMENTS

- Scheduled thorough examinations (on a routine or planned basis) to identify those problems more likely to occur as a consequence of age, severity of duty, and environmental condition
- Intermediate inspections (i.e., intrusive visual inspection to assess the general condition of enclosures and interconnecting systems)
- The frequencies should be derived based on factors such as
  - Legislative regulations, if any
  - International/national codes and standards
  - Manufacturer recommendations
  - Severity of duty
  - Deterioration rates
  - Consequences of failure
  - Availability of redundant feeders/systems and the specific requirements of the process units
  - Environmental conditions
  - Possibility of inadvertent damage
  - Associated equipment's scheduled examinations (e.g., pumps in the case of motors)
  - Unit turnaround

16.3.2.3 CONDITION MONITORING PRACTICES

Specific methods that need to be practiced and are relevant to the operation of electrical equipment include

- Thermography, for identifying the condition of electrical connections (e.g., busbar connections/breaker jaw contacts)
- Vibration analysis for assessing bearing condition
- Noise analysis (partial discharge) for assessing the condition of the switchgear
- Oil analysis for monitoring the condition of transformer windings and phase current analysis for examining motor stator and rotor condition

16.3.3 Electrical Equipment/Systems

16.3.3.1 SWITCHGEAR AND STARTERS

The practices indicated below are applicable to LV/MV switchgears from simple isolators to VCBs, starters including the associated auxiliary devices, and the interconnecting circuits.

The switchgear structure and connections should be given the following overall maintenance. All maintenance work should be performed with the primary and control power circuits de-energized.

- Thorough cleaning of the equipment (panel, busbars, and circuit breakers), preferably using a heavy-duty vacuum cleaner to remove all dust and other accumulations.
- Checking and cleaning circuit breaker-racking mechanism and lubrication of jackscrews and gears with lubricant.
- Checking of primary disconnecting device contacts for signs of abnormal wear or overheating. Discolorations of the silvered surfaces are not normally harmful unless an atmospheric condition causes deposits such as sulfides on the contacts. If necessary, deposits should be removed with a good grade of silver polish and a thin coat of contact lubricant should be applied.
- Checking tightness and continuity of all control connections and wirings.
- Insulation systems must be inspected closely for signs of overheating, cracking, tracking, and other defects. Insulation strength tests must be performed in accordance with the IEEE guidelines.
- Inspection of the main contactors for excessive wear and overheating must be undertaken and the mechanisms checked for freedom of movement. It is important that manufacturer manuals are referenced for equipment-specific detailed instructions.
- All terminals should be checked for firmness and signs of overheating.
- Power and control cables should be examined together with the connected equipment.
- The accuracy of protective devices should be checked against manufacturer's characteristics and the recorded set points should be verified. For this purpose, low-voltage secondary injection will be necessary. Primary injection should be performed during unit turnaround, when there has been some dismantling of the primary/secondary circuits on current transformers, or when maloperation is suspected.
- Fuse type and ratings should be checked against design specification and records.
- The correct functionality of control/protection/indication/interlocks/intertripping circuits should be checked against the relevant schematic diagrams as part of the inspection program. In addition to the examination checks, trip and closure controls should be operated wherever practicable at least once a year.
- Earthing conductors should be inspected and continuity assessed. All terminations must be checked for firmness.
- Circuit breaker shutters and locking mechanisms should be checked for freedom of movement and correct function with the inhibiting mechanical and electrical interlocks proven.
- Many types of switchgears are used in widely varying conditions. The frequency for examinations can be expected to vary from one site to another. A 2- to 3-year interval of inspection is desirable on the basis of the process unit run length. More frequent intervals (annually) are required for equipment having onerous

duties (e.g., motor starters subjected to frequent stop/starting, duplicate transformer and radial feeder having redundancy).

16.3.3.2 BUSBARS

- A busbar system will require isolation, which can often affect the operating units. Therefore, their examination is normally performed during plant turnaround or after a severe fault fed by the system.
- Covers should be removed and the busbars and connections should be checked for evidence of overheating or weakening of the insulation.
- All bus mounting bolts and splice connection bolts should be checked for tightness.
- After cleaning, megger and record the resistance to ground and between phases of the insulation of buses and connections. Because definite limits cannot be given for satisfactory insulation resistance values, a record should be kept of the reading. Weakening of the insulation from one maintenance period to the next can be recognized from the recorded readings. For MV systems with 2.5-kV megger, the desirable value should be above 5000 Mó.
- Bus-zone protection CTs should be examined as part of the busbar examination. Relay operability should be verified by primary injection and the trip setting proven.

16.3.3.3 CABLES AND ACCESSORIES

- Insulation resistance tests between cores and from cores to earth should be performed on all power and control cables.
- Terminals should be examined for signs of overheating and confirmation of soundness.
- Glands should be examined to confirm mechanical condition and the electrical integrity of the earth continuity where appropriate. Glands fitted to equipment in hazardous areas must be checked and their suitability to the hazard zone confirmed
- The examination of cables may be subject to scheduled inspection on an individual basis. However, it is a more appropriate and acceptable practice to include cable examinations as part of the connected equipment's examination schedule.

16.3.3.4 POWER/DISTRIBUTION TRANSFORMERS

- Inspections of transformers should be made on a regular basis. The frequency of inspection should be based on the importance of the transformer, the operating environment, and the severity of the loading conditions. Typical regular inspection data can include load current, voltage, liquid level, liquid temperature, winding hot-spot temperature, ambient temperature, leaks, and general conditions.
- Load currents are a very important part of the recommended regular inspections. If the observed current in any phase exceeds the rated full-load value, and the rated maximal temperature is exceeded, steps should be taken to reduce the load.
- Overvoltages and undervoltages can be detrimental to the transformer and the load it serves. The cause should be investigated immediately and corrective action should be taken to bring the voltage within acceptable limits.
- Transformers are rated to carry their nameplate load in kilovolt-amperes/megavolt-amperes with a given heat rise when the ambient temperature is at a standard level. Exact values are stated on the nameplate.
- Temperature gages and readings should be regularly taken and recorded. If the gage is also equipped with a maximum temperature indicator, readings from both indicators should be recorded and the maximal temperature indicator should be reset. Excessive temperature indicates an overload or perhaps some interference with the normal means of cooling.
- The liquid level should be checked regularly, especially after a long period of low load at low ambient temperature when the level should be at its lowest point. It is important that liquid be added before the level falls below the sight glass or bottom reading of the indicator.
- Pressure/vacuum gages are commonly found on sealed-type transformers and are valuable indicators of the integrity of the sealed construction. The readings should be compared to the recommendations of the manufacturer as to the normal operating ranges.
- All connections should be inspected for signs of overheating and corrosion. Insulators and the insulating surfaces of bushings should be inspected for tracking, cracks, or chipped skirts, and the gasketed bases should be inspected for leaks. The insulating surfaces should be cleaned of any surface contamination. Damaged insulators or bushings should be replaced. Leaks should be repaired. Pressure-relief devices should be inspected to ensure that there are no leaks or corrosion and that the diaphragm or other pressure relief device is intact and ready to function. A cracked or leaking diaphragm should be replaced at once.
- The tank, cooling fins, tubes, radiators, tap changer, and all gasketed or other openings should be inspected for leaks, deposits of dirt, or corrosion. Leak repair, cleaning, and painting should be done as required. Infrared inspection can be used to detect fluid levels as well as flow restrictions in cooling tubes.
- The tank ground should be inspected for corrosion or loose connections. A grounding electrode resistance test should be made.
- The conservator tank, inert gas atmosphere, and dehydrating breather equipment should be inspected and tested according to the manufacturer's instructions.
- If liquid is to be added, it should be given a dielectric breakdown test. The liquid to be added should be at least as warm as the liquid in the transformers.
- In addition to the primary and secondary insulation tests, an additional insulation test must be performed between the primary and secondary windings at the same test voltage as the low voltage side. For safety reasons the winding not under test must be earthed.
- For a conservator type oil insulated transformer, insulating oils should be sampled and subjected to a water content and strength test. Oil levels must be checked and breather silica-gel changed as required.
- Gas analysis of large transformers is to be performed on critical duties to give an early indication of incipient winding failure. The frequency can vary from 1 to 3 years depending on the criticality, loading, etc.
- Tap changers should be examined for signs of overheating and their operating mechanisms should be checked.

- Buchholz relays should be tested and the trip and alarm functions proven. Oil and winding temperature indicators must also be inspected and calibrated.
- Fans/pumps and their drivers must be examined as part of the transformer program and in accordance with the motor and switchgear inspection and maintenance requirements.
- Transformer frame and neutral earthing must be closely examined with the mechanical and electrical integrity assessed.
- Because transformers are normally very reliable, examinations need only be performed at intervals on the order of 3–4 years. However, nonintrusive intermediate inspections including oil sampling tests should be performed at more frequent intervals (e.g., annually).

16.3.3.5 ROTATING ELECTRICAL MACHINES

The various classes of rotating equipment have many common features in routine maintenance (i.e., electrical and mechanical). The practices indicated are of a general nature and are not intended to cover special applications.

- Evidence of dirt, dust, moisture, oil, and grease on the winding should be noted, and the winding should be cleaned thoroughly with the solvent solution. After a major cleaning, a drying process is to be done to restore the insulation to a safe level for operation.
- Insulation systems must be periodically strength tested in line with IEEE 43 recommendations. For machines online of voltages greater than 440 V, where low insulation values are apparent, a polarization index test should be performed and the extent of deterioration since the last test should be evaluated.
- Phase current analysis is an additional technique that may be considered as a noninvasive alternative to dielectric loss analysis (DLA) or partial discharge analysis (PDA).
- On HV machines, during machine overhaul, the condition of windings including wedges and overhangs must be established.
- The terminals and cable/winding tails must be examined for signs of overheating and the soundness of the terminals must be confirmed. The condition of terminal boxes, cables, and glands must also be examined.
- Compliance checks should be performed in accordance with requirements for equipment in hazardous areas.
- Bearings should be subject to monitoring in accordance with the site's condition monitoring policy. External inspection at the time of greasing will determine whether the bearings are operating quietly and without undue heating.
- The bearing housings can be opened to check the condition of bearing and the grease as per the vibration analysis results. The bearing and housing part should be thoroughly cleaned and new grease should be added. Standard greasing practices should be strictly adhered to as per manufacturer recommendations.
- The general condition of the frames must be inspected with particular attention being given to the fan and couplings.
- Cooling systems must be examined to ensure airways and filters are free from debris and obstructions. Anticondensation heater insulation and continuity must be tested and the control function proven.
- Earthing bonds must be examined to confirm mechanical and electrical integrity.
- Where protection CTs are accessible, they must be examined and the soundness of the terminations checked.
- All machines should be subject to nonintrusive inspection at more frequent intervals to confirm the integrity of the machine's external condition and compliance with Ex-certification. During normal operation, visual and physical monitoring of parameters such as temperature, sound, and load current should be performed to enable identified potential abnormalities.

16.3.3.6 FIXED LIGHTING INSTALLATIONS

In process plants, the light fittings and circuit cables are exposed to inadvertent damage in addition to general deterioration due to age and environmental conditions. To ensure their integrity, routine inspection is necessary with emphasis on the systems installed in hazardous areas.

- Inspection of luminaries should be included in the lamp-changing programs. Where block lamp-changing programs are undertaken, sampling can be considered.
- The lighting system cables, junction boxes, and control switchgear examinations should also be undertaken during re-lamping.
- Cables must be examined for proper glanding and signs of damage and overheating. Circuit breakers and switches must be examined in accordance with the requirements.
- Luminaries should be examined and their electrical and mechanical integrity should be confirmed.
- Ex-certified equipment must be inspected in accordance with the requirements of hazardous area equipment.
- Emergency fittings provided with integral batteries and associated electronic controllers should be examined in accordance with the requirements of power electronic equipment.
- Where emergency lighting installations are provided as total systems with central batteries and separate cabling and control equipment, the inspection and testing should take into consideration both the components of the system individually and the total operation of the system.

16.3.3.7 EARTHING AND BONDING SYSTEMS

- Earthing bonds attached to all electrical equipment (e.g., switchgear and motors, etc.) must be examined with the mechanical and electrical integrity established.
- Earth electrodes must be closely examined. Where practical, they should be disconnected and the impedance should be measured. *Note:* This may only be performed when plant operating conditions permit.
- Earth nests must be closely examined and the mechanical integrity assessed. Terminations should be broken and inspected to ensure that electrical continuity is not impaired.
- All connections to structures, tanks, vessels, and towers must be closely examined with the electrical and mechanical integrity assessed. Where practical, terminations should be broken and inspected to ensure that continuity is not impaired.

- The earth bonding system to the roof on floating roof tanks should be closely examined and the electrical and mechanical integrity assessed. Where practical, terminations should be broken and inspected to ensure that continuity is assessed. Scraping earths must be closely examined and the integrity of the bonding assessed.
- Neutral earthing resistors must be inspected and the mechanical and electrical integrity confirmed. The resistance must be measured and the value assessed against the design specification.
- When the equipment or any part of the associated circuit is in a hazardous area, care must be taken to ensure that the testing does not in itself create a hazard.
- At loading terminals, flexible-bonding systems should be closely examined with the mechanical and electrical integrity established. Earth monitoring systems must be closely inspected with the functionality of monitoring/interlocks and alarm functions proved.
- The earthing associated with electrical equipment should normally be included in the equipment's routine examination schedule.
- For systems installed in hazardous areas, inspections should be performed at more frequent intervals on the basis of a site's particular circumstances and environment. Typically, for loading gantries, flexible connections may need to be checked at weekly intervals.
- Tank and vessel earthing systems are to be normally included in their respective inspection schedule.

16.3.3.8 PORTABLE AND TRANSPORTABLE ELECTRICAL EQUIPMENT

- All portable equipment including extension leads must be inspected and approved as suitable for the purpose intended. The equipment must be registered and a record maintained of subsequent inspection findings.
- Portable equipment for use in the field (plant) should be tagged with a label that clearly shows when the equipment must be re-examined.
- The plug, sockets, and the operating voltage should be examined to ensure compatibility with the systems onsite.
- For all equipment there must be a careful inspection for signs of damage or deterioration, including, for example, the casing, weatherproof seals, the plug/sockets, terminals, cables, and anchoring devices.
- The special features of certified (Ex-equipment) should be checked for compliance. Certification labels must be firmly attached.
- Transforming equipment must be inspected and its electrical integrity checked. For isolating transformers, the insulation between primary and secondary windings must be verified and the output voltage checked for compliance with factory standards.
- Protective devices where fitted should be tested and their functionality should be confirmed.
- Equipment provided with basic insulation and having an earthed metal frame for protection must have the earth conductor subjected to a substantial current continuity test. The insulation must also be measured. *Note:* For this purpose, a portable appliance tester may be useful.
- Portable generators must have
  - Windings to frame the IR measured
  - Controls examined and functionally tested
  - Protection tested.
- The inspection of welding equipment should ensure that separate earth-free terminals have been provided.
- Portable testing equipment must be regularly inspected and calibrated against standard supplies. This is particularly important for equipment used to test at high voltage (i.e., phasing sticks). Leads used with test equipment must also be closely examined and their electrical and mechanical integrity established.
- As a guide, industrial equipment should be examined on an annual basis.

16.3.3.9 INVERTERS AND CHARGERS/STATIC DEVICES (INCLUSIVE OF BATTERIES)

- Examination in accordance with manufacturer's recommendations, including a proof test of protective devices, electrical integrity checks, and operational functionality, must be performed.
- Nonintrusive inspection shall include a check of any air filter and ventilation fans. Capacitor banks, chokes, transformers, and components generally must be checked for signs of overheating.
- Full examination may, depending on the arrangement, require the system to be taken out of service or put on bypass. This may inconvenience plants or jeopardize reliability of critical supplies. It is therefore common practice to include the full examinations in plant overhaul programs.
- Nonintrusive inspections will depend to a large extent on the local operating and environmental conditions. However, as a general guide, a frequency on the order of 1 year would be appropriate.
- Routine operating checks should be performed on a weekly/monthly basis as per the criticality and environment conditions, with the critical parameters being
  - Checking of input voltage, output voltage, and output current to be within limits
  - Checking of battery trickle charge current
  - Checking of diagnostic alarms and annunciation
  - Checking of abnormal heat and noise
  - Checking status of boost charger "auto mode"
- Periodic inspection of battery banks should be performed for ensuring the health of the batteries. For lead acid/nickel cadmium batteries, the routine visual inspections should include electrolyte levels, cracks in jars, evidence of corrosion at terminals/connectors, ambient temperature, ventilation, etc.
- Back-up battery systems must be regularly inspected and maintained in accordance with the manufacturer recommendations. It is important to ascertain that batteries can continue to support loads for the periods specified. Therefore, load tests (discharge) must be performed and the performance checked against the battery discharge characteristic.

16.3.3.10 VALVE ACTUATORS

- Integral motor and contractor insulation should be tested and inspected for signs of overheating on insulation, terminations, and contacts.
- Control circuits must be verified against schematics. Integral torque and limit switches must be checked for correct settings.

- The condition of the frame and cable glanding must be assessed and the compliance with the Ex-certification must be confirmed.
- Nonintrusive inspection of actuators, including Ex-certification checks, should be performed at a frequency of 2 years. Major examinations, including limit and torque switch checks, should be performed at frequencies on the order of 4 years.

16.3.3.11 HAZARDOUS AREA EQUIPMENT

- The Ex-certification of all components and the methods of installation must be examined for compliance with the classification requirements of the area.
- Enclosures, glasses, seals, gland rotating elements, special flanges, etc., should be examined closely for defects that could impair the Ex-effectiveness.
- Weather proofing systems must be checked and effectiveness established.
- Insulation of the equipment/systems must be measured. Terminations must be proven sound.
- Earth bonds should be checked for soundness and the earth resistance and loop impedance must be measured.
- An electrical apparatus must not be opened in a hazardous area until it has been properly isolated (including the neutral from its source of supply and precautions taken against its reinstatement).
- For pressurized Ex "P" equipment, the special requirements are as follows:
  - Protective gas must be sampled and proven to be free of contaminants.
  - Pressure/flow must be checked for adequacy.
  - Pressure/flow alarms, indicators, and interlocks must be tested and functionally must be checked.
  - Start-up purge cycle equipment must be inspected and tested in accordance with specifications.
  - The condition of ducting must be assessed and alarms must be tested.
  - The condition of pressurized enclosures must be inspected.
- For increased safety (Ex "e") & Type N protection (Ex "n"), the adequacy of motor air gaps and running clearances must be checked along with the condition of gasket healthiness.

16.4 INSTRUMENTATION MAINTENANCE

16.4.1 Objectives

- Higher availability and reliability
- Minimize downtime
- Prevent unscheduled interruption
- Ensure safety of equipment and people
- Minimize effect on environmental pollution.

Maintenance activities are classified into the following categories:

- *Breakdown/corrective maintenance:* Emergency/unscheduled maintenance driven by breakdown/failure.
- *Preventive maintenance:* Scheduled, periodic, fixed-interval maintenance program with thresholds established to indicate when potential problems could happen.
- *Predictive maintenance:* Maintenance program that is based on trend detection through data analysis that gives an insight into likely causes of impending failures. Advanced maintenance action is initiated accordingly, which prevents an impending failure.
- *Shutdown maintenance:* Scheduled, fixed-interval (based on plant shutdown schedule), preventive maintenance plan. Generally used with opportunity for reducing failures.
- *Special repairs:* Comprises modifications, retrofit, redesign/corrective engineering, technology upgrades, software/release upgrades (in conjunction with hardware upgrade, if necessary).

An effective maintenance management should broadly encompass the following:

- Skilled personnel with commensurate technical qualifications/training.
- Availability of special tools and test equipment/facilities.
- Established work procedure and work instructions.
- Careful planning to minimize MTTR.
- Strategies toward increasing mean time between failures (MTBF).
- Effective failure analysis system/procedure, incorporating FMECA.
- Standards for calibration equipment. Standards should be derived from parameters established by the National Bureau of Standards (NBS).
- Realistic (on the basis of experience and OEM recommendations) calibration and test frequencies.
- Use of recommended practices of OEMs on specialized systems/instruments/hardware.
- Coordinate spare parts management ensuring availability in time.
- Perform maintenance audit once every 3 years/as per experience or circumstances.
- Assess system obsolescence from time to time on the basis of technology trends/product releases and initiate upgrading plan.
- Conduct failure analysis of all failures to determine the root cause and ensure that the knowledge is put to use to prevent similar failures.

16.4.2 Control Measures for Improving Maintenance Effectiveness

- Ensure a mechanism is in place for authorization of programmable logic controller (PLC)/interlock logic bypassing and that the bypass has been removed subsequently and the logic/protection system is fully operational.
- Maintain backup of all distributed control system (DCS)/PLC software, programs, logic/interlock ladder diagrams on CDs/pen-drives and create facility for proper preservation. Put in place a suitable responsibility matrix for the same. Also, ensure that they are updated at quarterly intervals or per experience and circumstances. Updating should also be ensured after every modification/upgrade job.
- *Recordkeeping:* Maintain history and trend of equipment performance. "As found" and "as calibrated" data should be made available through PC-based systems. Facility for "work order" information should also be incorporated.
- *Documentation control:* Document updating should be performed for all modifications, changes to loop schematics/hook-up drawings, piping and instrumentation diagrams (P&IDs), interlock logic/ladder diagrams, trip settings, calibration ranges, etc., immediately upon completion of the job

- Test/calibration equipment traceability for accuracy, resolution, etc.
- Rodent control measure/treatment in and around control rooms housing DCS, PLC, and other electronic hardware and communication cables that are susceptible to damage.
- Ensure positive pressurization of the control room to prevent ingress of airborne dust and gaseous contaminants. Air curtains and double doors at all entrances to control rooms should be maintained.
- Ensure presence of air handling unit (AHU) filters/chemical filters as necessitated by control room ambience category.
- Ensure presence of humidity control in control room air conditioning and that it is in operation. High humidity accelerates destructive corrosive effects. On the other hand, low humidity may cause electrostatic discharge problems with the electronic equipment.
- Ensure that a periodic survey is done to maintain and enhance the control room ambience.
- Perform an audit of DCS and PLC systems through the OEMs as necessitated after a reasonable period of operation and driven by failure trends or as per OEM recommendations vis-à-vis necessity for a stagewise upgrade to adopt the latest technology, facilities, and features.
- Implement online continuous monitoring of control room ambience.
- Ensure that coatings conforming to severity class on DCS/PLC hardware are applied on electronic modules and printed circuit boards.

16.4.3 Spares Philosophy

- In general, 5 % for all field instrumentation, subject to a minimum of one number of each size and type.
- *DCS/PLC:* Nonredundant cards/hardware should be 5 % in general or at least one number of each type. Redundant cards/hardware should be at least one number against each type.
- *Control valves:*
  - One number plug and seat assembly and seal rings for each valve under cavitation/flashing/high-pressure services.
  - 5 % in general for
    - Diaphragm of actuators
    - Gland packings
    - Positioner spares
    - Bonnet gasket set
- *Annubar/pitot tube:* One set of gasket, “O” ring, packings, and needle valve.
- *Rotameter/level troll:* One number float, torque-tube assembly, PCB for each range, and set of packing for each size and type.

16.5 CIVIL MAINTENANCE PRACTICES

Civil maintenance is primarily associated with the maintenance of all buildings/structures, roads, environmental protection, sanitation, and drainage-system-inclusive general housekeeping in the refinery. In addition, repair of furnace refractory/castables/CF blankets, all paintings (normal/epoxy-based), specialized paintings in the tanks/vessels, tank cleaning, fire proofing, etc., are also taken care of by civil maintenance. The following areas are broadly covered under civil maintenance.

16.5.1 Buildings

Office buildings, control rooms, workshops, the operator’s cabin, and other buildings in the refinery are repaired and maintained regularly. Scheduled visual inspection of the buildings is done every year. The designer’s specification of the materials and application procedure for repair is followed for maintenance.

16.5.2 Structures

The flare stack, chimneys, cooling tower, piping structures, equipment structures, etc., are included in this category. The inspection of these is performed along with maintenance and inspection shutdowns of the plant or related activities. The designer’s specification of the materials and application procedure for repair is followed for maintenance. The remaining life assessment of concrete stacks and chimneys is performed before the estimated design life or any remarkable deterioration is observed during routine visual inspections. The repair/rectification is only performed under consultation of designer, if required.

16.5.3 Roads and Culverts

All refinery and peripheral roads, culverts, hard surface areas under piping, tank dykes, etc., are maintained as per requirements. Annual maintenance after monsoon season is performed for all of the observations.

16.5.4 Environment Protection and Sanitation

A refinery primarily deals with crude oil and has various unwanted gases that are not environmentally friendly. Cooling water is used as a cooling media of the process and can become contaminated during refinery operations. Planting new trees and their regular maintenance and horticulture activities are done to preserve the environment and comply with legislative requirements. Water quality is also monitored regularly and the necessary treatment is done to meet legislative requirements.

16.5.5 Drainage System

Hydrocarbon and water waste are unavoidable in refinery operations. These wastes are suitably drained to desired locations for further treatment and disposal as per the environmental norms. Repair and maintenance of all such drains are done on a regular annual basis in dry seasons.

16.5.6 Refractory and Insulation

Refinery operations require several furnaces, reactors, columns, vessels, and a vast network of process piping that requires application of various refractory and insulation jobs to meet the process requirements as well as to achieve reliable operation of the equipment. A similar requirement is also applicable for steam-generation systems. Selection, procurement, and application of all such refractory, castable, and insulating materials are performed. Maintenance activities are normally done during the planned maintenance and inspection activities of the equipment or during an available opportunity. The designer’s specification and manufacturer’s application procedures are applied for the maintenance activities.

16.5.7 Paints and Epoxy Coating

Atmospheric corrosion of all external surfaces of steel/concrete is inevitable because of climatic conditions and the refinery operational environment. Also, internal corrosion and deterioration of the equipment occurs because of various process conditions. Hence, suitable painting is done on such equipments/structures as per the corrosion expert's advice. High-temperature aluminum paints are applied on the external surface of metallic stacks, chimneys, and the equipment/piping operating at higher temperatures. Epoxy painting is done at the internal surface of tanks, vessels, heat exchanger water-side components, etc., as per the advice of corrosion experts. The surface preparation required for normal painting, high-temperature aluminum painting, or epoxy painting is religiously maintained as per Swedish standards, and painting is done as per the application procedure provided by the manufacturer.

16.5.8 Storage Tank Cleaning

Crude oil, intermediate products, and finished products are stored within the refinery premises itself. The storage is in tanks, vessels, and Horton spheres. The capacity of the storage tanks ranges between 1000 and 75,000 m^3 and above. The quantity and quality of sludge generation varies depending on the products handled in the tank. The number of tanks is optimized and kept at a minimum because of space limitations and the cost of the product handling system through the tank. This necessitates the meticulous planning and tight cleaning and maintenance schedule of the tanks wherever required for maintenance. Cleaning of tanks containing varieties of sludge is also a skillful job and is generally handled by a mechanized system. The tank cleaning schedule is maintained as per the inspection schedule of the tanks.

16.6 INSPECTION PRACTICES

16.6.1 Scope

The inspection function in the refineries is to protect assets from deterioration and evaluation of equipment integrity for continued service. It provides technical support through troubleshooting and condition monitoring. Inspection activities involves base data generation (design and operating data, metallurgy, thickness of the materials, metallurgical microstructure of critical high temperature equipment, etc.), health assessment of the equipment, corrosion study based on the operating conditions, failure analysis, development of repair/welding procedures, metallurgical upgrade, and application of various nondestructive tests (NDTs)/destructive tests (DTs) for investigations, etc. Inspection is also responsible for remaining life assessments of equipment, decision of plant shutdown frequency, finalization of the inspection/equipment replacement plan, and upkeep of documentation systems. Inspection is to ensure that refinery operations are safe, smooth, and reliable for the intended company's profitability and that they meet all statutory obligations of the state/country. Inspection of equipment is usually performed in three stages, i.e., during manufacturing, precommissioning, and in-service inspection. The discussion in this chapter will be limited to in-service inspection.

16.6.2 Inspection Philosophy

The in-service exposure of equipment causes deterioration because of corrosion and environmental factors, and inspection is to ascertain that the physical/metallurgical condition during service is safe and reliable for plant operation. The inspection frequency and type of inspection depend on the nature of deterioration. Thickness loss, localized corrosion, environmental cracking, and metallurgical degradation are the main considerations during inspection. To assess the health of the equipment, predict the life expectancy of the equipment, and decide plant/equipment shutdown for repair/replacement, inspection develops a systematic method for identifying the deteriorated components, structures, and equipment in a cost-effective manner without compromising safety. It provides sound technical evaluation of equipment conditions by way of various monitoring systems and suggests technoeconomical measures. Inspection develops and standardizes inspection frequencies, techniques, tools and instruments, documentation systems, spare management systems, etc. Quality assurance of all projects and modification activities, repair and maintenance activities, selection of materials, development of repair procedures, etc., is done within the framework of international codes and practices.

16.6.3 Inspection Methods

In general, two types of inspection methods are used for health assessment of equipment or material:

1. *DT (destructive testing):* This method is not used for an operating refinery.
2. *NDT (nondestructive testing):* Most commonly used in operating refineries. A brief description of the NDT used in refinery inspection follows.

16.6.3.1 VISUAL INSPECTION

Visual inspection is a nondestructive examination method used to evaluate an item by observation for surface conditions and deformity. Direct visual examination may usually be made when access is sufficient to place the eye within 24 in. of the surface to be examined and at an angle not less than 30° to the surface to be examined. Mirrors may be used to improve the angle of vision, and aids such as magnifying lenses may be used to assist examination. In some cases, remote visual examination using visual aids such as mirrors, telescopes, boroscopes, fiber optics, cameras, or other suitable instruments may have to be substituted for direct examination.

16.6.3.2 PHYSICAL MEASUREMENT

Physical measurement of equipment or its integral parts is done to evaluate any dimensional change during operations, fabrications, or installation. Normally, diameter [inner diameter (ID)/outer diameter (OD)], thickness, grooves or pits, cracks, etc., are measured using micrometers, calipers, pit gages, or such instruments. The measurement is compared with the desired specifications for further actions.

16.6.3.3 DYE PENETRANT TEST

The liquid penetrant examination method is an effective means for detecting discontinuities, which are open to the surface of nonporous metals and other materials. Typical discontinuities detected by this method are cracks, laps, porosity, shrinkage areas, and laminations.

16.6.3.4 MAGNETIC PARTICLE TESTING

Magnetic particle inspection is a method for locating surface and subsurface discontinuities in ferromagnetic materials. While testing a piece with hidden defects the magnetic particles are sprayed over the area to be tested and the object is magnetized. The fine magnetic particles are attracted and are held in a place to indicate the defects in true form and orientation.

16.6.3.5 ULTRASONIC TESTING

Ultrasonic testing is a method that uses sound waves having a very high frequency beyond the audible range of the human ear. The properties of sound waves are very similar to light waves in that they can be focused, reflected, and refracted. This phenomenon is used in ultrasonic testing. Ultrasonic pulses are transmitted to the specimen under examination, and measurement is made of the time taken for the wave to reach the opposite surface or an intermediate flaw. This will locate the position of the flaw from the surface. This is of particular advantage when only one surface is accessible.

16.6.3.6 EDDY CURRENT EXAMINATION

Eddy current inspection is based on the principles of electromagnetic induction and is used to identify or differentiate between a wide variety of physical, structural, and metallurgical conditions in electrically conductive ferromagnetic and nonferromagnetic metals and metal parts. The method uses attenuating currents in the radio frequency range (50–5000 kHz) of the electromagnetic spectrum for detection of surface and near-surface defects in the electrically conducting materials.

16.6.3.7 RADIOGRAPHY

Radiography uses the penetrating capacity of ionizing radiation such as X rays and gamma rays to produce a shadow of the internal condition of a job on a recording medium. The recording of an area of interest on the film by ionizing radiation is known as radiography.

16.6.3.8 CREEP MEASUREMENT

Gauging is a measurement of bulging within an allowable limit of furnace tubes to be decided for replacement beyond the permissible limit.

16.6.3.9 THERMOGRAPHY

Infrared thermography is a temperature-based technique that produces thermal images of an object on the basis of the infrared radiation emitted by them.

16.6.3.10 ALLOY ANALYSIS

Positive material identification of the different metallurgy used in the refinery is done by an alloy analyzer to confirm the actual materials used in the system against specifications. The check confirms the different grade of alloys with the percentage chemical compositions through assay. X-ray-based analyzers are currently used more than the previously used gamma ray isotope-based instruments.

16.6.3.11 HARDNESS TEST

The hardness test is a measure of the ductility of CS/AS materials to confirm for intended use. It is used in alloy steel components after heat treatment for desired services, also in Carbon Steel for stressed services like caustic/high thickness (more than 19 mm) weldment etc.

16.6.3.12 LEAK TEST

A leak test is the identification of a thorough defect in a wall of a tight assembly or component, pipe, or system using a liquid or gas under differential pressure. The test may be done from an inside compartment to outside or vice versa. A leak test is needed to check the integrity of fabricated components and the system for pressure vessels, nuclear reactors, electronic valves, vacuum equipment, gas containers at pressure, etc. It is always measured as the leak rate with units as cubic centimetre per second.

16.6.3.13 HYDROSTATIC TEST

A hydrotest is the process of filling equipment such as a tank, vessel, exchanger tubes/shell, furnace/boiler tubes, and pipings with water/liquid at the appropriate pressure and checking for any leakage. The test confirms the strength of the equipment as well as the integrity. In this test, properly calibrated pressure gages are selected based on the complexities and size of the system/equipment as well as the pressure requirement. Normally, a minimum of two pressure gages are used that have ranges such that the pointer should approximately be showing at the center of the test pressure on the dial.

16.6.3.14 IN SITU METALLOGRAPHY

In situ metallography is an onsite evaluation of the metallurgical degradation of high-temperature equipment. The metallographic kit contains a replica with portable hand tools for taking a microstructure of the area of interest. The sequential bank of the microstructure helps in deciding the remaining life of the equipment vis-à-vis its reliability for safe operation.

16.6.3.15 THICKNESS LOSS MEASUREMENT

Health of the equipment/piping is ascertained by wall thickness measurement, and the operating life is decided based on the remaining thickness and derived corrosion rate.

16.6.3.16 VIDEOSCOPIC INSPECTION

Inspection at inaccessible areas is done with this instrument.

16.6.3.17 BOROSCOPIC/FIBEROSCOPIC INSPECTION

Inspection at inaccessible areas is done with this instrument.

16.6.3.18 EQUIPMENT FOR HEALTH ASSESSMENT

The equipment for refinery operations are broadly classified into three categories.

1. Static equipment
    - Furnace
    - Power boiler
    - Columns
    - Reactors
    - Vessels
    - Heat exchangers
    - Tankages
    - Horton spheres
    - Stack/chimney
    - Pressure safety valves/temperature safety valves
    - Tank-mounted safety reliefs
    - Rupture discs
    - Expansion bellow
2. Rotary equipment
    - Compressors
    - Pumps
    - Blowers
    - Turbines

3. Piping
    - Process piping
    - Utility piping
    - Valves and fittings
    - Gaskets

16.6.4 Inspection Criteria, Frequency, and Schedule

16.6.4.1 BROAD CRITERIA ADOPTED FOR INSPECTION FREQUENCY

- Corrosion/erosion properties of process fluid, chemicals, and catalysts. Rate of deterioration, remaining corrosion allowances, deterioration pattern, etc.
- Criticality of the equipment (cost, size, operational criticality and dependency, material availability, etc.)
- Operational requirement
- Statutory requirement

The inspection frequency is decided based on the criticality of the equipment and facilities and the inspection requirement, whether in-service inspection is possible, or if equipment/system isolation is desired. The inspection schedule is prepared accordingly.

The following inspection programs are implemented in the refinery:

- *Planned inspection:* The equipment or system is inspected thoroughly after isolation from service during plant operation without compromising the plant efficiency.
- *On-stream inspection:* It is performed when the equipment/plant is in service. It helps in determining the extent of general damage and deterioration. It also helps in identification and rectification of unsafe conditions arising out of faulty operation. The observations form the basis to determine the extent of repairs/further investigations to be performed during the shutdown. During on-stream inspection, monitoring of the critical operating parameters of rotary/static equipment of process units and TPS/utilities is conducted, and immediate suggestions on corrective actions by operations, process, and maintenance teams is initiated. The monitoring points are as follows:
    - *Furnace:* COT, pressure drop across each pass, skin temperature, presence of any hot spots, box temperature, burner flame condition, flue gas outlet temperature, draft, falling of refractory, casing plate temperature, stack temperature, etc.
    - *Column:* Overhead temperature should be above dew point temperature.
    - *Exchangers:* Pressure-temperature survey for identification of fouled exchangers/coolers affecting efficiency.
    - *Vessels/accumulator:* Accumulator or reflux drum pH/chloride/iron/copper, desalter salt content upstream and downstream, adequacy of dosing systems such as ahuralan, ammonia, caustic, demulsifier, etc.
    - *Boiler:* Boiler feed water pH/alkalinity/conductivity/phosphate/silica/dissolved oxygen, superheater steam pH, superheater skin temperature, flue gas temperature, burner flame condition, etc.
    - *Cooling water quality:* Flow, pressure temperature, pH, sulfur-reducing bacteria, Langlier index (contributes to fouling), etc.
- Crude analysis for presence of salt, sulfur, and TAN levels.

16.6.4.2 UNPLANNED INSPECTION

- Breakdown inspection and failure analysis
- Special inspection
- Operational/process requirement inspection

16.6.4.3 SHUTDOWN (TURNAROUND) INSPECTION

The inspection is performed when the equipment/plant is taken out of service during a planned unit shutdown. The thorough internal and external inspection of all equipment and piping systems is performed during the shutdown. All parts of the equipment are thoroughly inspected and corrective action is taken for safe run until the next planned shutdown.

A schedule of on-stream inspection for equipment and facilities is given in Table 16.2.

TABLE 16.2—On-Stream Inspection Schedule of Equipment and Facilities

	Daily	Weekly	Quarterly	Annually
Heater	Routine as per checklist	Casing temperature	Thermography	
Reactor/ column/ vessel	Routine as per checklist. Temperature indicative of paint.	Skin temperature of lined vessel		
Dosing system	Dosing at individual points			
Tanks				Premonsoon inspection
Piping	pH of cooling water system	Corrosion probe in jacketed lines	Impressed current measurement of cathodic protected lines. Corrosion coupons.	General condition of piping with supports.

16.6.4.4 HEAT EXCHANGER INSPECTION SCHEDULE

After the initial commissioning of the plant, the first inspection of the heat exchanger, cooler, and condenser shall be performed as per the designers/licensor's recommendations or after 1 year of service, whichever is sooner. In general, the following frequency of inspection shall be adopted, which can be improved based on the equipment condition and inspection findings from time to time.

- Heat exchangers in corrosive service—2 years
- Heat exchangers in noncorrosive service—4 years
- Condensers—2 years
- Coolers—2 years

16.6.4.5 UNIT SHUTDOWN SCHEDULE

The inspection schedule is prepared by a joint decision of process/production and maintenance/inspection considering all aspects as mentioned earlier and given in Table 16.3. Tools used for inspection are given in Table 16.4. Instruments used for inspection are given in Table 16.5 and special instruments used are given in Table 16.6.

TABLE 16.3—Frequency of Unit Shutdown

Sr. No.	Unit	Maintenance and Inspection Frequency (years)
1.	CDU/VDU/NSU	4
2.	OHCU	4
3.	HGU	4
4.	RFCCU	2
5.	CCRU	2
6.	DHDS	4
7.	SRU	2
8.	SWSU	2
9.	ARU	2
10.	BBU	4
11.	MEROX	4
12.	VBU	4
13.	BOILERS	1
14.	LUBE BASED PLANTS	4
15.	WAX PLANT (DEOILING UNIT)	4

TABLE 16.4—Tools Used for Inspection

Thermal Chalks	ID/OD Calipers/ Vernier Calipers	Go/No-Go Gage	Screw Gage
Measuring tape/scale	Intrinsically safe torch	Nonwashable marking chalks	Marker pens
Ball pein hammer	Files and emery papers	Wire brush	Inspection mirrors
Illuminated mirror	Dial gage	Magnifying glass	Weld gage
Surface profile gage	Radiation survey meter	Radiography film viewer	Personal radiation alarm meter
Pocket dosimeter	Hydrometer	Spirit level	Wire gage
Buffing tools	Heavy-duty engraver	Light-duty drill	Scraper

TABLE 16.5—Instruments Used for Inspection

Ultrasonic Thickness Meter	Portable High-Temperature Infrared Thermometer	Thermo Hunter	Low-Temperature Infrared Thermometer
pH meter	Pit gage	Ultrasonic hardness tester	Dye-penetrant kit
Magnetic particle inspection kit	Radiography arrangements with dark room	Boroscope and fibroscope	Paint thickness gage
Holiday detector	Optical densitometer	Microscope	Hardness tester
Vacuum box testing instrument			

TABLE 16.6—Special Instruments

Ferrite Meter	Alloy Analyzer	Digital Camera	Binoculars
Ultrasonic leak detector	Theodolite	Internal rotary inspection system (IRIS)	Tank bottom floor scanner
Metallography kit	Eddy current tester/remote field eddy current tester		

16.6.5 Major Inspection Points of Equipments

16.6.5.1 UNFIRED PRESSURE VESSELS (COLUMNS, REACTORS, AND VESSELS)

Corrosion-prone areas in columns/reactors/vessels include

- Bottom head and shell of fractionators processing high-sulfur crude oils are susceptible to sulfide corrosion.
- Top heads and upper shell of distillation columns are prone to chloride attack in the form of pitting corrosion.
- Fractionation and distillation column, knockout drums, and reflux drums in the presence of wet H_2S or cyanides are prone to cracks in welds and their HAZ.
- Corrosion and erosion will take place in the shell directly opposite to the steam inlet and inlet streams.
- Corrosion occurs where two dissimilar metals are in close contact (cladded/uncladded zone).

16.6.5.2 INTERNAL INSPECTION OF COLUMNS

All parts of columns should be inspected for corrosion, erosion, hydrogen blistering, cracking, and lamination. Thickness measurements should be taken on heads, shells, and nozzles to know the extent of deterioration. The top dome and shell should be checked for pitting. The depth of pits/grooves is measured by a pit depth gage. For wet H_2S, amine or caustic service, magnetic particle testing (WFMPT) is done in welded seams to detect surface cracks. Connected nozzles should be checked for internal corrosion. Supports for internals such as trays, baffles, screens, grids, piping, etc., should be visually checked. The general condition of internals such as trays and packing material should be checked for corrosion. The flash (feed) zone should be thoroughly checked for erosion/corrosion of an impingement plate attached with the shell. The bottom dome and shell near the draw-off nozzle are critically inspected for pitting corrosion. The shell opposite of the steam injection nozzle should be checked for impingement.

16.6.5.3 INSPECTION OF CLADDED COLUMNS/ REACTORS

Cladding protects the base metal from erosion/corrosion. SS 410S, SS 316L, and Monel are some of the cladding materials used. Careful visual inspection of the lining is required for checking corrosion, erosion, bulging, etc. Light hammer taps will identify corroded and cracked sections of lining. Thickness measurements at designated locations should be done to check the bonding of cladded metal with base metal. The junction of the cladded and uncladded zone should be checked for galvanic corrosion. Weld joints and HAZ should be checked for cracks. Pneumatic testing of nozzle liners should be done.

16.6.5.4 INSPECTION OF GUNITE/REFRACTORY LINED VESSELS

Visually inspect gunite/refractory lined vessels to check for spalling and cracks. Hot-spot locations are to be carefully checked. The lining is to be checked for bulging and looseness by light hammer tapping. The thickness of the shell is to be measured from outside.

16.6.5.5 STATUTORY EXTERNAL INSPECTION OF VESSELS

- Inspection of all vessels should be done as per the existing rules of the country/state.
- External inspection should be conducted at least every 5 years or whenever the opportunity is available.
- The frequency of inspection and hydrotest of boilers, pressure vessels, and Horton spheres should be religiously performed per the Power Boiler Act and pressure vessel regulations of the country/state.

16.6.5.6 FIRED HEATERS

A fired heater is an internally insulated enclosure where the heat liberated by the combustion of fuels is transferred to fluid contained in tubular coils.

16.6.5.6.1 Inspection Points for Furnaces

- *External inspection of heater tubes:*
    - Check for sagging, bowing, and bulging. Sagging and bowing should not exceed 0.5 times the diameter of the tube. Tubes should be checked for bulging, especially those that are subjected to flame impingement. If the increase in the diameter of the tube at the bulge is 5 % or more, the tube is rejected. In the case of reformer tubes, the increase in diameter is limited to 3 %.
    - Check for oxidation, scaling, deposits, corrosion, cracks, and grooving.
    - Check for roll leaks and plug leaks in the case of plug- and header-type heaters in heavy oil/coker units.
    - All weld joints of heater tubes should be thoroughly inspected for any crack or serious defects.
    - Magnetic particle inspection (MPI), DPT, radiography, and ultrasonic flaw detection, etc., may be used as per requirement.
    - Wear/grooving at all tube support locations should be checked.
    - Ultrasonic thickness survey of tubes should be done along the length to determine the metal loss and rate of deterioration. The outermost curvature of bends, such as near the weld joint of the bend with tube, and upstream and downstream of tube weld joints, etc., are critical areas for corrosion/metal loss.
    - In the convection section, the last few rows of tubes at the exit of flue gases should be checked for external corrosion due to the dew point of flue gases. The accessible studded tubes should be inspected for any sign of oxidation of studs due to overheating or corrosion due to sulfurous deposits.
- *Tube supports:* Tube supports are generally made of 25Cr-20Ni (HK-40) material. Tube supports are prone to oxidation, corrosion, and cracking at high temperatures. Tube supports are prone to sigma phase formation due to prolonged exposure at high temperatures, which makes them brittle at room temperature. All supports should be inspected for cracks.
- *Refractory lining (castables, CF blanket/module):* The refractory lining should be visually inspected for breakage, crumbling, and open joints. The clearance in expansion joints of the lining should be checked for deterioration from heat/debris. Clearance should be filled with asbestos rope/ceramic fiber. After major refractory repairs, it should be dried/cured properly before commissioning.
- *Furnace casing and accessories:* Exposed parts of heater casing should be visually inspected for signs of any damage, paint peeloff, etc. Casing should be inspected for thinning/perforation due to acidic flue gas corrosion. Header boxes should be checked for warping because this leads to excess air in the heater resulting in additional fuel consumption. Proper alignment of burners is essential because misaligned burners will lead to flame impingement on radiation tubes and damage of burner housing. Burner tips should be checked for oxidation, corrosion, and choking.
- *Thermocouple connections:* Weldments of thermocouple tips on radiation and convection tubes often crack in service. The weld should be DP checked during every planned inspection.

16.6.5.6.2 Hydrostatic Testing

A hydrostatic test should be performed in all heater tubes in every planned shutdown. Hydrostatic test pressure should be 1.5 times the maximum operating pressure (corrected for temperature or shutoff pressure of pump). Testing should also be done whenever tubes or fittings are replaced involving a hot job in the system. During the test, inspection should be done for the heater to locate any leak. Austenitic stainless steel tubes should be hydrotested with demineralized (DM) water or water having a chloride content less than 20 ppm.

16.6.6 Heat Exchanger

The heat exchanger is equipment that is used for the heating or cooling of a fluid without intermixing.

16.6.6.1 HYDROTESTING OF EXCHANGERS

- All heat exchangers should be tested at 1.5 times the design pressure when the shell or tube is new or any major repair or replacement has been performed. The periodic test pressure is calculated on the basis of 1.5 times the maximal operating pressure, pump shutoff pressure if directly connected to a pump, or safety valve test pressure mounted on the shell or tube side of the heat exchanger.
- Wherever tube-side pressure is higher than shell-side pressure then it should be preferably tested at the tube-side test pressure, provided that the design condition of the shell permits or vice versa.
- Pressure gages used in the hydrotest should be freshly calibrated and two gages of the same range should be used. The range of the pressure gage should be generally double the intended maximal test pressure, but in no case should the range be less than 1.5 or more than 4 times the test pressure (30 % more than the test pressure).
- DM water should be used for hydraulic tests if material of construction is austenitic stainless steel.

- The duration of the test should not be less than 30 min, and a pressure gage should be installed at the highest point.

16.6.6.2 PROCEDURE FOR TESTING

Testing of the shell and tube exchangers is normally done in three stages and with water as the test media. If the water ingress in the equipment is not desirable, other suitable test media should be selected (e.g., kerosine).

- *Shell test:* Shell tests facilitate detection of individual tube leaks, if any. Soundness of shell weld joints/gasket joints is confirmed. In the case of floating head types, a separate test ring is required to conduct the shell test. In the case of a roll leak, rerolling of the tube is done using suitable expander and taking due care for overexpansion. In the case of a tube leak, both of the tube ends are plugged with tapered plugs. It is desirable to remove the test fluid from the shell by air before doing the tube test.
- *Tube test:* In this case tubes are pressurized and tested under tensile stress. Here floating head gasket/channel cover gaskets are also tested. Tube leaks are detected, but identification of individual tube tests is not possible here.
- *Cover test:* Pressurization of the shell side after boxing up of the shell cover is done. The test pressure should be equal to the shell test pressure. This facilitates total exchanger component integrity for operation.
- *Individual tube test:* This is done to discover the leaky tube in the bundle assembly by pressurizing each tube.
- *Testing of box coolers:* The coil should be pressurized and checked for leaks from the pipe, bends, gasket joints, etc. The shell side should be tested by water fill.

16.6.6.3 AIR FIN FAN COOLERS

The segment should be pressurized hydraulically and checked for leaks through plugs, rolls, and gasket joints and for any drop in pressure.

16.6.6.4 BREECH LOCK EXCHANGERS

Having low alloy steel material of shell is susceptible to temper embrittlement. Hence, to avoid risk of brittle fracture due to pressurization at ambient temperature, the metal temperature of the shell side should be maintained at 93°C during test. The skin temperature of the shell should be maintained throughout the test period. Pressure above 20 % of the design pressure should not be exceeded before attaining a temperature of 93°C. Pressure should be raised to the shell side differential test pressure and maintained for 1 h. The shell side should be pressurized to the shell test pressure and the tube side should be simultaneously pressurized to the tube test pressure, ensuring that at no time is the differential test pressure between the shell and tube exceeded. Depressurization after testing should be done similarly. Pressure should be held for a minimum 1 h before inspection.

16.6.6.5 COMBINED FEED PLATE HEAT EXCHANGERS

Because the metallurgy of construction is austenitic stainless steel, DM water is used for a hydrotest. Due consideration of maintaining differential test pressure is always simultaneously given during pressurization of the exchanger at both sides as indicated above.

16.6.6.6 TUBE PLUGGING

In the case of tube leaks, the tube is isolated with a plug at both ends. The metallurgy of the taper plug should be the same as the tube metallurgy to avoid galvanic corrosion. The taper plug should have an included angle of 5.5° or less. The plug dimension depends on the tube size and thickness. A maximum of 20 % plugging is recommended to meet the production efficiency.

16.6.7 Storage Tanks

16.6.7.1 INSPECTION FREQUENCY OF TANKS

Visual external inspection of all storage tanks should be performed once a year. The detailed external inspection along with a thickness survey of tanks should be conducted as per the following unless otherwise guided by state statutory requirements (see Table 16.7).

TABLE 16.7—Frequency of External Inspection of Tanks

Sr. No	Fluid Stored	External Inspection Interval (years)	
		With Corrosion-Rate-Based Assessment	Without Corrosion-Rate-Based Assessment
1.	Crude oils, vacuum gas oil, cycle oil, SKO, MTO, ATF, HSD, gas oil, MS, naphtha, benzene, toluene, ethanol, MTBE, LDO, JBO, bitumen, lube oil, grease, industrial water, amines, etc.	5	3
2.	Fuel oil, RCO, LSHS, vacuum residue, slops, caustic	3	3
3.	Acids (concentrated)	2	2
4.	Acids (dilute)	1	1

16.6.7.2 INTERNAL INSPECTION

All storage tanks should be subjected to detailed inspection as per the following unless otherwise guided by state statutory requirements (see Table 16.8).

TABLE 16.8—Frequency of Internal Inspection of Tanks

Sr. No	Fluid Stored	Internal Inspection Interval (years)	
		With Corrosion-Based Assessment	Without Corrosion-Based Assessment
1.	Crude oils, fuel oil, RCO, LSHS, vacuum residue, vacuum gas oils, cycle oil, SKO, MTO, ATF, HSD, gas oil, MS, naphtha, benzene, toluene, ethanol, MTBE, LDO, JBO, bitumen, lube oil, grease, industrial water, caustic, amines	Years determined by corrosion rate and integrity assessment or 15 years, whichever is lower	10
2.	Slops	Same as above	8
3.	Acids (concentrated)	Same as above	4
4.	Acids (dilute)	Same as above	1

16.6.7.3 INSPECTION OF TANK ROOF MOUNTINGS

Tank mountings such as breather valves/P&V valves, relief valves, flame arresters, etc., should be ensured clean and operable after every monsoon. Floating roof drains, shell sealing, and emergency roof drains should be inspected before every monsoon.

16.6.7.4 TESTING OF TANKS

Bottom vacuum testing is performed using a metal testing box 6 in. wide by 30 in. long with a glass window at the top. Suitable connections, valves, and gages should be provided to maintain a partial vacuum of 3–5 psi (g) on the box. With the help of a soap solution, the bottom plate weldment should be checked for any defect.

16.6.7.5 HYDRAULIC TESTING OF THE TANK

Atmospheric tanks, which are designed to withstand less than 0.5 lb/ft^2 (g) pressure over the static pressure of the liquid contained in the tanks, are normally tested only by filling the tanks with water up to the curb angle in a fixed roof and up to safe filling height in floating roof tanks. If water is not available, a carefully controlled air test using an air pressure not exceeding 2 in. of water pressure may be applied. In this case, a soap solution is applied on all suspected areas of the tank for leak detection. Only fresh water or good quality water with a pH between 6 and 8.3 should be used for testing. In the case of a longer duration of water holding time in the tank, suitable corrosion in inhibitors should be used. The hydrotest should be performed at a temperature of 4°C and above. Water filling rates should be decided based on the soil condition and tank design. In the case of a stable foundation, the rate may be considered as 1.5 m/h. Only an approved filling rate holding time should be applied during testing. In the case of floating roof tanks, a low filling rate of not more than 0.2 m/h should be used until the roof is floated. Thereafter, the filling rate may be increased to the specified filling rate. For roof drains, after inspection the pressure testing should be done at 3.5 kg/cm^2. For heating coils, after thorough inspection and necessary repair/replacements, coils should be hydrotested at 1.5 times the operating pressure.

16.6.7.6 TESTING OF ROOF

Fixed roof tanks are tested by applying internal air pressure not exceeding the weight of the roof plates and applying a soap solution to the weld joints. Alternatively, vacuum testing can be performed. A floating roof should be tested for a smooth up and down movement. Stability of the roof should be checked by pouring water on the floating roof equivalent to 10 in. of rainfall. The stability of the floating roof of the tank should be checked both for single deck/double deck by puncturing any two adjacent pontoon compartments with no water or live load.

16.6.7.7 NONDESTRUCTIVE EXAMINATION FOR TANK INSPECTION

- Ultrasonic thickness measurement
- Ultrasonic corrosion testing—automated ultrasonic scanning
- Ultrasonic shear wave testing to find out discrimination between lamination and inclusions
- Acoustic emissions testing for online assessment of storage tank floor
- Magnetic floor testing for detecting top-side pitting and under-side corrosion and holes on the tank floor
- Low-frequency electromagnetic technique to map corrosion of tank bottom plate on product and soil sides

16.6.8 Off-Site Piping Types

- Above-ground—insulated/with heating coil/jacketed lines/uninsulated
- Underground

16.6.8.1 INTERNAL CORROSION

- Uniform corrosion due to low/high pH
- Localized corrosion in crevices, bends, etc.
- Preferential attack on weld
- Stagnant areas—in dead ends, etc.
- Condensation/two-phase systems.
- Internal lining damage
- Stress corrosion cracking
- High-temperature failures
- Hydrogen attack
- Areas downstream of chemical injection points
- Naphthenic acid/polythionic acid corrosion

16.6.8.2 EXTERNAL CORROSION

- Corrosion under insulation
- Soil-side corrosion of underground lines
- Atmospheric corrosion—sulfurous/acidic environment
- Spillage/impingement
- Corrosion at soil/air interface

16.6.8.3 STRESS-RELATED FAILURE

- Overpressurization
- Vibration—as in pump connected piping
- Support failures—inadequate supporting system or stuck up
- Thermal stresses due to continuous wetting/drying in connected piping
- Fatigue due to cyclic loading NDT techniques for piping
- Ultrasonic thickness survey

16.6.9 Safety Mountings/Devices

For equipment and process safety, the pressure vessels and storage tanks are provided with the following mounting:

- Pressure safety relief valve
- Temperature safety valve
- Rupture disc
- Pressure and vacuum relief valve

The routine testing and revision of these valves are performed as per the inspection schedule, which is prepared based on legal requirements, government acts, designer's recommendations, and operational safety requirements.

16.6.10 Inspection Documentation

The following inspection recording and documentation should be generated:

- Drawings—one set of original as-built drawings.
- Equipment data card.
- Equipment data record card—to be prepared from equipment passport.

- History sheets—to be maintained chronologically.
- Inspection checklists for all categories of equipment and piping (includes on-stream, shutdown inspection, and external and internal inspections as per the requirements). The checklist is to be religiously filled in for each equipment inspection.
- Inspection observation and record sheet—visual observations, dimensional checks, and thickness records are to be maintained.
- Radiography films—to be stored for 5 years.
- All test certificates.
- Calibration chart.

SUGGESTED READING

1. *API Guide for Inspection of Refinery Equipment,* Chapter 7, “Exchangers, Condensers, and Cooler Boxes."
2. Standards of Tubular Exchanger Manufacturers Association.
3. ASME Pressure Vessel Code, Section 8.
4. API 660, *Shell and Tube Heat Exchanger for General Refinery Services*.
5. BS 3274, *Specification for Tubular Heat Exchangers for General Purposes*.
6. API 653, *Tank Inspection, Repair, Alteration, and Reconstruction*.
7. API 510, *Pressure Vessel Inspection Code*.
8. Indian Oil’s In-House Inspection Manual.
9. ISO Standards for Vibration Measurement.
10. Vibration Charts from IRD Mechanalysis.
11. Indian Oil's Reliability Improvement Report, 2005.

APPENDIX 1—Preventive Maintenance Checklist for Centrifugal Pumps—Half-Yearly

Unit		**Frequency**	**Half-Yearly**
Equipment Type	**Centrifugal Pump**	**Tag No.**	
Sap Order No.		**Date**	

Sr. No.	**Description of Job**	**Done**	**Not Done**	**Not Applicable/ Remarks**
1.	Drain bearing oil, flush, and refill.			
2.	Examine oil bottle for leaks and proper operation.			
3.	Clean/replace oil filters of AOP and MOP.			
4.	Check gland leak and adjust.			
5.	Check mechanical seal and seal pot condition. Refill the pot.			
6.	Check mechanical seal API flushing/quenching plan condition. If required, clean the orifice, filter, and cooler.			
7.	Check for proper locking of cartridge seal on position.			
8.	Check cooling water lines/lube oil lines for flow and leaks.			
9.	Decouple and check coupling condition.			
10.	Check alignment and rectify, if needed (based on CM observations.			
11.	Check coupling guard condition.			
12.	Check foundation bolts and tighten if necessary.			
13.	Clean suction strainer of pump. Repair if any.			
14.	Check piping and support/rectify.			
15.	Check that the surrounding area is clean.			
16.	Remarks (if any)/safety hazard.			

Recording of Parameters after Pump Commissioning

Vibration			**Suction Pressure**	**Discharge Pressure**	**Flow**	**Motor Amp.**	**Bearing Temperature**	**Casing Temperature** **Noise Level**
V	H	A						
		Special observation and status of the machine/online recording readings.						

(Field Maintenance Engineer)

Special tools required: laser alignment tool, coupling spanner, set of cap screw keys, vibration meter, thermometer, noise level meter.

Spares/consumables required: lube oil SS46, oil cup, coupling Shim pack set.

APPENDIX 2—Equipment Checklist for Plunger Piston Pumps/Diaphragm Pumps

Unit		**Frequency**	**Quarterly/Half-Yearly**
Tag No.		**Sap Order No.**	

Sr. No.	**Description of Job**	**Done**	**Not Done**	**Not Applicable/ Remarks**
1.	Check crank case oil condition; replace if required.			
2.	Check gear box oil condition; replace if required.			
3.	Check gland leak of slide valve, steam cylinder, and fluid cylinder; adjust if necessary.			
4.	Check for any looseness and leakage of crank case oil seal, isolator, deflector, etc.			
5.	Check for any abnormal sound/bearing sound/ valve knocking sound, etc.			
6.	Report safety hazard, if any.			
7.	Check alignment and rectify if needed.			
8.	Check function of NRV, PSV, pilot and slide valve.			
9.	Check lubrication of cylinder/plunger.			
10.	In addition to the above, the following checks should also be performed during the half-yearly schedule:			
11.	Check cylinder and piston for wear.			
12.	Check/tighten or replace gland package.			
13.	Check force feed lubricator functioning			
14.	Check and clean/repair/replace suction and discharge valves/valve seats.			
15.	Check foundation/foundation bolts for tightening.			
16.	Check discharge of pump.			
17.	Remarks (if any).			

(Field Maintenance Engineer)

Special tools required: valve maintenance tool, DE spanner 80 mm, and gland tightening tool.
Spares required: Set of gland packaging, set of oil seals, stuffing box seal gasket.

APPENDIX 3—Vibration Severity Ranges in Accordance with ISO 2372

Range of Vibration Severity in Velocity		**Examples of Quality Judgment for Separate Classes of Machines**			
Limits of Range, mm/s		**Small Machines Class I**	**Medium Machines Class II**	**Large Machines Class III**	**Turbo-Machines Class IV**
Peak	**RMS**				
0.40	0.28	A	A		
0.64	0.45				
1.0	0.71	B			
1.58	1.12		B		
2.5	1.8	C		B	
4.0	2.8		C		B
6.4	4.5	D		C	
10.0	7.1		D		C
15.8	11.2			D	
25	18				D
40.0	28				
64.0	45				
				A	A

A = Good
B = Usable (normal working condition)
C = Still acceptable
D = Unacceptable

APPENDIX 4—Guidelines for Types and Locations of Measurements and ISO Standards References for Vibration

Machine Type	Evaluation Parameters	Sensor Type	Measurement Locations	Direction	Standard Reference	Note
General rotating machines 10–200 revolutions/s (600–12,000 revolutions/min) • Electric motors • Pumps • Turbines	Displacement	Noncontact sensor	Shaft at each bearing	Radial	ISO 7919 Part 1 ISO 10816 Part 1	a
	Velocity	Velocity sensor or accelerometer	Each bearing housing, machine main structure	Radial *x* and *y*, axial *z*		
	Acceleration	Accelerometer	Each bearing housing	Radial *x* and *y*		
	Enveloped acceleration, ESP™	Accelerometer	Rolling element bearings	Radial		
	Spike Energy ™, HFD™, BCU™	Accelerometer	Rolling element bearings	Radial		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Large steam turbines with fluid film bearings • Power generation • Mechanical drive • Marine—usually two separate	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 2 ISO 10816 Part 2	b
	Velocity	Velocity sensor or accelerometer	Each bearing housing	Radial *x* and *y*		
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar	Axial *z*		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Small industrial steam turbines with fluid film bearings	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 3 ISO 10816 Part 3	
	Velocity	Velocity sensor or accelerometer	Each bearing housing and turbine hosing	Radial *x* and *y*		
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar	Axial *z*		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Turbines with rolling element bearings	Velocity	Velocity sensor or accelerometer	Each bearing housing and turbine hosing	Radial *x* and *y*	ISO 10816 Part 3	
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Large and medium industrial gas turbines with fluid film bearings	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 4 ISO 10816 Part 4	
	Velocity	Velocity sensor or accelerometer	Each bearing housing and turbine hosing	Radial *x* and *y*		
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar	Axial *z*		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Large generator with fluid film bearings	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 2 ISO 10816 Part 2	c
	Velocity	Velocity sensor or accelerometer	Generator housing	Radial *x* and *y*		
	Shaft axial position (if not rigidly coupled to deriver)	Noncontact sensor or shaft rider	Shaft end	Axial *z*		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Large pumps with fluid film bearings • Boiler feed • Circulating • Process	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 3 & Part 5 ISO 10816 Part 3 & Part 5	d
	Shaft axial position	Noncontact sensor or shaft rider		Axial *z*		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		

(*Continued*)

APPENDIX 4—Guidelines for Types and Locations of Measurements and ISO Standards References for Vibration (Continued)

Machine Type	Evaluation Parameters	Sensor Type	Measurement Locations	Direction	Standard Reference	Note
Medium and small pumps with fluid film bearings	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 3 ISO 10816 Part 3	d
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar	Axial *z*		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Medium and small pumps with rolling element bearings	Velocity	Velocity sensor or accelerometer	Each bearing housing and turbine hosing	Radial *x* and *y*	ISO 10816 Part 3	d
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Vertically mounted pumps • Reactor coolant	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 5 ISO 10816 Part 5	
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar	Axial *z*		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Large electric motors with fluid film bearings	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 3 ISO 10816 Part 3	
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar	Axial *z*		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Medium and small motors with rolling element bearing	Velocity	Velocity sensor or accelerometer	Each bearing and motor housing	Radial *x* and *y*	ISO 10816 Part 3	
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Compressors • Package centrifugal (four-poster), with fluid film bearings and rigid housing	Relative displacement	Noncontact sensor	Each bearing, pinion housing, and ball gear shaft	Radial ± 45°	ISO 7919 Part 3 ISO 10816 Part 3	
	Velocity	Velocity sensor or accelerometer	At each gear mesh	Radial *x* and *y*		
	Phase angle reference and RPM	Optical or mechanical sensor	Each shaft	Radial		
Compressors • Centrifugal process	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°	ISO 7919 Part 3 10816 Part 3	e
	Shaft axial position	Velocity sensor or accelerometer	Thrust collar of shaft end	Radial *x* and *y*		
	Phase angle reference and RPM (if driving through a gear box)	Optical or mechanical sensor	Shaft	Radial		
Compressors • Reciprocating with fluid film bearings	Relative displacement	Noncontact sensor	Piston rod and each bearing housing	Axial *z* and radial ± 45°	ISO 7919 Part 6 ISO 10816 Part 6	
	Velocity	Velocity sensor or accelerometer	Rod housing	Radial *x* and *y*		
	Position reference	Optical or mechanical sensor	One drive rod or piston at TDC, or crank shaft	Radial		
Compressors • Screw type with two interlocking shafts, fluid film bearings	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°		
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar	Axial *z*		
	Phase angle reference each shaft	Optical or mechanical sensor	Each shaft	Radial		
Compressors • Screw type with two interlocking shafts, rolling element bearings	Velocity	Velocity sensor or accelerometer	Bearing caps and compressor housing	Radial *x* and *y*	ISO 10816 Part 6	
	Phase angle reference each shaft	Optical or mechanical sensor	Each shaft	Radial		

Machine Type	Evaluation Parameters	Sensor Type	Measurement Locations	Direction	Standard Reference	Note
RIC engines, or reciprocating internal combustion machines, rolling element bearing	Displacement	Noncontact sensor, velocity sensor, or accelerometer	Bearing caps, main body, attached components	Axial z and radial ± 45°	ISO 7919 Part 6 ISO 10816 Part 6	
	Velocity	Velocity sensor or accelerometer	Bearing caps, main body	Radial x and y		
	Acceleration	Accelerometer	Bearing caps, main body, cylindrical heads	Axial or radial		
Gears—large with fluid film bearings	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial ± 45°		
	Velocity	Velocity sensor or accelerometer	Bearing caps and gear case	Radial x and y		
	Shaft axial position	Noncontact sensor or shaft rider	Shaft ends	Radial z		
Gears—with rolling element bearing	Velocity	Velocity sensor or accelerometer	Bearing caps and gear housing	Radial x and y		
Fans—large radial with fluid film bearings • Cooling tower fans	Relative displacement	Noncontact sensor	Bearing housing casing	Radial ± 45°	ISO 7919 Part 3 ISO 10816 Part 3	f
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar of shaft end	Radial z		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Fans—medium and small with rolling element bearing	Velocity	Velocity sensor or accelerometer	Each bearing cap and fan housing	Radial x and y	ISO 10816 Part 1 ISO 10816 Part 1	
Centrifuge	Relative displacement	Noncontact sensor	Shaft at each bearing (if accessible)	Radial ± 45°		
	Velocity	Velocity sensor or accelerometer	Housing	Radial x and y		
	Shaft axial position	Noncontact sensor or shaft rider	Thrust collar	Axial z		
	Phase angle reference and RPM	Optical or mechanical sensor	Shaft	Radial		
Pulp refiners	Relative displacement	Noncontact sensor	Shaft at each bearing	Radial x and y		
	Velocity	Velocity sensor or accelerometer	Bearing caps	Radial x and y		
	Phase angle reference and RPM	Noncontact sensor or shaft rider	On shaft ends	Radial z		

Notes: [a] Also refer to specific machine entry in table.

[b] Orthogonal measurements at 45° are recommended for condition monitoring. x and y locations are acceptable.

[c] Measuring both the DC displacement and the dynamic displacement is always a recommended practice. It is more important for hydroelectric turbines because of the relatively larger radial bearing clearances.

[d] Pump vibration varies significantly with operating condition, and ideal operation at the best efficiency point (BEP) will have the least vibrations. Operating continuously at a point other than the BEP will produce increased vibrations.

[e] If not directly coupled, two key references are required.

[f] On large axial flow fans, if the bearing housings and drive shafts are not accessible, accelerometer vibrations on the housing, x and y direction, are required.

The above appendix gives guidelines for types and locations of measurement with respect to ISO standards. Depending on the level of vibration present in the equipment and its characteristics, it is possible to indicate likely reasons that might be inducing vibration. The following are the major factors that induce vibration in equipment:

- Unbalance
- Misalignment
- Mechanical looseness
- Bearing problems
- Gear problems
- Resonance problems
- Rotor rubbing
- Flow-induced vibration
- Electrical problems
- Belt drive problems

APPENDIX 5—Fired Heater Inspection Checklist

Unit: Date:
Equipment no.:

1. TUBE AND FITTINGS INSPECTION
    a) RADIATION
        Visual inspection
        i) Tube condition:
        ii) Fittings condition:
        iii) Weld joint:
        iv) Tubes seating on support:
        Thickness check
        i) Tube:
        ii) Fittings:
    b) CONVECTION
        Visual inspection
        i) Tube condition:
        ii) Fittings condition:
        iii) Weld joint:
        iv) Tubes seating on support:
        Thickness check
        i) Tube:
        ii) Fittings:
    c) SUPERHEATER COILS
        Visual inspection
        i) Tube condition:
        ii) Fittings condition:
        iii) Weld joint:
        iv) Tubes seating on support:
        Thickness check
        i) Tube:
        ii) Fittings:
2. TUBE SUPPORTS INSPECTION
    a) RADIATION
        i) Tube hangers:
        ii) Guides:
        iii) Spigots:
    b) CONVECTION AND STEAM COILS
        i) Tube sheets:
3. THERMOCOUPLES
    a) Radiation
        i) Number of thermocouples:
        ii) Visual inspection of welding:
        iii) DP of weld joint:
    b) Convection
        i) Number of thermocouples:
        ii) Visual inspection of welding:
        iii) DP of weld joint:

4. REFRACTORY LINING INSPECTION
    a) RADIATION
        i) CF lining:
        ii) Castable:
    b) CONVECTION
        i) CF lining:
        ii) Castable:
    c) FLOOR
        i) Castable:
        ii) Bricks:
    d) Stack
        i) Castable:
5) MISCELLANEOUS ATTACHMENTS
    a) Explosion doors:
    b) Dampers:
    c) Flue gas ducts:
    d) Header box:
    e) Peephole (field of view):
    f) Inspection doors:
6) BURNERS
    a) Numbers installed:
    b) Condition:
7) AIR PREHEATER
    a) Duct lining and insulation:
    b) Glass module:
    c) Cast module:
8) SOOT BLOWERS
9) EXTERNAL PAINTING
10) FOUNDATION
11) STRUCTURES
12) HYDROTEST
    a) Date:
    b) Media:
    c) Pressure
13) STRESS RELIEVING
14) RADIOGRAPHY
15) REMARKS

INSPECTED BY:

APPENDIX 6—Pressure Vessels Inspection Checklist

Unit: Date:
Equipment no.:
Service:
REASON FOR INSPECTION
Shutdown
On-stream
Breakdown

1) INTERNAL INSPECTION
    a) Top zone
        i) Scaling nature
        ii) Dome
        iii) Shell
        iv) Welding
        v) Nozzle welding
        vi) Internals
        vii) Spouts and counterspouts
    b) Middle zone
        i) Scaling nature
        ii) Shell
        iii) Welding
        iv) Nozzle welding
        v) Internals
        vi) Spouts and counterspouts
        vii) Impingement plate
    c) Bottom zone
        i) Scaling nature
        ii) Shell
        iii) Welding
        iv) Nozzle welding
        v) Steam coils
2) EXTERNAL INSPECTION
    a) Foundation and foundation bolts
    b) Insulation
    c) External corrosion
    d) Ladder and staircase
    e) Nozzle flanges
    f) Bosses and nipples
    g) Grounding connections
    h) Testing nipple and liners on nozzle
3) THICKNESS SURVEY OF EQUIPMENT INCLUDING ALL NOZZLES Yes/No
4) CONDITION OF INTERNAL LINING
5) REPAIR, IF ANY
6) CORROSION COUPONS Yes/No
7) REMARKS

INSPECTED BY:

APPENDIX 7—Heat Exchanger Inspection Checklist

Date:
Unit: Equipment no.: Service:
Brief description of last inspection
Whose requirement IP/PN
Bundle pullout Yes/No
Agency Contractor/MRS
Cleaning Mechanical/chemical/both mechanical and chemical
No. of tube Total
  Already plugged
  Recent plugging
  Total plugging
Shell
Shell nozzles
Channel
Channel nozzles
Painting
Tubes
Baffle
Floating head
FH seat
Anodes
Hydraulic testing
Shell (kg/cm^2): Tube (kg/cm^2):
Recommendations

INSPECTED BY:

APPENDIX 8—Storage Tank Inspection Checklist

Tank No. **Service:** **Inspection Date:**
Type of inspection: External/internal

OBSERVATIONS OF EXTERNAL INSPECTION

1.0	**Tank Pad Foundation**	**Y/N**	**Observations**
1.1	Foundation pad is free from cracks settlements/erosion/ vegetation growth etc.		
1.2	No voids found between annular plate extensions and foundation surface.		
1.3	Foundation slope is satisfactory to avoid water stagnation.		
1.4	Tank is free from abnormal/ uneven settlement.		
2.0	**Annular Plate Extension**	**Y/N**	**Observations**
2.1	Annular plate extensions are free from corrosion, pitting, and scales, and the painting condition is satisfactory.		
2.2	Annular plate thickness readings are satisfactory.		
3.0	**Shell Plates (External)**	**Y/N**	**Observations**
3.1	Shell plates are found free from corrosion patches, pitting, and scales, and the painting condition is satisfactory.		
3.2	Shell plates are free from abnormal dents/buckles.		
3.3	Shell plates are free from sweating/leaks/cold weld/repairs/ patch plates.		
3.4	Reinforcement pads are in satisfactory condition at nozzles.		
3.5	Wind girders are found in satisfactory condition without corrosion patches and sagging.		
3.6	Supports for connected piping/ nozzles are in satisfactory condition without unduly stressing the shell plates.		
3.7	Shell plates, nozzles, steam coil nozzles, manholes, cleanout doors, etc., thickness readings are satisfactory.		
3.8	Condition of foam/sprinkler lines and foam deflectors plates was satisfactory.		
4.0	**Cone Roof Plates (Fixed Roof)**	**Y/N**	**Observations**
4.1	Roof is free from corrosion patches and painting condition is satisfactory.		
4.2	Thickness readings of roof plates are satisfactory.		
4.3	Flame arrestor condition (if provided) is satisfactory.		
4.4	Roof vents condition is satisfactory.		
4.5	Foam system/hydrant lines condition is satisfactory.		
5.0	**Floating Roof**	**Y/N**	**Observations**
5.1	Roof is free from corrosion patches and painting condition is satisfactory.		
5.2	Roof plates weld joints are found satisfactory without any sweating/ leaks.		
5.3	Roof is free from patch plates/cold weld repairs.		
5.4	Thickness readings of roof plates are satisfactory.		
5.5	Pontoon compartments are free from leaks/sweating/corrosion and painting condition is satisfactory.		
5.6	Primary seals are in satisfactory condition (neoprene sheet and foam).		
5.7	Condition of weather shrouds was satisfactory.		
5.8	Deck support legs and pipe sleeves are in satisfactory condition.		
5.9	Main drain including sump and NRV/emergency drains are checked and conditions are okay.		
5.10	Roof drain valve was found opened.		
5.11	Condition of rim vents/PV valves/ breather valves was satisfactory.		
5.12	Sample/dip hatch pipe condition and rollers/brass sleeves are in satisfactory condition.		
5.13	Rolling ladder and its runway condition are satisfactory.		
5.14	Condition of foam dam plates are satisfactory.		
6.0	**Appurtenances/Attachments**	**Y/N**	**Observations**
6.1	Condition of earthing are satisfactory. • Between floating roof and ladder • Between rolling ladder and shell • Between shell and earth		
6.2	Condition of insulation and claddings are checked and found satisfactory in insulated tanks.		
6.3	Sealing of insulation around manways and nozzles are satisfactory.		

(*Continued*)

APPENDIX 8—Storage Tank Inspection Checklist (Continued)

OBSERVATIONS OF INTERNAL INSPECTION

6.4	Condition of staircase, handrails, etc., and paintings are satisfactory.		
6.5	Condition of siphon drains was satisfactory.		
6.6	Condition of cleanout doors was satisfactory.		
7.0	**Bottom Plates and Internals**	**Y/N**	**Observations**
7.1	Bottom plates' painting condition is satisfactory.		
7.2	Shell plates' painting condition is satisfactory.		
7.3	Roof plates and structure painting condition is satisfactory.		
7.4	Condition of outer rim of pontoons including painting (in fixed roof tanks) was satisfactory and no appreciable corrosion/pitting was observed.		
7.5	Condition of weld seams in first two courses (horizontal and vertical joints) is found satisfactory without grooving, pinholes, and cracks.		
7.6	Shell plates are free from closely located deep pitting.		
7.7	Shell plates are free from patch plates/cold weld repairs.		
7.8	Shell to bottom plate joint is found satisfactory.		
7.9	Edge settlement is within the reasonable limit.		
7.10	Bottom plate weld seams are in satisfactory condition.		
7.11	No appreciable corrosion/pitting on bottom plates was observed.		
7.12	Bottom plates are found without patch pipes/cold weld repairs.		
7.13	Bottom plate thickness readings were satisfactory and no appreciable thickness loss was observed.		
7.14	Swivel joints and their piping conditions were satisfactory. Swivel joint revisioning and hydrostatic testing was done at 3.5 kg/cm^2 and was found to be satisfactory.		
7.15	Roof support column and its reinforcement pad (if provided) are in satisfactory condition.		
7.16	Structural under roof plates viz. rafters, fasteners, gussets, etc., are checked and found to be satisfactory.		
7.17	Condition of Sacony mixture (nozzles/supports/pipe) is satisfactory.		
7.18	Steam coils (if any) are surveyed for thickness, supports, and hydraulically tested at 13.5 kg/cm^2. Condition found satisfactory.		

8.0	**Details of Tanks Nozzles/Manholes/Clean Outdoors**		
	Nozzle Identity	**SIZE/NB**	**Observed Thickness**
8.1	Inlet		
8.2	Outlet		
8.3	Roof drain		
8.4	Siphon drain 1. 2.		
8.5	Shell manway 1. 2.		
8.6	Recirculation line		
8.7	Jet mixture 1. 2.		
8.8	Temperature gage		
8.9	Foam connections 1. 2.		
8.10	Steam coils 1. 2.		
8.11	Cleanout doors 1. 2.		
8.12	Any other nozzles		

9.0	**Any Other Specific Observations, If Any**

INSPECTED BY:

APPENDIX 9—High-Pressure Boilers Checklist

Date:

VISUAL INSPECTION

1) STEAM DRUM
    - Internal:
    - External:
2) MUD DRUM
    - Internal:
    - External:
3) ECONOMIZER COILS
4) SUPERHEATER ASSEMBLIES
    - Platen superheater
    - Final superheater
5) DESUPERHEATER (DESH)
6) SUPPLY TUBES
7) WATER WALL TUBES
8) WATER WALL HEADERS
9) RISER TUBES
10) SATURATED LINKS
11) REGENERATIVE PREHEATER
12) STEAM COIL PREHEATER
13) DUCT EXPANSION BELLOWS
14) SOOT BLOWERS
15) SAFETY VALVES
16) SKIN THERMOCOUPLES
17) BURNERS
18) ALLOY ANALYSIS
19) RADIOGRAPHY
20) STRESS RELIEVING
21) REFRACTORY
22) THICKNESS SURVEY
23) PAINTING
24) SAFETY VALVE FLOATING
25) HYDROTESTING

INSPECTED BY:

APPENDIX 10—Pipeline Inspection Checklist

PIPELINE IDENTITY:

Inspection Date:

SN	Checklist Points	Y/N	Observations
PHYSICAL CONDITION			
1.1	Ground clearance of the piping is adequate.		
1.2	Pipeline is free from any visible sweating/leakage.		
1.3	Pipeline is free from dents, cracks, scratches, impingements, and any mechanical damages.		
1.4	Pipe is accessible for inspection under the culvert.		
1.5	Pipeline route is clear without vegetation in aboveground portion.		
THICKNESS SURVEY			
2.1	Thickness survey conducted for aboveground portion. The results are satisfactory to continue to operate the pipeline (attach thickness survey).		
2.2	Thickness survey conducted in underground piping on sample basis after removal of wrapping/coating and found satisfactory.		
SUPPORTS			
3.1	Condition of supports (with respect to damage/distortion in concrete pedestal, roller GI pipe, sinking of support, etc.) is satisfactory.		
3.2	Saddle plates provided at the pipe supports are welded all along the periphery to prevent water ingress.		
3.3	Piping is anchored properly near the expansion loops.		

SN	Checklist Points	Y/N	Observations
CORROSION AND ITS PROTECTION			
4.1	Painting condition of the aboveground pipeline throughout its length found satisfactory.		
4.2	Pipeline outer surface are found without deep pitting/corrosion attack, etc.		
4.3	Check for wrapping/coating of pipelines crossing roads/dykes/boundary walls and also for proper sealing of the sleeve pipes at ends.		
THERMAL INSULATION			
5.1	Insulation/cladding of pipe is found satisfactory.		
5.2	Steam tracer lines are free from leakage.		
LPDS & OTHER TAP-OFF FITTINGS			
6.1	All branch pipelines including tap-off points for instruments and sampling points are surveyed and general conditions found satisfactory without cracks/leakage.		
6.2	Blinds used at the dead ends are satisfactory.		
6.4	All flange joints are leak free.		
6.5	Expansion joints are found to be free of leaks.		
7.0	Any other observations		

INSPECTED BY:

APPENDIX 11—On-Stream Inspection Format of CDU/VDU/NSU

DATE:
THROUGHPUT: m^3/hr
TYPE OF CRUDE: LS/HS
REMARKS/AREAS OF CONCERN:
SKIN TEMPERATURE.

Furnace	Design Limit ^{0}C	Maximum Skin Temperature (^{0}C)	Visual Condition of Furnace
Crude heater			
Vacuum heater			
NSU heater			

Heater Draft: (mm of WC): **CDU heater:**
VDU heater: **NSU heater:**
COLUMN TOP TEMPERATURE
ATMOSPHERIC COLUMN TOP TEMPERATURE–
LIMIT: —/— °C (Min)
VACUUM COLUMN TOP TEMPERATURE–
LIMIT: —/— °C (Min)
pH AND CHLORIDE OF SOUR WATER

Overhead Accumulator	pH (Limit: 5.5–6.5)	Chloride (Limit: <20 ppm) (Previous Day's Result)	Fe (Limit: <1 ppm) (Previous Day's Result)
-VV-01			

DESALTER Yes/No Water injection ________ m^3/hr
OPERATING:
DPC 1201/1202 ________ kg/cm^2 ________ Temperature: °C
SALT CONTENT OF CRUDE:
Pre-Desalter: Post-Desalter (Limit: < 0.5 ptb):
CHEMICAL DOSING PUMPS:
CORROSION INHIBITOR: Yes/No
AMMONIA: Yes/No
NEUT. AMINE: Yes/No
DEMULSIFIER: Yes/No
CAUSTIC: Yes/No
TSP: Yes/No

INSPECTED BY:

APPENDIX 12—On-Stream Inspection Format of CCRU

DATE:

THROUGHPUT, m^3/h (HYD./REFORMER):

A) HEATERS

		Skin Temperature (°C)					**Arch. Temperature °C**	**Flame Condition**
Heater No.	**Cot °C**	**Pass 1**	**Pass 2**	**Pass 3**	**Pass 4**	**Design Limit**		
-F-101								
-F-102								
-F-204								

STACK TEMPERATURE 1. IFP HEATERS:
2. NON-IFP HEATERS:

B) COLUMNS

	Top Temperature °C		
Column No.	**Observed**	**Limit**	**Inhibitor Dosing (Y/N)**
-C-101			
-C-201			

C) pH VALUES

Vessel No.	**Ph Values**		**Remarks**
	Observed	**Limit**	
-V-102			
-V-104			
-V-701			

D) STATIC EQUIPMENT UNDER MAINTENANCE:

E) REMARKS/AREAS OF CONCERN:

INSPECTED BY:

APPENDIX 13—On-Stream Inspection Format of VBU

THROUGHPUT (m^3/h): DATE:

A) HEATER

		Skin Temperature °C		
Tag No.	**Cot**	**Observed (Max)**	**Limit**	**Flame Imp. (Y/N)**
-F-01				

B) COLUMN

	Top Temperature °C		
Tag No.	**Observed**	**Limit**	**Inhibitor Dosing (Y/N)**
-C-01			

C) Ph VALUE

	Ph Values		
Tag No.	**Recorded**	**Limit**	**Remarks**
-V-01			

D) STATIC EQUIPMENT UNDER MAINTENANCE:

E) REMARKS:

INSPECTED BY:

APPENDIX 14—On-Stream Inspection Format RFCCU

THROUGHPUT (m^3/h) DATE:

1. FEED HEATER

Skin Temperature, °C				**Box Temperature, °C**	
T. No.	**Pass 1**	**Pass 2**	**Limit**	**Radiation**	
				Arch	
				Stack	
Flame Condition:				COT: Draft: mm WC	

2. RR–SECTION TEMPERATURE

Equipment	**Limit, °C**	**Dense Bed, °C**	**Dilute Phase, °C**
RG-1			
RG-2			

3. MAIN FRACTIONATING COLUMN

Top Temperature (°C):	**Overhead pH:**

4. FLUE GAS COOLER (07-LW-00-001): Generation: T/h

Bfw			**Blowdown**		
Parameter	**Limit**	**Observed**	**Parameter**	**Limit**	**Observed**
pH	> 9		Condition (μmho/cm)	<2500	
Silica (ppm)	<.02		Silica (ppm)	<10	
Residual N_2H_4	>0		PO_4 (ppm)	<15	

CHEMICAL DOSING:

Morpholene: Y/N	**Hydrazine: Y/N**	**Trisodium Phosphate: Y/N**

1. STATIC EQUIPMENT UNDER MAINTENANCE:
2. REMARKS:

INSPECTED BY:

APPENDIX 15—On-Stream Inspection Format (OHCU/HGU/DHDS)

A. OHCU DATE:

1. FURNACE

Furnace	**F-01**	**F-501**	**F-502**	**F-503**
Max Skin Temperature				

2. COLUMN TOP TEMPERATURE

Fractionator		**Stripper**	

3. AHURALAN INJECTION/WATER INJECTION (YES/NO)

Debutanizer Column	**Stripper Column**	**DM Water In Reaction System**

4. STATIONARY EQUIPMENT UNDER MAINTENANCE:

REMARKS

B. HGU

1. REFORMER HEATER

	Skin Temperature (Max Limit– °C)					
Cell	**T# 1**	**T#15**	**T#30**	**T#45**	**T#60**	**T#75**
South-AB						
North-CD						

2. COLD COLLECTOR SKIN TEMPERATURE (MAX LIMIT– °C):
3. CHEMICAL DOSING (MORPHOLINE/HYDRAZINE/TSP) YES/NO
4. pH (LIMIT): STEAM DRUM ________
   DEAREATOR ________
5. STATIONARY EQUIPMENT UNDER MAINTENANCE:

REMARKS

C. DHDS

1. FEED HEATER SKIN TEMPERATURE (MAX LIMIT– °C):
2. CHEMICAL DOSING (CORROSION INHIBITOR) YES/NO

Stripper Column		**Stabilizer Column**	

3. STATIONARY EQUIPMENT UNDER MAINTENANCE:

REMARKS:

INSPECTED BY:

APPENDIX 16—CPP On-Stream Inspection Report Format

Date:

Unit	Load (T/H)	Flame Condition	Raph Air		Raph F Gas		Remarks
B#1							
B#2							
B#3							
HRSG							

Equipment/ Stream	Parameter	Limit	Observed	Remarks
	pH	8.8–9.2		
	Dissolved O_2	5 ppb (max)		
	Silica	0.01 ppm (max)		
	Conductivity	0.3 μó/cm (max)		
	Residual hydrazine	0.01–0.02 ppm		
Drum water B1/B2/B3	pH	9.2–10.0		
	Silica	2.0 ppm (max)		
	Conductivity	200 μó/cm (max)		
	Residual phosphate	5–20 ppm		
Superheated steam	Silica	0.02 ppm (max)		
Chemical dosing	Hydrazine Morpholine Phosphate	Yes/No Yes/No Yes/No		
Note: Any static equipment failure/under maintenance:				

INSPECTED BY:

APPENDIX 17—On-Stream Inspection Format of SRU Block

Date:

A) BBU (U-10)
HEATER (10-F-001)

Max Skin Temperature (Limit–°C)	**Box Temperature (°C)**	**COT (°C)**	**Flame Condition**

Static equipment under maintenance:
B) BBU (U-10)
COLUMNS

	Top Temperature °C		**Remarks**
	Limit	**Observed**	
-C-01			
-C-02			

- pH VALUES

Refinery SWS Limit (6.0–7.0)		**OHCU SWS Limit (6.0–7.0)**	
-V-01 Sour Water	-C-01 Stripped Water	-V-02 Sour Water	-C-03 Stripped Water

Static equipment under maintenance:
C) ARU (U-21)
COLUMN (21-C-02)

Top Temperature (°C)		**Inhibitor Dosing (Yes/No)**	**Remarks**
Limit	Observed		

Static equipment under maintenance:
D) SSRU (U-44)
- MCC Box
- Stack Top Temperature (Limit > 190 °C)

E) SRU (U-22)

INSPECTED BY:

APPENDIX 18—Special Tools/Gadgets Used In Mechanical Maintenance

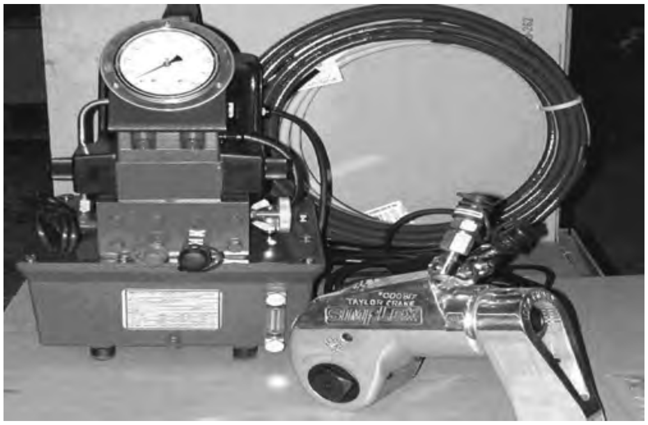


Figure 16.8—Hydraulic torque wrench.

Figure 16.9—Scissor lift.

Figure 16.10—The bundle puller.

Source (Figures 16.8–16.10): Maurya, S.L., Ghosh, A., Paranjape, D.B., and Kacker R., “Indian Oil's Reliability Improvement Report (Refineries Division),” Indian Oil Corporation Ltd., New Delhi, India, 2005.

17

Corrosion Inspection and Control in Refineries

Jorge L. Hau[1]

17.1 INTRODUCTION

Crude oil by itself should not be corrosive to metals, but when extracted, it contains water, sulfur-organic compounds, nitrogen compounds, salts, organic acids, and other contaminants that make it corrosive to metals and alloys used to manufacture equipment and piping. The use of high temperatures and pressures in oil refining processes can create particular corrosive environments. Additions made to the process as raw material or as catalysts can also create particular corrosive environments to these metallic materials. Thus, the materials of construction of pressure vessels, heat exchangers shell and tube bundles, air coolers, piping, piping accessories, column trays, packing material, and other pieces of equipment can be subjected to a rather large variety of corrosion and other damage mechanisms. If not properly recognized and managed, they can lead to increased risk of material failures. Successfully and safely operating the petroleum refining industry is thus the challenge facing corrosion engineers in this industry. This chapter provides a brief overview of the topic of refining industry corrosion and, to a lesser extent, corrosion control and inspection. This topic is very extensive so readers are encouraged to refer to other books related to the subject [1–4].

Understanding the petroleum refining process is of paramount importance to material engineers, corrosion engineers, and inspection personnel involved in this industry. Descriptions of these processes are found elsewhere in this manual. In this chapter, the unified numbering system (UNS) is used to refer to corrosion resistant metals and alloys; more generic names are used for most common materials.

17.2 WET CORROSION

The crude oil is fed to the crude distillation unit where steam is injected into the distillation tower to aid fractionation. Steam is also used in ejectors to create vacuum in vacuum distillation units, sometimes in the coils of furnaces as velocity steam to reduce residence time and internal coke formation, and as stripping or heating medium in many parts of the oil refining processes. Thus, steam and water are necessary parts of the refining petroleum process but, at the same time, they represent a source of wet corrosion.

17.2.1 Crude Unit Overhead Corrosion

The corrosion that is the subject of this section includes the top trays or packing, the overhead piping of the atmospheric distillation tower, the reflux line at the top of the distillation tower, the heat exchangers, and the condensers, pumps, and drums in the overhead system. Because of the high temperatures used in atmospheric and vacuum distillation units, calcium and magnesium chloride salts present in the crude oil hydrolyze to form hydrogen chloride (HCl) gas, which, in the presence of moisture and water, forms corrosive hydrochloric acid. Sulfur and organic acids also thermally decompose in the furnace and form hydrogen sulfide (H_2S) and carbon dioxide (CO_2). It has been stated that organic acids can also form by thermal degradation of crude oil components such as naphthenic acids. All these acid gases separate from the liquid and go to the top of the distillation tower and the overhead system, together with steam, naphtha, and light end products (butanes, propane, ethane, and methane). At the typical crude unit overhead temperatures of 90 °C to 180 °C, the overhead stream becomes corrosive when water condenses and dissolves these acid gases. Presence of other contaminants such as oxygen, ammonia (NH_3), amines, and other chemicals, adds to the species contributing to corrosion problems in the overhead system. Most of the corrosion and other damage mechanisms affecting metallic materials in oil refining are described in API RP 571 [5].

Crude unit overhead corrosion is widely described in the literature [6–8]. Amine-based products unintentionally or intentionally added to the crude oil can also separate from the crude oil during distillation and move upward in the tower. The amines, NH_3, or both can combine with HCl and form ammonium chloride salts (NH_4Cl), amine hydrochloric salts, or both and become a source of fouling and severe corrosion for the upper trays or packing beds in the distillation tower.

Some units have a preflash column where light naphtha and lighter components are removed from the feed and either sent directly to the crude overhead system or processed separately in downstream units. A preflash column overhead may operate at a temperature low enough that it can face similar corrosion problems as the atmospheric tower overhead system. Because this corrosion depends on water condensation, the overhead system temperature is a determining factor. The tower top temperature in some units is near or below the water dew point and hence water starts condensing within the top of the tower. Naphtha is raw gasoline that does not condense within the atmospheric column but goes overhead as vapors together with water vapor. Units with a two-stage overhead system are designed so that the first stage does not condense water but only naphtha; the remaining naphtha and water condense in the second stage. The corrosion problems in these systems occur in the second stage and are similar to those in single-stage overhead systems. Thus, depending on the unit design and operation, the tower top temperature may

---

[1] Shell Projects and Technology, Shell Global Solutions (U.S.), Inc., Westhollow Technology Center, Houston, TX, USA

vary and water condensation is expected to occur when the temperature of the overhead vapor stream reaches the dew point that depends also on the pressure in the system and the water vapor content. However, condensation can also occur upstream of the initial condensation point in cold spots caused by loss of insulation on the tower and overhead piping, cold weather, or even by cold reflux entering the column. This is referred to as shock condensation.

In spite of the several mitigation methods used for crude overhead corrosion control, the corrosion and fouling problems persist in many refineries. There have been problems with desalting [9], tower top temperature variation, spot or shock condensation, and presence of tramp bases or other uninvited contaminants. There have also been concerns about the presence of no extractable chlorides [10] because of reported problems. These are usually non-water-soluble organic chloride compounds that are not removed by desalting. They only partially hydrolyze in the crude heaters and the HCl thus produced joins the HCl normally produced by inorganic chloride salts. The remaining non-hydrolyzed portion of the organic chlorides is carried away with the naphtha and upper side streams. Attempts have been made to identify the impact of amine contaminants [11] and amine-based H_2S scavengers [12] on the corrosion in crude distillation units. All these factors may cause loss of pH control, loss of corrosion inhibition, increased initial condensate corrosion, increased fouling by hydrochloric neutralization salts and increased pitting or localized corrosion under deposit. When water separation is inefficient, the naphtha reflux may carry some of the neutralized water to the tower and once there, salts may deposit on trays and packing as this water evaporates. If these salts form or fall on draw-off trays, they can also be taken with the side stream to downstream units.

17.2.1.1 CORROSION-RESISTANT MATERIALS FOR CRUDE OVERHEAD CORROSION

Carbon steel is still the most common metallurgy used for heat exchanger tubes in the crude distillation unit overhead systems. Some units have crude feed/overhead vapor exchangers to start heating the feed with the overhead vapor stream. Most crude units have overhead condensers that could be of the shell/tube bundle type or fin fan air coolers. In the case of cooling water condensers, this water is normally oxygenated and the life of carbon steel bundles may be limited because the tubes suffer corrosion on the cooling waterside and the process side as well. Standard austenitic stainless steels of the series 300 could resist the general corrosion, but because of their susceptibility to chloride SCC (Cl SCC), they are not normally used. Austenitic stainless steels of the series 300 are also susceptible to under-deposit chloride-induced pitting on both the cooling waterside and process side. Duplex stainless steel S31803/S32205 and super duplex stainless steel S32750 can be used instead of 300 series stainless steels. Cu-Ni alloys C70600, C71500, and N04400 have been used. Admiralty brass metals C44300, C44400, and C44500 are used, but they are susceptible to NH_3 stress corrosion cracking (NH_3 SCC).

Alloy N04400 has traditionally been used as clad material, trays, packing, and other internal components in the crude distillation tower top. It is resistant to the HCl corrosion prevailing in the crude distillation unit overhead for most conditions but it has also failed by severe corrosion. The corrosion of trays, packing, and demister made of alloy N04400 and trays made of super austenitic stainless steel alloy N08367 have been attributed to amine hydrochloric or NH_4Cl salt corrosion. The environment developed under these deposits is aggressive enough to completely dissolve these alloys, particularly if the components are made of thin metal sheets. Alloy N06625, N10276, grade 2 titanium, or grade 12 titanium may offer better corrosion resistance but when there are problems related to fouling and corrosion with these salts inside the distillation tower, it is best to treat the source and thus prevent salt deposition from occurring. Grade 2 is commercially pure unalloyed titanium; grade 12 titanium (Ti 0.8Ni-0.3Mo) is alloyed with nickel and molybdenum. Alloy Ti-0.3Mo-0.8Ni (grade 12) has applications similar to those for unalloyed titanium (grade 2) but has better strength and corrosion resistance. Changing the metallurgy of the internal components at the top of the tower should be the last resort.

17.2.1.2 VACUUM UNIT OVERHEAD CORROSION

Most of the subject of overhead corrosion and control is devoted to atmospheric crude units, but vacuum distillation column overhead can also suffer similar corrosion problems even though most vacuum units operate without added steam and are therefore drier. Even if there were steam in the vacuum distillation tower, it would not condense because of the vacuum in the overhead system; this is until the overhead stream reaches the condenser shells. Some salts do not hydrolyze in the atmospheric crude distillation furnaces but in the vacuum distillation furnaces. The resulting hydrogen chloride vapor moves to the top of the vacuum distillation column and vacuum column overhead system. HCl corrosion can hence occur in the condenser shells, the outside surface of the tubes in these condensers, and in the receiver drum (the hot well). Because of the higher temperatures normally used in the furnaces of vacuum units, as compared with crude distillation unit furnaces, further decomposition of sulfur species occurs that produces H_2S that travels to the vacuum tower overhead. Organic nitrogen compounds can also decompose and produce NH_3. Some refineries inject amine neutralizer and filmer inhibitor into the overhead system of the vacuum distillation unit to control corrosion. Oxygen can enter the vacuum system with air leaking connections and accelerate corrosion. Some corrosive organic acids may form because of this oxygen and contribute to the corrosion of carbon steel. In general, however, vacuum overhead system corrosion is far less severe than corrosion in crude unit overhead systems.

17.2.2 Wet H_2S Corrosion and Cracking

There is a considerable amount of published literature on the subject of wet H_2S cracking of steels [13]. The wet H_2S environment is defined as that having a total sulfide concentration greater than 50 ppmw in the aqueous phase or even at least 1 ppmw if the pH is lower than 4.0. In the gas phase, when handling only gases, the requirement is to have more than 0.0003 MPa partial pressure of H_2S [14]. It is not uncommon to have 50 ppmw or more total sulfide in the water collected in the overhead systems of both atmospheric and vacuum distillation. The pH of this water is usually higher than 4.0, but without neutralization the pH can certainly decrease to less than 4.0. Therefore, if these definitions are applied, the carbon steel equipment in the overhead systems of both atmospheric and vacuum distillation units would have to be considered in wet H_2S service. This means that pressure vessels in this service should comply with certain requirements when newly fabricated [15–17] and the refinery should comply with certain inspection practices for pressure vessels in service [18]. These actions add cost to the construction of new equipment and to the maintenance of existing equipment because of the special inspection required for crack detection and other wet H_2S-related damage mechanisms.

The required pressure and stress level to activate wet H_2S SCC is not addressed in these recommended practices and standards dealing with this topic. If the pressure is vacuum or near atmospheric in the overhead systems, there is no driving force for cracks to propagate through thickness, except for the residual stresses. Residual stresses may be as high as the yield strength of the steel but are confined to a small area beyond which crack growth will arrest. The typical operating pressure at the overhead system of crude distillation columns is 0.10–0.21 MPa so the required design for pressure vessels, piping, heat exchanger shells, and fin fan cooler header boxes can be thin-wall construction. The wall thickness is a determining factor for the hardness and the residual stress of carbon steel weldments. Welding thin wall vessels may neither result in hard heat-affected zone (HAZ) nor in high residual stresses in common carbon steels used to fabricate refinery equipment using standard welding methods and procedures. However, shallow single pass welds used as internal attachment welds or to fill pits may result in hard HAZ and welds susceptible to wet H_2S SCC, and these should be avoided. These attachment welds should be made using at least two passes and high heat input for welding. Equipment with pitting damage should be evaluated to determine whether they need to be repaired or left as they are. If repairs are required, proper repair procedures should be used.

It is found that some refineries include their crude and vacuum overhead system equipment in wet H_2S service and some do not. A risk-based inspection approach [19] is recommended to deal with these inspection issues. A strategy is often adopted to remove items from the special wet H_2S cracking inspection list when two or three separated inspections have already been performed, each after at least one unit run, and no indications are found. This would be valid provided the operating conditions remain unchanged.

The wet H_2S damage mechanisms are more relevant in refinery process units that handle higher H_2S concentrations than crude distillation. The high temperatures used in processes like visbreaking, fluidized catalytic cracking unit (FCCU), delayed coker, and other thermal cracking processes produce significant amount of H_2S. In hydroprocessing the desulfurization occurs by converting organic sulfur compounds into H_2S that is then removed from the treated product.

The wet H_2S phenomenon involves the corrosion reaction of H_2S with the steel and the generation of hydrogen, which, rather than combining with another hydrogen atom and evolving as gas that moves away from the steel, it enters and diffuses into it. Just by being inside the steel, if this is harder than about 22 HRC (Rockwell hardness, scale C), this dissolved hydrogen can cause H_2S SCC. The phenomenon is dependent on hydrogen flux, but it will not occur if the steel is not hard enough, the stress is not high enough, or both.

Susceptibility to wet H_2S damage not only depends on the corrosive environment but also on the carbon steel type. Hydrogen-induced cracking (HIC) and hydrogen blisters (H_2 blisters) depend on cleanliness of the steel. Even if the steel is not harder than 22 HRC, as hydrogen atoms diffuse through the steel, they can be trapped in nonmetallic inclusions, combine with another hydrogen atom to form hydrogen gas within these defects, and build up enough H_2 pressure to create a HIC. If the HIC were well inside the wall thickness, the crack would not be apparent from the surface and would be detectable only by ultrasonic inspection means. If the HIC is close enough to the steel surface, the build-up of H_2 pressure at the defect can cause a bulge on the surface and thus it produces a H_2 blister. HIC can occur isolated, randomly distributed, or aligned in a step-like form, in which case it is referred to as step-wise cracking. In the presence of high-tensile stress, several HICs can form aligned in the through-wall direction, one form of which becomes SOHIC (stress-oriented hydrogen-induced cracking). The most critical wet H_2S damage is SCC followed by SOHIC, HIC, and H_2 blisters.

HIC and H_2 blistering can form a single and large crack extending parallel to the vessel wall or numerous and rather small cracks. If there is concern with the integrity of the vessel due to widespread H_2 blistering, HIC, or both, a window is sometimes cut to remove the most affected area and an insert plate is welded in place. The usual recommendation is to post-weld heat treat (PWHT) after weld repair, but if H_2 blisters or HIC are left in the steel that is not replaced the H_2 trapped will cause high-temperature hydrogen attack at the temperatures and times typically used in PWHT [20]. There have also been instances where residual HIC has developed into very large bulges during post-weld heat treatment as the steel softens and the hydrogen pressure inside these existing HIC greatly increase with increasing temperature during this heat treatment.

The concern about wet H_2S corrosion service is mainly with pressure vessels. Most refineries do not specify post-weld heat treatment or inspection for wet H_2S SCC for carbon steel piping made of seamless fully killed low strength carbon steel (e.g., ASTM A-106, grades A and B). Seamless pipe circuits have only circumferential welds to join pipe with pipe, and branch connection and attachment welds. Butt welds in these piping circuits are made with multipass welding where subsequent weld beads soften the weld pass and associated heat affected zone underneath. It was once stated that welding piping from outside only would leave a compressive residual stress system that does not favor SCC. However, occurrence of stress cracking in alkaline media, such as caustic and amine, has demonstrated that this is not true; there is a residual tensile stress system at the welds of these piping circuits; otherwise caustic or amine SCC would not occur. Thus, hardness is most likely the reason wet H_2S stress cracking does not occur in seamless low strength carbon steel type ASTM A-106 grades A and B. Also, the threshold level of the tensile stress required to cause SCC is believed to be much lower for alkaline SCC than for wet H_2S stress cracking. The presence of cyanides (HCN) is known to considerably increase hydrogen flux because they destroy the protective iron sulfide layer. Carbon steels exposed to hydrofluoric acid (HF) may experience damage [21] in a very similar manner as in wet H_2S environment. The HF environment is present in the HF alkylation process.

17.2.3 Ammonium Bisulfide Corrosion

H_2S and NH_3 react to form ammonium bisulfide (NH_4HS). The concentration of NH_4HS is not very high in visbreaker, FCC, delayed coker, and fluidized coker units, which is why carbon steel is still suitable for most equipment and piping used in the recovery units where light end products from these units are fractionated.

NH_4HS corrosion is a well-known concern in hydroprocessing units. The reactor effluent stream is cooled from about 120 °C–200 °C to 37 °C–66 °C using fin fan coolers. This system has been known as the reactor effluent air cooler (REAC), although shell/tube bundle cooling water exchangers are also used. The main problem is fouling due to the presence of NH_4HS [22]. To avoid NH_4HS salt deposition water wash is necessary to dissolve and wash away this salt, but in doing so water is introduced that becomes corrosive itself. Thus, the corrosion is associated with salt deposition and concentrated NH_4HS solution. High fluid velocities have the effect of removing the protective iron sulfide layer that forms on the metal surface and thus greatly accelerate the corrosion.

Oxygen introduced by the water injected into the hydrocarbon stream can accelerate corrosion. Chloride present in the feed or introduced by the use of catalytic reformer hydrogen does not seem to make NH_4HS corrosion any worse but NH_4Cl salt can start precipitating at a temperature higher than that for NH_4HSI. NH_4Cl salts formed upstream of the wash-water injection point can cause fouling and severe under deposit corrosion if these salts absorb moisture.

The problems with REAC corrosion have persisted [23] in otherwise noncorrosive conditions for unfavorable fluid distribution to the condenser system. The cause of corrosion is reasonably well understood, but it is recognized that is a complex phenomenon that depends on a larger number of variables, other than just the presence of H_2S/NH_3, NH_4HS concentration, and velocity. There is usually a bank of air coolers, several cooling water shell/bundle exchangers, or both in the REAC. The design of the incoming piping to these condensers is a significant variable, a balanced design being preferred because of equal distribution of hydrocarbon and wash water and minimum differences in velocity among the several condensers.

Recent research results were published [24] that depart from rules of thumb previously applied to these systems. The statement that corrosion is low at NH_4HS concentration of 2 wt % or less still seems valid, with the added information that the effect of velocity at this concentration is only marginal. At intermediate NH_4HS concentration of 2 to 8 wt %, low to moderate corrosion was observed, significantly increasing with velocity. At intermediate NH_4HS concentration greater than 8 wt %, moderate to high corrosion was observed, significantly increasing with velocity. The H_2S partial pressure was found to be a major factor that was deemed necessary to consider when predicting corrosion rate. The velocity limit of 6.1 m/s was found to be too conservative at low NH_4HS concentration and low H_2S partial pressure and too liberal at high NH_4HS concentration and high H_2S partial pressure. The presence of hydrocarbon mixed with the sour water resulted in significant reduction of corrosion, as compared with sour water without it. Super duplex stainless steel S32750 and super austenitic stainless steel N08367 exhibited far more corrosion resistance than duplex stainless steel S31803/S32205. Alloy N10276 was the most corrosion resistant of all the alloys tested.

In the field, there are additional factors that may play important roles on the NH_4HS corrosion. The wash water is usually injected into a 100 % vapor stream and, as this stream cools down, hydrocarbon starts condensing either in a fin fan cooler bank or cooling water exchangers. Part of the injected wash water may vaporize to condense back into water when it cools down. Thus the water quality and source, wash water rate, the location of the injection point, whether it is multiple or single, if it has quill or a spray nozzle, will all matter. Among all these factors, the flow regime plays a major role [25]. Best practices for water washing in hydroprocessing units have been described [26] to address some of these topics.

In the inlet or outlet piping of the REAC system, NH_4HS corrosion is expected to be more pronounced at the extrados of elbows, the impingement side of the tee and, in general, where there is high turbulence or a change in the direction of flow in single liquid phase flow condition.

17.2.4 Ammonium Chloride Corrosion

When present, chlorides from HCl in hydroprocessing reactors can combine with NH_3 and produce NH_4Cl. Several cases of NH_4Cl corrosion have been reported in the REAC system [27], the fractionator feed preheat exchangers [28], and also in the stripper column overhead [29]. NH_4Cl corrosion could be very aggressive to carbon steel and other alloys. Its presence can also encourage chloride SCC (Cl SCC) [30] in austenitic stainless steels. The catalyst in catalytic reformer units is activated with addition of chloride compounds that may become the source of HCl that is carried with the H_2 that is used in hydroprocessing. Nickel base alloys N06625 or N08825 may be required to resist this aggressive corrosive environment. However, as mentioned earlier, the remedy actions should first attempt to eliminate the source of chloride whenever possible, rather than to go directly for upgrading the metallurgy. Catalytic reformer H_2 is often passed through chloride traps, absorbers, or pressure swing adsorption to remove the HCl before using it in hydroprocessing plants.

17.2.5 Acid Corrosion

There are other process units in the oil refining industry that are corrosive because of the process itself. For instance, the catalyst in alkylation is pure HF [31] or sulfuric acid [32], both very corrosive to metals and alloys. The materials used in HF and sulfuric acid service have been fully described elsewhere [33,34]. Polymerization unit is a different process in that solid phosphoric acid catalyst is used. Because this catalyst is fragile, fine catalyst particles may break and be carried away downstream. At the normal reactor temperature and pressure, there is no concern of corrosion, but these fine particles may be carried away downstream of the reactors, where they may react with water or moisture and form phosphoric acid that may corrode both piping and vessel walls where the wet material deposits on the surface.

17.2.6 Dead Legs and Injection Points

The corrosion rate in dead legs can vary significantly from adjacent active piping and hence, they represent places demanding special attention. Dead legs include points both at the stagnant end and the end at the connection to an active line. Several corrosion mechanisms associated with injection points have become apparent to refineries over the years. Many of these problems have resulted in highly localized deterioration and even piping failures. The approach has been to also treat them as separate inspection circuits that demand special attention and thorough inspection on a regular basis. Both topics, dead legs and injection points, have been covered in piping inspection code [35], and inspection practices for piping system components [36]. There is a technical committee report by NACE International on the subject of refinery injection and process mixing points [37]. The use of quills or injectors is always advisable. There are many design considerations and aspects that need to be taken into account to achieve trouble-free injection points.

17.2.7 Sensitization

Solution annealing is a heat treatment used in 300 series stainless steels and it consists of heating the material up to a temperature above 1066 °C and holding it long enough for the carbon to go into solution. After this, the material is quickly cooled to prevent the carbon from coming out of solution. Solution annealed material is in its most corrosion-resistant and ductile condition. Sensitization in the steel occurs from chromium depletion along austenite grain boundaries due to chromium carbide precipitation during welding these types of austenitic stainless steels or during high-temperature operations, higher than 370 °C.

In certain corrosive environments, sensitized austenitic stainless steels may suffer intergranular corrosion or even intergranular SCC. Because of this, low carbon grade or stabilized grade S32100 and S34700 are used. Stabilizing heat treatment performed after the material has been solution annealed enhances the sensitization resistance of these stabilized grades. The stabilizing heat treatment is to tie up the carbon with the stabilizing elements (either Ti or Nb) and thus leave no carbon available for sensitization. Sensitization is more likely in the presence of coke at temperatures high enough for carburization to occur; this would provide more carbon to the steel for the sensitization phenomenon.

17.3 SCC

There are a number of SCC mechanisms that may affect the materials in oil refining equipment and piping. The SCC mechanism caused by wet H_2S and HF corrosion was already described. This mechanism is basically delayed cracking due to hydrogen embrittlement. In the more general cases of SCC, the cracks form and grow by anodic dissolution, which is the typical mechanism that does not depend on the material hardness or strength level, although cold working usually has an adverse effect. The cracking process in this case involves the direct action of corrosion on the cracking formation and growth mechanism. In all cases of SCC, three contributing factors are required, the presence of tensile stress, the wet corrosive medium, and the susceptible material or metallurgical condition.

17.3.1 Polythionic Acid SCC (PTA SCC)

PTA SCC refers to a branched intergranular SCC that can occur in sensitized austenitic stainless steels. PTA refers to the family of acids that can form by the oxidation and hydrolysis of iron sulfide films that formed on the austenitic stainless steel surface during service. This sulfide film formation cannot be avoided because these steels, under high-temperature sulfidic corrosion conditions, will naturally form it; moisture and air are naturally present in the environment as soon as the equipment or piping is opened to the atmosphere for maintenance or inspection. The required material condition is being sensitized. Because the sulfide scale forms on the inside surface, PTA SCC starts on the inside surface and propagates through wall thickness toward the outside surface.

Soda ash neutralization procedure is used to prevent PTA SCC. Decoking furnace tubes is often done by mechanical means, using coke cutting “pigs” pushed with water, which should also contain similar amount of soda ash for neutralization purpose. The aqueous soda ash solution is also recommended for hydrotesting austenitic stainless steel heater coils, pressure vessels and piping in this service likely to produce PTAs. After using this alkaline water, it is of paramount importance that all the remaining solution is drained, particularly the low points in the system that can concentrate carbonate and chlorides that can cause either chloride SCC or caustic type SCC upon heating.

Applying all these measures to prevent PTA SCC is time consuming and costly. Thus, determining when they are really required or not can be gainful. There is an increasing amount of austenitic stainless steel being used to deal with high-temperature sulfidic corrosion, naphthenic acid corrosion, or both in crude and vacuum distillation units. The furnaces heat the feed to about 370 °C in atmospheric distillation and up to 400 °C in vacuum distillation. This sets the temperature the metals will be exposed to outside the furnaces. Thus, in the case of crude units, the temperature may be below the range required for sensitization. However, furnace tubes can be exposed to at least a 50 °C to 100 °C higher temperature than the fluid inside the tubes; thus, they are expected to be more susceptible to sensitization and, hence, to PTA SCC. Only a few instances of PTA SCC have actually been reported to occur in crude and vacuum distillation units.

PTA SCC occurs when there is not operating pressure. The stress causing it is the residual stress present in weldments or that arising from lack of flexibility in piping circuits and piping-to-equipment connections. If it occurs and propagates through thickness, the cracking is detected during the start-up procedure or soon after the unit returns to service, requiring a new shutdown for inspection, repair, and replacement. Thus, it can be a costly event, not only because of the maintenance cost involved in the repair job but also due to the loss of production.

The reported sensitization temperature ranges for stabilized grade S32100 and S34700 steels is 400 °C–815 °C. Operating temperature for hydroprocessing units may vary from 300 °C to 450 °C. Thus, in some low-severity hydroprocessing units, the piping and feed/effluent exchanger temperature would be below the sensitization range but, as mentioned earlier, furnace tubes can experience higher temperature and are hence more likely to sensitize in service.

The most established corrosive environment leading to high PTA SCC potential is that containing hydrogen with significant amount of H_2S. Some hydroprocessing units use sweet hydrogen (with no H_2S), so this corrosive environment would not form but at the reactor where the conversion of organic sulfurs species to H_2S occurs and is carried downstream. Some other hydroprocessing units use sour recycle hydrogen (with H_2S) so this H_2/H_2S corrosive environment would be present at the hydrogen injection point and downstream.

Hydroprocessing reactors usually have their internal surfaces protected by a layer of austenitic stainless steel to provide for the necessary corrosion resistance to high-temperature sulfidic corrosion in the presence of a H_2/H_2S environment. The protective layer of austenitic stainless steel may be a weld overlaid layer or clad. The clad material is applied to the base metal by hot rolling or explosion. Hot-rolled clad forms a metallurgical bonding with the base metal, while the explosion bonding is a solid-state welding process that uses the forces of controlled detonations to accelerate one metal plate onto another and thus create a diffusionless bonding. Because of the problem with hydrogen-induced clad disbonding during service, weld overlay is preferred, with the added beneficial effect that low carbon and chemically stabilized weld overlays appear very resistant to PTA SCC if the operating temperature is below 455 °C.

The PTA SCC concern should be limited to austenitic stainless steel exposed to high-temperature sulfidic corrosion with and without H_2. Extending the practices to prevent PTA SCC in austenitic stainless steels exposed only to H_2S or NH_4HS wet service may be overly conservative.

17.3.2 Chloride SCC

Chloride SCC refers to a branched cracking that can occur in austenitic stainless steels independently of whether they are sensitized or not. Usually in nonsensitized austenitic stainless steels the cracking is transgranular, but if the steel is sensitized it can also occur intergranularly. The chloride SCC has been a potential damage mechanism for austenitic stainless steels used in oil refineries. The potential for external chloride SCC under thermal insulation has been recognized and recommended practices have been issued [38] to address this potential problem. The problem occurs when water and chloride enter the insulation material. The chlorides can be from the insulation material itself or external sources, more frequently coastal atmospheres, nearby chloride-containing chemical processes, wash water, fire protection deluge systems, and process spillage. The hot metal surface concentrates the chlorides by evaporation. Equipment that cycles through the water dew point is particularly susceptible because of chloride concentration.

Most external chloride SCC failures occur when the metal temperature is in the hot water range, 50 °C to 150 °C, and less frequently when the temperature is outside this range. Water is usually necessary and it is generally believed that it will not occur at temperatures where water cannot exist in liquid form. An apparent temperature threshold of about 50 °C–60 °C has been observed, below which cracking probability becomes very low. Sufficient tensile stress must be present for chloride SCC to occur. Protective coating systems have been recommended for austenitic stainless steels under insulation.

Chloride SCC can also occur due to presence of chlorides in the process environment inside equipment and piping. Oxygen is usually necessary, but this may vary with the nature of the aqueous solution. For instance, dilute aqueous solutions do not cause chloride SCC if completely free of oxygen [39]. The simultaneous presence of H_2S and chlorides has a synergistic effect even causing chloride SCC in the absence of oxygen. The presence of molybdenum, as an alloying element, tends to inhibit chloride SCC. Low pH aggravates chloride SCC at least until cracking is initiated; thereafter, the pH conditions within cracks become acidic and do not necessarily coincide with those of the bulk environment. Although it has not been possible to find a safe low-chloride concentration, it has been customary to specify a maximum of about 50 ppmw chlorides for water that is used for hydrotesting, washing, or flushing austenitic stainless steel equipment and piping. Kerosene or naphtha has been used instead of water to perform hydrotesting in heater tubes.

Because of the concern of chloride SCC, corrosion and material engineers are sometimes forced to select alloys other than austenitic stainless steels for equipment and piping in the oil refining industry. Duplex stainless steels have become popular [40] in this respect, but these steels have temperature limitations. It is not recommended to use duplex stainless steels beyond about 280 °C–340 °C. Prolonged exposure to temperatures exceeding these limits may cause undesirable metallurgical changes in duplex stainless steels. Nickel-based alloy N08800 and N088250 are resistant to chloride SCC. In general, nickel-base alloys are often used under wet operating conditions because of their resistance to chloride SCC.

17.3.3 Caustic SCC

Caustic sodium hydroxide (NaOH) is used in many petroleum refinery applications in a wide range of concentrations and temperatures. Caustic SCC of carbon steel equipment and piping has been a well-known phenomenon. It is an intergranular SCC mechanism producing multiple branched cracking. The caustic soda service chart [41] is still used today to determine the temperature and concentration, beyond which carbon steel may become susceptible to caustic SCC. Post-weld heat treatment is effectively used to mitigate the problem because it significantly reduces the residual stress. However, above certain temperature level and given caustic concentration, even low stresses may still result in cracking, in which case not even post-weld heat-treated carbon steel is suitable for hot caustic service.

Austenitic stainless steels [42] and even nickel-based alloys may become susceptible to caustic SCC at relatively high temperatures. With austenitic stainless steels, the morphology of cracking is often transgranular and indistinguishable from chloride SCC but intergranular cracking is also observed. Because chloride is a common contaminant in caustic, SCC failures in caustic environment may not be conclusively ascribed to either chloride or caustic. Also, although caustic is the most common SCC encountered, other alkali metal compounds may cause similar SCC problems. For instance, carbonate SCC has occurred in low points that have not been properly drained after alkaline washing done with soda ash to protect austenitic stainless steel piping systems in hydroprocessing units from PTA SCC. These pockets of alkaline water tend to dry out and thus significantly increase the alkaline concentration; SCC may then occur in hours when warming up the unit for start up. Because of this potential problem, some refineries have selected nickel-based alloy N08800 or N088250 for small-bore connections at low points in these austenitic stainless steel piping systems to reduce the SCC problem.

Duplex stainless steels and alloy N04400 may also experience SCC under certain conditions of concentrations and temperatures. Alloy N06600 is preferred to alloys N08800 and N088250, which may crack by caustic SCC more easily than alloy N06600. The technically correct metal for the greatest immunity to caustic SCC is nickel, either N02200 or N02201 sometimes used as clad material.

17.3.4 Alkaline SCC

There are other common substances that can cause intergranular SCC in carbon steels, usually with multiple fine-branched cracks. A list of the most common alkaline environmental cracking mechanisms affecting carbon steels in oil refining services is given in the literature [15]. These are caustic; alkanolamine-containing CO_2, H_2S, or both; and alkaline sour waters containing carbonates. Alkanolamine solutions are widely used in oil refineries and gas plants to remove H_2S, CO_2, or both from hydrocarbon streams in the liquid or vapor phase, in plants referred to as amine units. Amine SCC is dealt with in the API RP 945 [43]. There is a dependence of the amine SCC and the metal temperature above which cracking is most likely. Thus, post-weld heat treatment is recommended for carbon steels in amine units depending on the type of amine used and the operating temperature. The temperature limit varies from 60 °C to 88 °C. There is no temperature limit for monoethanolamine.

Not only the normal operating temperatures should be considered, but also the effects of heat tracing and steam-out on the metal temperature of carbon steels in contact with the amine or caustic solution. Equipment and piping have been known to crack during steam-out due to the presence of amine. The same concern arises when performing any kind of hot work on existing carbon steel equipment and piping in amine units. These should be thoroughly cleaned before attempting steam-out or before conducting repairs or alterations involving welding. Washing and flushing the equipment and piping with copious amounts of water to remove any residual amine or caustic contamination achieve this. As a conservative precautionary measure, refineries may apply post-weld heat treatment to every carbon steel equipment and piping in amine and caustic units, irrespective of the operating temperature. This is usually the case for carbon steel piping and equipment handling lean amine.

Intergranular SCC in carbon steels has been reported in the FCC main fractionator overhead systems [44] and attributed to carbonate SCC. It has been recently noticed that as the FCC feed is hydrotreated to reduce its sulfur content, new conditions are created that favor carbonate SCC [45]. The Task Group 347 of NACE International recently issued a technical committee report on this subject [46]. When metallographic cross-sections of damaged carbon steels are examined, the damage consists of intergranular oxide-filled branched cracks, indistinguishable from caustic and amine SCC. Similar type of damage has been found in buried pipelines in certain soil environment [47]. Post-weld heat treatment is normally applied to prevent carbonate SCC in oil refineries.

Alkaline SCC also can occur in carbon and low-alloy steels in anhydrous ammonia service [48]. The list of all possible cracking mechanisms that could affect metals and alloys commonly used in the oil refining industry has not been exhausted here, but the description of each of them is outside the scope of this chapter; a description was given for most common ones.

17.4 DRY CORROSION

Like high-temperature oxidation of metals, dry corrosion occurs in the absence of water. It is attributed to sulfur, naphthenic acids, or both. Once the temperature of the crude oil feed reaches or exceeds about 230 °C, problems with high-temperature sulfidic corrosion and naphthenic acid corrosion may begin. Both corrosion mechanisms are temperature/velocity dependent; therefore, the most critical parts are the places and locations where the temperature and the velocity or turbulence is the highest. These locations are typically furnace tubes, furnace outlet piping, transfer line (from the furnace to the distillation tower), pumps, and downstream control or pressure let down valves. The internal components and wall of the distillation towers can also be affected.

Depending on the amounts and aggressiveness of the sulfur species and naphthenic acids present, the potential for corrosion could continue to occur in the side stream piping circuits and bottom lines of distillation towers, including the associated heat exchangers, drums, and pumps. The atmospheric bottoms are fed to the vacuum unit where the potential for high-temperature sulfidic corrosion and naphthenic acid corrosion continues. Actually, naphthenic acid corrosion is typically more critical in vacuum distillation units than in crude distillation units. The vacuum tower bottoms are fed to visbreaker, delayed coker, or fluidized coker units, but the corrosion concern in these units is more high-temperature sulfidic corrosion rather than naphthenic acid corrosion. For side streams, the potential for these two corrosion mechanisms continues in all the downstream units for as long as the operating temperature reaches or exceeds about 230 °C.

17.4.1 High-Temperature Sulfidic Corrosion in the Absence of Hydrogen

The modified McConomy curves have been generally useful for predicting corrosion rates for various steel alloys in refining process streams based on total sulfur present [49,50]. The original McConomy curves were published in 1963 by the API Subcommittee on Corrosion [51]. They were hand-fitted curves through widely scattered points obtained by industrial surveys containing field and laboratory corrosion rates. The predicted corrosion rates were those on the curves, and these were found to be overly conservative and were later modified. A corrosion rate multiplier factor was then provided to account for sulfur content from 0.05 to 5 wt %. The curves show increasing corrosion rate in a logarithmic scale from practically 0 mm/year to about 2.54 mm/year, at increasing temperature on a lineal scale, from about 260 °C to 400 °C. There are seven roughly parallel curves from top to bottom corresponding to carbon steels, 1–3 wt % Cr steel, 4–6 wt % Cr steel, 7 wt % Cr steel, 9 wt % Cr steel, 12 wt % Cr steel (S40500, S41000, S41008), and 18Cr/8Ni austenitic stainless steel.

Crude oils having less than about 0.6 to 1.0 wt % sulfur are usually referred to as sweet and those having higher sulfur content are known as sour. The definition is arbitrary but has been the basis for making material selection. When high-temperature sulfidic corrosion becomes significant, upgrading the metallurgy from carbon steel to 5Cr–½Mo steel is preferred, rather than to 1¼Cr–1½Mo and 2¼Cr–1Mo steels that would not offer significant corrosion resistance over carbon steel. Higher alloyed steels 7Cr–½Mo and 9Cr–1Mo do offer further resistance to sulfidic corrosion and are also used. Ferritic stainless steel type S40500 or martensitic stainless steel type S41000 or S41008 is even better but these steels are not often used as solid plates to fabricate pressure vessels or piping because of difficulties of welding. These 12 wt % Cr steels are widely used for distillation trays, packing material, and clad though. All of the austenitic stainless steels of the series 300 have excellent resistance to high-temperature sulfidic corrosion.

Crude distillation units designed for processing sweet crude oils are basically constructed with carbon steel, with limited use of 5Cr–½Mo steel, usually located in the tubes in the furnace, and stainless steel type 12 wt % Cr steel for trays and other internal components in the atmospheric and vacuum distillation towers, as well as side stream strippers. As the potential of high-temperature sulfidic corrosion increases, so does the use of 5Cr–½Mo, 9Cr–1Mo, and S40500, S41000, or S41008. Thus, crude units designed to process sour crude oils are recognized because they contain appreciable amounts of these alloyed steels. The tubes in the furnaces are of particular concern because the metal temperature is higher than in piping and equipment. The furnace outlet piping, transfer line piping, and flash zone where the feed enters the distillation columns can also be a concern because of high velocities, particularly in vacuum unit transfer lines where velocities may be 60–140 m/s or higher.

Many refineries were originally designed and constructed to process sweet crude oils. As sweet crude oils become scarce and more expensive, the trend has been to process sourer and more acidic crude oils. Thus, it is not uncommon to find refineries that have and are processing these sourer crude oils in units that still have carbon and 5Cr–½Mo steels in places where the modified McConomy curves would predict higher corrosion rates than they are actually experiencing. This is not to say that the modified McConomy curves are not correctly predicting the corrosion because in cases of piping failures or early detection of corrosion during on-stream inspection programs, it is often found that the measured corrosion rates coincide reasonably well with those predicted by the modified McConomy curves. In this sense, they could be considered upper bound predictions.

Although it is still the practice to specify the total sulfur content, it is now known that certain organic sulfur compounds, referred to as reactive sulfur, are mostly responsible for high-temperature sulfidic corrosion. These are the organic sulfides, disulfides, polysulfides, and mercaptans. Noncorrosive sulfur compounds are the nonreactive compounds, and they are mainly the various thiophenes. Although it seems obvious that the correlation between sulfidic corrosion and corrosion rate should be based on the amount of reactive sulfur content, most laboratories are equipped only to determine the total sulfur content and thus this is still widely used today.

Higher corrosion rates than those predicted by the modified McConomy curves have also been reported in cases where significant concentrations of mercaptans are present [52]. An industrial survey [53] recently showed that corrosion rates could be higher than predicted by these curves in the hydrogen-free portion of desulfurizing units, specifically the fractionation and distillation facilities downstream of hydrotreaters and hydrocrackers. They reported that some hydroprocessing units experienced aggressive corrosion rates, while many did not. In some cases, hydrocarbon streams with low sulfur content, in the order of ppm (weight), caused significant corrosion.

On the other end, there are well-known cases of corrosion being lower than those predicted by the modified McConomy curves in distillation units processing heavy and extra heavy crude oils. Some of these units are processing sourer crude oils than those for which they were originally designed and have shown corrosion rates lower than those predicted by the modified McConomy curves. Clearly, this indicates that oil refineries cannot rely on these curves alone and that the reliability of the plant still depends much on inspection, with particular attention being paid to steels that are supposed to be experiencing higher corrosion rate.

17.4.2 H_2S/ H_2 High-Temperature Sulfidic Corrosion

Hydroprocessing units require the use of hydrogen that, together with H_2S, creates special high-temperature sulfidic corrosion environments that are much more aggressive than sulfidation in the absence of hydrogen. The corrosion rate predictions are made using the Couper-Gorman curves [54] where the correlation was established with the presence of H_2, temperature, and mole % of H_2S, starting with less than 0.002 (20 ppm by volume) to higher than 1.0 %. There are two categories for the prediction of the corrosion rate, naphtha, used for naphtha and light distillates such as kerosene and diesel, and gas oil, used for all other hydrocarbons and H_2 without hydrocarbon present. The latter refers to the handling of hot recycle hydrogen that can contain significant amount of H_2S with only traces of hydrocarbons.

Carbon steel is the most susceptible steel to H_2S/H_2 high-temperature sulfidic corrosion; increasing chromium content to 5 wt % or less provides only a marginal improvement. Corrosion resistance is modest with increasing chromium content up to 9 wt %; a minimum of 12 wt % Cr steel is required to see a more significant increase in corrosion resistance. In general, most units processing gas oils or heavier hydrocarbon streams make use of austenitic stainless steels in the feed/effluent heat exchangers, the piping in and out of the furnace, the furnace tubes, the reactor, and the reactor effluent piping back to the feed/effluent heat exchangers. Some units processing naphtha or even diesel do not extensively use austenitic stainless steels but Cr-Mo or even carbon steels. As in the case of sulfidic corrosion without H_2, actual corrosion rates measured in the field are sometimes lower than predicted by the Couper-Gorman curves. Thus, these could also be considered upper bound predictions. Austenitic stainless steels have performed well and usually experience negligible corrosion rates in this service.

17.4.3 Naphthenic Acid Corrosion

Even though naphthenic acid corrosion has been recognized for many years [55], it is still the subject of research and publications [56,57]. The rule of thumb has traditionally been to consider a neutralization number (or total acid number [TAN]) of 0.5 mg KOH/g as the threshold beyond which naphthenic acid corrosion may begin occurring and therefore when it is required to use more corrosion-resistant steels.

As the severity of naphthenic acid corrosion increases, the problem starts occurring in the vacuum furnace tubes, the vacuum furnace outlet piping, the vacuum transfer line, as well as the piping circuits handling heavy vacuum gas oil (HVGO) and the overflash in the vacuum tower. At this stage, problems with naphthenic acid corrosion may also start appearing in the atmospheric distillation unit. The places most likely to suffer naphthenic acid corrosion are again the furnace tubes, furnace outlet piping, transfer line, and the flash zone where the feed enters the distillation column. There are usually fewer problems with naphthenic acid corrosion in the diesel and kerosene sections of the crude units, although there have been recent reports claiming naphthenic acid corrosion in the kerosene section [58]. Likewise, there are usually fewer problems with naphthenic acid corrosion in the LVGO section of vacuum distillation units. In most cases, the bottom stream from the crude and vacuum distillation towers appeared less corrosive than the crude itself and the gas oil streams. In the case of atmospheric bottoms, naphthenic acid corrosion typically becomes a problem only at the vacuum furnace and downstream.

Naphthenic acid content in naphtha, kerosene, and diesel streams going to hydrotreater units has not yet been of concern with regard to naphthenic acid corrosion. Gas oils may have the potential to cause naphthenic acid corrosion in these units, but it has been a concern only upstream of the injection point of hydrogen and where the temperature is higher than about 230 °C–250 °C. Experience has shown that naphthenic acid corrosion does not occur or it is negligible downstream of the hydrogen injection point [59]. It does not occur downstream of heaters in delayed coker units either, but in this case it is because the naphthenic acids decompose at the outlet temperatures of about 500 °C.

Recognizing that there is a complex interaction between two competing corrosion mechanisms, the corrosion rate determination tables found in API Publication 581 contemplate both sulfidation and naphthenic acid corrosion but are still based on total sulfur (wt %) and TAN. In any case, the tables tend to reflect the observed phenomenon that low sulfur produces higher naphthenic acid corrosion and that sulfur inhibits naphthenic acid corrosion and thus reduces the corrosion rate with increasing sulfur. The fact is that simple ways of accurately predicting corrosiveness have not yet been found.

17.5 OTHER DAMAGE MECHANISMS

17.5.1 High-Temperature Hydrogen Attack

The use of hydrogen at high temperature and pressure creates conditions for high-temperature hydrogen attack. Thus, this material degradation mechanism applies to hydrogen reformer, catalytic reformer, and hydroprocessing units. Recommended practices for the selection of materials in high-temperature hydrogen attack service is described in detail in API RP 941 [60]. Material selection is based on the so-called Nelson curves. These are curves with a temperature scale on the vertical axis versus partial pressure of hydrogen on a horizontal axis. There are empirical curves for carbon steel, 1Cr–1½Mo, 1¼Cr–½Mo, 2¼Cr–1Mo, 2¼Cr–1Mo–V, 3Cr–1Mo, and 6Cr–½Mo steels. Conditions of temperature and hydrogen partial pressure below the curve delineate the safe zone of no attack; the zone of high-temperature hydrogen attack is on and above the curve. There used to be a C–½Mo steel curve located between the carbon steel and 1Cr–1½Mo curve but this was deleted because of reported cases of hydrogen attack in C–½Mo steel under this curve. Currently, the applicable curve for C–½Mo steel is the carbon steel curve.

The API has issued a document that describes the technical basis for this recommended practice. The validity of the Nelson curves as currently published in API RP 941 is confirmed in this document and the presence of stainless steel clad material, even for ferritic stainless steel clad, is given a credit, while currently this is not the case. In general, hydroprocessing units use either Cr-Mo steel or austenitic stainless steels in all the hot areas of the process because of the H_2S/H_2 sulfidic corrosion potential. Because of this, there is no concern of hydrogen attack; all these steels offered sufficient resistance to it, except for old reactors and feed/effluent exchangers that were built in C–½Mo steel. The most common areas of hydrogen attack concern are those that were originally fabricated in carbon steel or C–½Mo steel and that are close or slightly exceed the limit condition for hydrogen attack, because of the downgrading of C–½Mo steel or operational changes made in the units or the process after they were designed and commissioned.

Even though there have been no reported instances of high-temperature hydrogen attack in Mn–½Mo steels, the API RP 941 makes no distinction between this and the conventional C–½Mo steel. Experiments led by the author with one-side accelerated test suggested that Mn–½Mo was superior to C–½Mo steel. Manganese is a noncarbide-forming element, and the argument has been that not enough information has been gathered to support this claim. This is an area that certainly requires confirmation because there are still some old Mn–½ Mo steel reactors in hydroprocessing units that have been treated just as C–½Mo steel. The results of these one-side accelerated tests conducted with both C–½Mo and Mn–½Mo steel in the normalized and annealed condition using 1 °C/min cooling rate are shown in Figure 17.1. The best hydrogen attack resistance was observed in the normalized heat treatment condition. C–½Mo steel in the annealed condition exhibited the same resistance to hydrogen attack as carbon steel. Similar trend was obtained for Mn–½Mo steel, but in this case the resistance of Mn–½Mo in the annealed condition (its worst heat treatment condition) was superior to C–½Mo steel in the normalized condition (its best heat treatment condition). Tests were also conducted to assess the effect that the cladding has on increasing the hydrogen attack resistance. Calculation was made so that the hydrogen partial pressure at the clad-base metal interface was the same as the hydrogen pressure used in the test for the sample without clad and yet, hydrogen attack proceeded 7.5 times faster without clad. This finding confirmed a protection effect of having an austenitic stainless steel layer on the C–½Mo steel. Tests were not conducted with ferritic or martensitic stainless steel clad.

Existing C–½Mo steel equipment operating above the carbon steel Nelson curve is subject to regular and costly inspection for hydrogen attack. This kind of inspection poses problems in that the clad or weld overlay does not allow access to the internal surface and the damage in the form of intergranular fissuring is not detectable by conventional

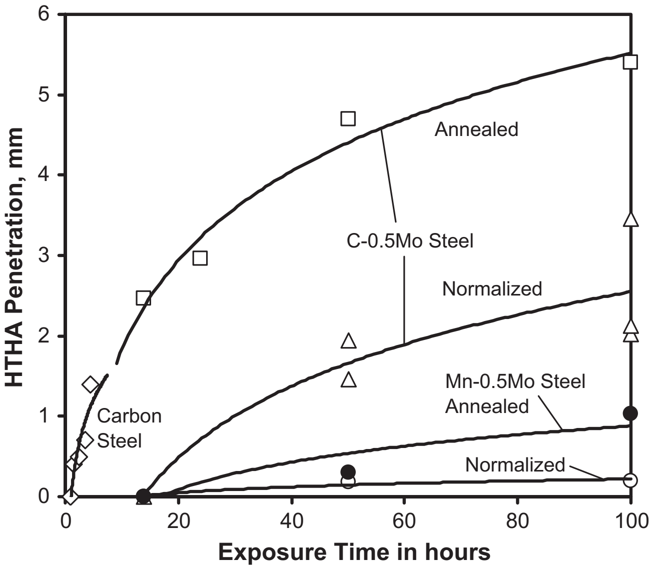


Figure 17.1—Accelerated short-time hydrogen attack tests results obtained at about 550 °C and 13.8 MPa hydrogen pressure and using carbon steel, C–½Mo, and Mn–½Mo steels.

inspection methods. The API RP 941 includes a summary of the available inspection methods used, emphasizing the limitations and detection capabilities.

17.5.2 Creep

Creep is a well-known damage mechanism affecting metals and alloys operating at high temperatures. Creep rupture and cracking develop relatively slowly with time at stress levels that are lower to those necessary to cause plastic yielding. Some construction and design codes establish adequate design stress based on creep strength. If the design temperature is below the limits where these metals and alloys are known to suffer creep, the design is then done in the elastic range, as it would at room or ambient temperature.

In the absence of corrosion or other damage mechanisms, alloys operating below the creep regime will provide unlimited useful life. Even within the creep regime, if the temperature is on the low side of the range, the time to rupture may be so large that it is practical to consider unlimited useful creep life. The approach has been to establish allowable stresses as the stress required to cause creep rupture or a given amount of creep strain at the end of so many hours of exposure. In practice, because the values used in the design are higher than the operating temperature and pressure, equipment, piping, and tubes usually exceed the designed life and still may have significant amounts of remaining life after many years of service. Creep damage can still occur in places of excessive stress concentration or arising because of lack of flexibility in piping but, in general, pressure vessels and piping in oil refineries are designed with overly conservative safety margins.

Furnace tubes pose a different problem in that the temperature of the metal is higher than the fluid temperature. In cases such as a hydrogen manufacturing unit, the temperatures are so high that special alloys are used and even so, the tubes have limited life because of creep damage. In general, however, in most common oil-refining processes, the use of alloy steels is determined more on the basis of sulfidic corrosion, naphthenic acid corrosion, or both. In cases where these corrosion mechanisms do not apply, it is common to use carbon steel, 1¼Cr–½Mo, or 2¼Cr–1Mo steels, depending on the design pressure and expected maximum metal temperature. API Standard 530 [61] provides the method most commonly used to calculate heater-tube thickness in petroleum refineries. Both API Standard 530 and RP 579 [62] provide methods for assessing the remaining life of heater tubes. The predictions of remaining life are as good as the historical data on which they are based; oversimplifying the assumed conditions may lead to under- or overestimations [63] that render the approach useless.

Heater tubes in petroleum refineries are also designed with enough safety margins for prolonged service, and most tube failures in refineries can be attributed to overheating by flame impingement, coke build-up inside the tubes, irregular flow, and operational upsets. Excessive overheating of the heater tubes under internal pressure may consume a large proportion of the available remaining creep life, and if this is not properly recorded in the history, it will be overlooked in remaining life assessments. The API RP 573 [64] describes the recommended practices to inspect heaters and heater tubes and also provides more detailed descriptions of the causes of deterioration.

17.5.3 Carburization, Metal Dusting, Sigma Phase Embrittlement, and Oxidation

Metals and alloys are generally susceptible to carburization when exposed to carbon-rich environment at high temperatures [65]. Carburization attack is a process whereby the carbon enters and diffuses into the metal and form internal carbides. This is possible because of the high temperatures that favor the diffusion process. As a consequence of carburization, the alloy suffers embrittlement and other mechanical property degradation. The carburizing environment in oil refineries is due to the crude oil, its distillates and hydrocarbon gases. Coke formed adjacent to the metal surface of tubes is the main source of carbon.

There are two main families of steels, namely ferritic and austenitic. Carbon steel, 1Cr–½Mo, 1¼Cr–½Mo, 2¼Cr–1Mo, 5Cr–½Mo, 7Cr–½Mo, and 9Cr–1Mo are ferritic steels. The solubility of carbon in ferrite is very limited (≤0.02 wt %). These steels begin to undergo a phase transformation from ferrite to austenite when reaching and exceeding the lower critical temperature, which varies from about 720 °C to 825 °C, depending on the alloy content. These steels are not used at or near the lower critical temperatures. The limiting design metal temperature given by API Standard 530 for heater tubes alloys is 540 °C, 595 °C, 650 °C, and 705 °C, for carbon steel, 1¼Cr–½Mo, 5Cr–½Mo, and 9Cr–1Mo steels, respectively. These limits set the alloy about 120 °C–180 °C below the lower critical temperatures.

Carburization may start being significant in these ferritic steels only above 650 °C–700 °C, but at these high-temperature levels the main concern should be strength and creep, rather than carburization, except under metal dusting conditions. Metal dusting is another form of carburization that generally results in pitting and wall thinning. It has been reported in catalytic reforming heater tubes, [66] but it is more commonly seen in chemical process plants [67]. Carburization is expected to significantly increase when ferritic steels reach or exceed the lower critical temperature, but when this happens they would soften significantly to the extent that they may have insufficient strength to withstand normal operating pressure or even its own weight.

Austenitic stainless steel can be used for temperatures higher than those allowed for ferritic steels. Typical application in the oil-refining industry is in furnaces as heater tubes. The internals of fluidized crack cracker unit (FCCU) regenerators are usually made of type S30409 steel, operating at about 730 °C, and this selection is made on the basis of strength as well as resistance to sigma phase formation. Although carburization does occur in this FCCU service, it is usually shallow. The main degradation mechanism of S30409 steel in FCCU regenerator service is sigma phase embrittlement [68]. Sigma phase is a nonmagnetic intermetallic phase composed mainly of iron and chromium that forms in ferritic and austenitic stainless steels during exposure at 560ºC–980ºC. It causes loss of ductility, toughness, and is generally strain intolerant at temperatures under 120ºC–150ºC, but it is believed it has little effect on properties in the temperature range where it forms. If this were so, it would appear that there should be little consequence as long as the affected components continuously operate at the elevated temperature. However, cracking could occur if the components were impact loaded or excessively stressed during maintenance work. Sigma phase formation competes with carburization. Sigma phase is usually observed in the bulk of the steel and carburization on the surface where the source of carbon is located. Excessive carburization depletes the austenitic matrix of chromium and thus weakens its resistance to sulfidic corrosion. Excessive wall thinning has thus resulted because of severe carburization followed by sulfidation.

17.6 DETECTION AND MEASURING TECHNIQUES

The techniques and methods used for the detection and measuring of degradation of materials depends on the mechanism and the oil-refining process. In the case of crude tower overhead corrosion, common corrosion monitoring techniques used are the measurement of pH, chemical analysis of the water for chloride and metal content, corrosion rate measurements on weight-loss coupons or corrosion probes (e.g., electrical resistance probes known as ER probes), and periodic ultrasonic thickness measurements. Process simulation [69] has been used to predict where water condensation and salt precipitation will start occurring and thus better define the corrosion control strategy. The whole process of controlling and measuring the crude distillation overhead corrosion is often under the responsibility of the vendors of the chemicals that are used for corrosion control.

In addition to the corrosion control programs, there should be an inspection strategy that regularly measures wall thickness by ultrasonic devices and, when possible, profile radiography, to detect and measure corrosion on selected places commonly referred to as thickness measurement locations or corrosion monitoring locations. These should include all dead legs, injection points, elbows, reducers, and tees. Equipment and piping in the crude distillation tower overhead system should be inspected at every available opportunity. Useful lives of tube bundles and tubes in fin fan coolers in this system should be noted, and replacement or retubing should be planned proactively, before the time to failure is reached. The alternative to achieve longer lives would be to upgrade to higher alloyed materials.

Inspection for the detection of wet H_2S SCC has traditionally been performed by wet fluorescent magnetic particle testing (WFMT), but more recently there is an increased use of alternating current field measurement (ACFM). WFMT requires cleaning the surface on both sides of the welds on the inside of the equipment and consists in applying a fine fluorescent magnetic powder in a liquid medium on the steel surface while also applying a magnetic field. Surface breaking cracks accumulate this fine powder that can be revealed with “black light.” It is a highly sensitive inspection technique for crack detection. In fact, experience has shown that it often detects shallow indications that disappear fairly easy with light superficial grinding. These scratch-like indications should well be defined as nonrelevant. If this is not done or properly clarified, the inspection files would give the impression that the wet H_2S cracking problem is more critical than it really is because they will contain records of inspections performed and indications found, without qualifying if they were relevant or not. The ACFM is an electromagnetic noncontacting technique that applies an alternating current flow in the skin near the surface. A magnetic field forms above the surface associated with this uniform current, and this will be disturbed if a surface-breaking crack is present. It is claimed that it requires less surface preparation than WFMT.

Shear wave ultrasonic inspection is used to size and learn more about crack indications. Automatic ultrasonic inspection (AUT) is also being used with the options of examining B-scan and C-scan for HIC damage. C-scan is a top internal ultrasonic view image of the metal; B-scan is a through-thickness ultrasonic side image. Visual inspection is still the most effective way to detect H_2 blistering.

The prediction, detection, and measuring of naphthenic acid corrosion have been a challenge. The TAN has traditionally been used to indicate the corrosion potential and acid content, and although it seems there is general agreement that it does not always work to indicate corrosiveness to oil refining equipment, it is still being widely used today. This is basically because there is not anything else universally accepted to use in its place. Alternative methods have been used where sulfur compounds are extracted first before measuring TAN in the sample or where the naphthenic acids are first extracted from the oil sample and then analyzed [70]. New approaches have been suggested to measure the naphthenic acid corrosion potential based on corrosivity tests to obtain an index known as “naphthenic acid corrosion index” or NACI [71] or the concentration of iron dissolved in the oil sample after exposure to naphthenic acid corrosion in Fe powder tests [72]. These two latter methods deal with the complex interaction between naphthenic acid corrosion and high-temperature sulfidic corrosion. In the former, the corrosion product film is indirectly measured and the naphthenic acid corrosion index is obtained by dividing corrosion rate by this corrosion product film weight. The method is based on the premise that naphthenic acid corrosion and high-temperature sulfidic corrosion are competing processes and that pure naphthenic acid corrosion would produce no corrosion product film while pure high-temperature sulfidic corrosion would produce a corrosion product film. Thus, a low naphthenic acid corrosion index would indicate that sulfidic corrosion dominates, a high naphthenic acid corrosion index would indicate that naphthenic acid corrosion dominates, and an intermediate naphthenic acid corrosion index would indicate inhibited naphthenic acid corrosion.

Conventional weight loss coupons are used in 48-h tests at 260 °C (500 °F) to determine the naphthenic acid corrosion index. In the Fe powder test, fine and pure iron powder is used in 1-h tests conducted at temperatures beginning at 140 °C, then at 40 °C increments through 380 °C. Some of the tests in the middle of this temperature range are duplicated to increase accuracy in the light of relatively large data scatter encountered. The amount of dissolved iron is determined for each test. These experimental points are plotted and curve fitted, usually with a third or fourth order polynomial equation within the temperature range 140 °C–380 °C. Examples are given in Figure 17.2 for two heavy crude oils. The maximum iron concentration obtained by the fitted curve is taken as the outcome of the test, about 33 and 220 ppmw for the crude oil in Figure 17.2, a and b, respectively.

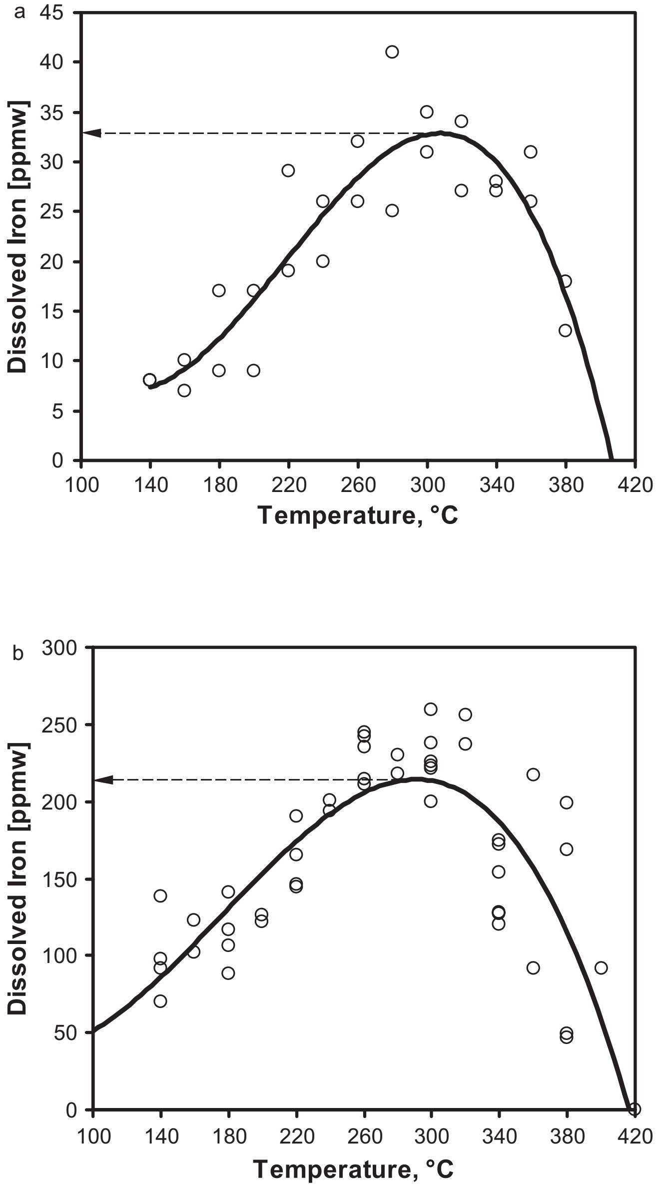


Figure 17.2—Fe-Powder test results of about 33 ppmw for (a) heavy crude oil 15.7 °API, 2.7 wt % sulfur, and TAN 1.3–1.5, and 220 ppmw for (b) heavy crude oil 10.8 °API, 2.7 wt % sulfur, and TAN 4.6–6.5.

This method is based on the premise that naphthenic acid corrosion produces soluble iron naphthenates while sulfidation would produce an insoluble corrosion product. Therefore, by filtering out all solids in the oil sample after the 1-h test and measuring the iron concentration only in the liquid oil sample, before and after the test, a number is provided that indicates the naphthenic acid corrosion potential. Zero amount of dissolved iron would imply no naphthenic acid corrosion in the Fe powder test, regardless of the extent of sulfidation that may have occurred and of the amount of iron consumed by its conversion to iron sulfide corrosion products.

It was found that the H_2S that evolves when heating a sample of sour crude oils and sour distillates during the iron powder test can react with at least part of the iron naphthenates that resulted from naphthenic acid corrosion, introducing an error since it reduced the amount of dissolved iron that was originally produced by naphthenic acid corrosion. To assess the phenomenon without the interference of sulfidation, pure liquid paraffin was used together with commercially available pure naphthenic acid. Extensive laboratory testing and research was conducted and to confirm previous findings made by the Fe powder tests, conventional autoclave weight-loss coupon tests were performed. Thus, adding 0.2, 0.5, 1.0, 2.0, and 4 wt % naphthenic acid to this clear mineral oil, the TAN increased from zero to roughly 0.5, 1.4, 2.7, 5.6, and 11.4 mg KOH/g, respectively. Fe powder tests were performed with these synthetic oil samples and the results were 7, 17, 192, 654, and 3350 ppmw dissolved iron, respectively. The standard weight loss coupon tests (48 h each) were conducted using these same synthetic oil samples. It was confirmed that corrosion rate increases with increasing TAN, but the additions of reactive sulfur species greatly inhibited naphthenic acid corrosion and modified this apparent TAN-corrosiveness correlation. Adding elemental sulfur and nonreactive sulfur species did not have any naphthenic acid corrosion inhibiting effect. The inhibiting effect of the reactive sulfur species started to become evident only at temperatures above 200 °C, when sulfidation was suspected to start occurring. A great number of sulfur species were tested and, although not expected to be found naturally in crude oils, butyl and methyl sulfoxide displaced the point of maximum iron dissolution from about 280 °C–290 °C to 140 °C. This finding was confirmed by weight-loss coupon tests. At 280 °C, pure liquid paraffin with 4 wt % naphthenic acid resulted in a corrosion rate range of 2.5–3.0 mm/y, in coupons made of carbon steel, 5Cr–½Mo, 9Cr–1Mo, and 12 wt % Cr steel. At 140 °C the amount of dissolved iron in the Fe powder test and the corrosion rate measured in weight loss coupon tests were negligible using this same synthetic oil sample. Adding 0.28 M (Molar) sulfoxide to this synthetic oil reduced the corrosion rate to 0.8 mm/year, 0.4 mm/year, 0.3 mm/year, and 0.03 mm/year at 280 °C, in carbon steel, 5Cr–½Mo, 9Cr–1Mo, and 12 wt % Cr steel, respectively. Thus, at this temperature they also experienced a naphthenic acid corrosion inhibiting effect. But at 140 °C, the corrosion rate range increased from practically zero to 1.3–8.7 mm/year for these four different steel coupons. That is, as high or higher corrosion than before adding any sulfur species but occurring at half the temperature level. This finding, originally made by the Fe powder test, demonstrated the complexity of the interaction effect between sulfidic and naphthenic acid corrosion, which makes prediction rather difficult.

The corrosion could then be attributed entirely to naphthenic acid corrosion when these synthetic oil samples with naphthenic acid doses did not have any intentionally added sulfur species. It was thus found that 5Cr-½Mo and 9Cr-1Mo steels offer some useful resistance to naphthenic acid corrosion when the TAN is relatively low (<1.5 mg KOH/g). For higher TAN, however, they start experiencing unacceptably high corrosion rates. When using the synthetic oil sample with TAN = 5.6 mg KOH/g and no sulfur at the same testing temperature of 340 °C, the corrosion rate for 12 wt % Cr steel was 0.5 mm/year. A corrosion rate of 0.5 mm/year would be unacceptable for a 12 wt % Cr steel tray component about 3 mm thick. If naphthenic acid corrosion occurs on both sides, the tray would disintegrate in 3 years of service. When using the synthetic oil sample with TAN = 2.7 mg KOH/g and no sulfur at the testing temperature of 280 °C and 340 °C, the corrosion rate for 12 wt % Cr steel decreased to 0.1 mm/year. This would also be unacceptable for packing material that is usually about 0.5 mm thick or less and would therefore disintegrate in 2 to 3 years of service. Based on these tests performed by using the same synthetic oil samples for Fe powder and autoclave tests, it was possible to establish a correlation between the amount of dissolved iron obtained at any given TAN and the corrosion rate obtained for the same TAN. This is illustrated in Figure 17.3. There was a significant difference in corrosion rate for a carbon steel tested at 280 °C and 340 °C, but the difference was insignificant for 12 wt % Cr steels. This type of correlation allowed translating Fe-Powder results into corrosion rates. For instance, 33 and 220 ppmw dissolved iron in the Fe-Powder tests in Figure 17.2 would translate into 0.28–0.60 mm/year and 10–20 mm/year, respectively, for carbon steel. In the case of 12 wt % Cr steel, the corresponding corrosion rate would be 0.2 mm/year for 220 ppmw dissolved iron.

Several other methods have been proposed to study or measure naphthenic acid corrosion where the emphasis is placed on the velocity or shear stress [73] exerted by the oil sample on the metal surface and on refreshing the oil sample to overcome the loss of TAN that occurred when the naphthenic acids decompose and are consumed during the 48-h test [74]. The nature, concentration, and composition of the naphthenic acids differ among different crude oils with different origins so adding commercially available naphthenic acids to these crude oils would change this and render the test useless for the purpose of determining which one is more or less corrosive than the other. Velocity or shear stress is one of the factors that play a role on naphthenic acid corrosion in piping and piping accessories, but to determine which crude is more or less corrosive than another, the velocity or shear stress factor should be kept constant in comparative tests. The longer the test duration the more likely the oil sample will degrade with time since naphthenic acids and sulfur compounds decompose. Lighter products (methane, propane, butane, light gasoline, and others) may also separate from the oil sample as they leave the solution and vaporize with increasing temperature during the tests. To overcome this, some autoclave tests are performed with a condenser that condenses the lighter products and returns them to the autoclave. However, the basic issue of being able to discriminate between sulfidation and naphthenic acid corrosion is not addressed by any of these methods and for any given amount of damage or corrosion there would not be an easy way to assert if it is sulfidation or naphthenic acid corrosion. Tests have been run to determine by how much the TAN is reduced because of the test exposure conditions, but KOH is found to also react with iron naphthenates so even if the acids had been completely consumed or destroyed, a TAN of zero will not be obtained.

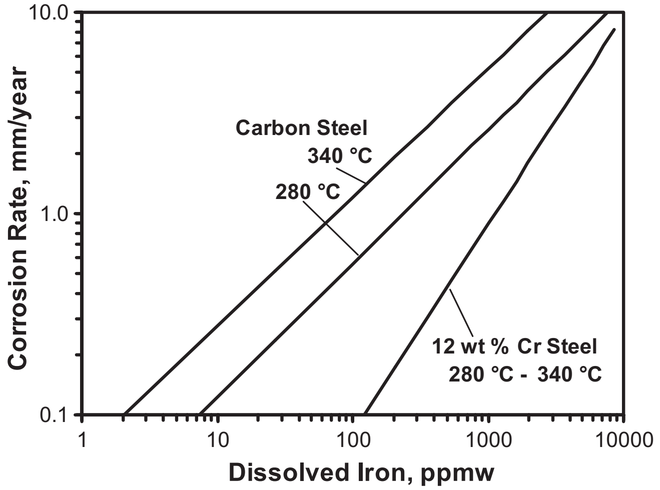


Figure 17.3—Correlation established between corrosion rate and Fe-Powder test results obtained by using clear paraffinic oil dosed with naphthenic acid, no sulfur species added.

It should also be mentioned that corrosion rate measured in weight-loss coupons has shown a dependence on exposure time. The corrosion rate is high with short exposure time and tends to decrease as the exposure time increases up to a point where it is believed it stabilizes and remains constant. Usually the exposure times are 8, 24, 48, 72, or longer. In comparison, corrosion rate in the field on actual equipment and piping is obtained after one or more years in service. Unlike autoclave tests, where the oil sample remains the same during the entire exposure time and their corrosive species may be consumed, degraded, or both, in the field the materials are exposed to the oil that is continuously replenished. So reproducing corrosion rates measured in the field by conducting autoclave tests with weight-loss coupons may not always be successful.

C–½Mo steel used to be selected for some high-temperature high-pressure hydrogen service, but this is not currently allowed. This created a special challenge in that many refineries and chemical process plants still have C–½Mo steel equipment operating within high-temperature hydrogen attack conditions above the carbon steel Nelson curve. The recommendation has been to regularly inspect these assets to make sure they remain free from hydrogen attack and replace if damage is found. The API RP 941 describes the most common inspection methods used to detect high-temperature hydrogen attack. Advanced ultrasonic backscatter technique has found increasing use in this respect [75].

The task of developing techniques and methods that would allow determining if C–½Mo steel can stay in service or needs to be removed and replaced is very attractive. The concept of "bad $M_{23}C_6$ carbide" was introduced in 1996 [76] and carbide extraction replication was then used to analyze the type of carbide in an attempt to be able to tell if that particular C–½Mo steel has high-temperature hydrogen attack resistance that resembles the old C–½Mo steel curve or the existing carbon steel Nelson curve. The presence of bad carbides was supposed to indicate similar hydrogen attack resistance than carbon steel and those not having this bad carbide were likely to still comply with the former Nelson curve for C–½Mo steel. This approach has been abandoned because it could not been confirmed and because of contradictory results obtained elsewhere.

17.7 PREVENTION METHODS

The techniques and methods used for the prevention of the degradation of the material also depend on the mechanism and the oil refining process. Water wash is often used in oil-refining processes to dissolve contaminants and wash hydrocarbon streams. In the case of crude distillation units, the first step used to prevent corrosion is to desalt the feed and use caustic NaOH injection downstream the last desalter. Desalters remove the salts together with solids and sediments from the crude oil but the process is not 100 % efficient. Typical target is to reduce the salts to about 3 ppmw (weight). The injection of caustic into the desalted crude oil feed stream is called primary neutralization and it is to reduce the effect of these hydrolyzable salts by converting them to sodium chloride (NaCl) that is more stable, does not hydrolyze as much, and stays with the liquid that falls and collects at the bottom of the distillation column that is usually fed to the vacuum distillation unit. Some refineries do not use it because Na tends to increase the fouling tendency by coke formation in the tubes of furnaces in downstream units.

Chemicals are added to the crude oil at the desalting stage to aid the operation, which uses wash water that is then removed as brine. Stripped sour water is usually used as desalter wash water but if excess NH_3 is still left in this water, it may make its way to the crude oil and ends up in the tower overhead system. Sour water is the process water that is collected in refining process units, commonly containing H_2S and NH_3, and is routed to the sour water stripper to remove these contaminants and thus become stripped sour water.

Secondary neutralization is achieved by injecting a neutralizer in the crude tower overhead system. Without this neutralization, the pH of the water that condenses in the overhead system may be as low as 1.0 at spots where water starts condensing. At these low pH values, HCl corrosion can occur at high rates in carbon steel (one or more mm/year). Either NH_3 or neutralizing amines may be used to adjust the pH to about 5.5 to 6.5. The neutralization product is a solid or molten salt that can cause severe under-deposit corrosion in carbon steel and some corrosion resistant alloys. Water wash is often used to wash out any salt deposit from the overhead system, in particular the tubes in the exchangers used to condense the crude overhead vapors. A filming amine is often used as corrosion inhibitor [77]. Ideally, the salt deposition point should be found downstream the injection point of wash water, and in principle, there should be no direct injection of NH_3 or other amine neutralizer into the tower top, the naphtha reflux or both, because of the potential to form these neutralization salts inside the tower.

In case of encountering wet H_2S stress cracking, the indications are usually removed by grinding and if the excavation is deep weld repair is usually necessary. If the damage is only in the form of HIC and H_2 blisters, a fitness-for-service (FFS) [78] evaluation is normally required to first determine if they can be left without removal and repaired. HIC-resistant carbon steel is often specified, but there have been doubts with increased susceptibility to SOHIC [79]. Also, HIC-resistant carbon steel equipment still requires the same kind of inspection for HSC as conventional steel. HIC-resistant steels are specially manufactured to have extremely low sulfur content (typically less than 0.003 wt %), plus the addition of a small amount of calcium (used to scavenge residual sulfur into a harmless non-planar inclusion) and hence less inclusions and nucleation sites for HIC but they can have marked pearlite banding, indicative of segregation along which HIC may still form. Carbon steel purchased as HIC resistant steel but not certified by HIC testing has also suffered HIC in severe service along the central segregation line. Some refineries prefer to use standard carbon steel clad with austenitic stainless steel for severe wet H_2S service because of the saving realized by not having to perform any inspection for wet H_2S cracking.

Corrosion in wet H_2S environment does not necessarily have to be high for the damage to develop. Carbon steel forms a protective iron sulfide layer that keeps corrosion rates low. Therefore, traditional on-stream inspection programs based on periodic ultrasonic wall thickness measurements to estimate corrosion rates will not give any indication of lower or higher potential for wet H_2S damage. The same precautionary measures to prevent cracking and damage in carbon steels as in wet H_2S service are applied in this HF alky service.

Organic thin-film coatings are not normally used to prevent corrosion and hence the wet H_2S environment because they are susceptible to become damaged by steam out procedures. Thermal spraying metals (e.g., Al) on the surface of the vessels could also be used. The success of both organic thin-film coating and thermal spraying methods is highly dependent on surface preparation and application; failures have been encountered where the coating or the thermal sprayed skin failed and exposed the base metal to corrosion.

Water washing is often used in the fractionation side of in visbreaker, FCC, delayed coker, and fluidized coker units to avoid fouling by NH_4HS salts, and this is also beneficial to reduce corrosion. In cases where the cyanide content exceeds 20 ppmw, polysulfide injection is also used to control its adverse effect on wet H_2S corrosion.

Historically, NH_4HS concentration has been measured at the downstream water separator and the values used to measure corrosiveness of the stream; concentration of 2 wt % or less is found to be noncorrosive to carbon steel. Piehl [80] referred to the Kp factor, which is the product of mole % NH_3 × mole % H_2S, and found that Kp values of 0.1 to 0.5 could be handled with carbon steel, provided the fluid velocities did not exceed 4.6 to 6.1 m/s. The rule of thumb has been to assume 6.1 m/s as the upper velocity limit for carbon steel. Because low velocity could also be detrimental, in that it could allow deposit formation, a lower limit has also been set at 3 m/s.

The measure used to prevent PTA SCC is standard practice in the petroleum refining industry [81]. The most common protection method is to use alkaline washing involving water with 1 to 5 wt % soda ash (Na_2CO_3), before opening the equipment and piping to the atmosphere. Some refineries follow these practices of protecting their austenitic stainless steels in their atmospheric and vacuum distillation units and some do not. In hydroprocessing units there is no question that PTA SCC can become active so soda ash washing the units prior to being opened is a common practice in these units. Most refineries apply the neutralization procedure in their hydroprocessing units, irrespective of the operating temperatures, the use of chemically stabilized or low-carbon austenitic stainless steels, and the feed quality. In the case of furnace tubes, it is based on the premise that all austenitic stainless steels will eventually sensitize and that there is the risk of PTA SCC failure. In the case of piping, reactors, heat exchangers, and other pressure vessels operating at temperatures below the known temperature range for sensitization, the concern has been the welds and heat-affected zones (HAZ). Here again, determining if soda ash wash is still required on chemically stabilized austenitic stainless steel grades can be gainful.

If materials other than austenitic stainless steels are used in hydroprocessing units in the regions where there is H_2S and H_2 at operating temperature exceeding 230 °C–250 °C, they should be inspected periodically to detect high corrosion rates and take the corresponding measures to avoid failures. This is usually done by ultrasonic thickness measurements or profile radiography, when applicable.

Many refineries were originally designed and constructed to process either sweet or only sour crude oils, and to begin processing naphthenic acid containing crude oils with these units that are not fully equipped with the proper corrosion resistance metallurgy for naphthenic acid corrosion has become a challenge. Under modern conditions when refineries start processing crude oils or blends for which they have not yet gathered sufficient field data about corrosion, it is necessary to implement and maintain an inspection program to determine the condition of all lines and equipment operating at temperatures above 230 °C–250 °C where high temperature corrosion could occur. This is intended to identify any locations that may suffer high corrosion rates and thus ensure the integrity of these assets. In cases where corrosion rates higher than normally experienced in the past are detected, the forecasted lives should be adjusted accordingly so opportune repairs or replacement can be planned and, in case the corrosion is excessively high, consideration should be given to metallurgically upgrading to more corrosion resistant materials. In the past, S31600 used to suffice, but under certain conditions it also corrodes by naphthenic acid corrosion, if the Mo content is lower than about 2.3–2.5 wt %. It still offers an excellent corrosion resistance to high-temperature sulfidic corrosion, but if there is the potential for severe naphthenic acid corrosion, the current practice is to use S31700 that should contain 3.0 to 4.0 wt % Mo. If there is potential for any naphthenic acid corrosion for thin packing material in crude and vacuum distillation units, the recommendation is to use S31700.

17.8 CASE STUDY REFINERY MATERIAL PROBLEMS

17.8.1 Vacuum Distillation Unit

The upper packing bed in a vacuum tower severely corroded by NH_4Cl salts, indicating the presence of NH_3 in the feed. The tower was being operated with excessively low temperature at the top. The source of NH_3 could not be accurately determined, but the problem was resolved by increasing the temperature at the top of the tower to displace the salt deposition point outside the vacuum column.

At least two refineries have experienced high-temperature sulfidic corrosion in 9Cr–1Mo steel vacuum bottom lines when processing a particular heavy (22° API) sour (3.3 wt %) and low or nonacidic (TAN <0.5 mg KOH/g) crude oil. The metallurgical upgrading was made to S31600 to resist it. The indication was that this corrosion was not naphthenic acid corrosion but a rather aggressive sulfidic corrosion, and this was confirmed by laboratory tests. Aggressive high-temperature sulfidic corrosion can cause significant corrosion in 5Cr–½Mo and 9Cr–1Mo steels when processing nonacidic crude oils.

Cases of naphthenic acid corrosion have occurred when processing crude oil slates made to meet a TAN of 0.5 mg KOH/g or less. Certain West African sweet and light crude oils [82] are well known in this respect, but some sweet and light crude oils from South America have also been reported to have caused naphthenic acid corrosion [83] at these rather low TAN values. In the light of these experiences, some refineries have lowered the limit to 0.3 mg KOH/g. These cases of corrosion caused by processing low TAN crude oils have been identified because 5Cr–½Mo, 9Cr–1Mo, and 12 wt % Cr steel have suffered corrosion with features consistent with what is expected from naphthenic acid corrosion. These steels are known not to resist naphthenic acid corrosion but are commonly used to resist high-temperature sulfidic corrosion.

The most critical areas for naphthenic acid corrosion are the HVGO section of the vacuum tower, where 12 wt % Cr steel random and structural packing material has dissolved; and 12 wt % Cr steel trays, structural support beams for trays and packing, and 12 wt % Cr steel clad have been severely attacked. Likewise, 12 wt % Cr steel vane type vapor distributors, vapor horns, or other inlet devices have also been affected in atmospheric and vacuum distillation towers. The corrosion occurring in the internal components of the distillation tower in crude and vacuum units seems to be the first stage of manifestation of naphthenic acid corrosion problems. Vacuum tower design appears to have an effect in that 12 wt % Cr steel can suffer severe corrosion in vacuum columns designed with packing beds and high wash oil rates while in older vacuum towers processing exactly the same feed, 12 wt % Cr steel trays and clad survived without suffering naphthenic acid corrosion [84]. HVGO withdrawn from the tower is normally used as wash oil for the lower packing bed when it is still hot and also for the HVGO packing bed, after the stream is cooled in heat exchangers. Naphthenic acids distill in the vacuum tower and partition into the different streams, depending on their boiling point. The HVGO is usually the stream that takes more of the naphthenic acids or the more corrosive ones. Thus, recycling it back into the tower may actually increase the amount of naphthenic acids in the column.

Also, naphthenic acids vaporize and when they condense directly on the metal surface of packing, trays, structural beams, or clad material in distillation columns, they have a TAN that greatly differs from the TAN of the feed that enters the crude unit. Under these circumstances, attempts to establish a correlation between TAN and actual naphthenic acid corrosion is pointless. The TAN of condensing naphthenic acids must be very high and probably has little correlation with the TAN of the crude oil from which it originated. Thus, the naphthenic acid corrosion occurring in distillation tower internal components differs from that occurring in fully liquid phase flow in piping, piping accessories, heat exchanger and heater tubes, pumps, and valves.

17.8.2 Hydroprocessing

A pipe failure occurred by excessive wall thinning occurring only at the top while at the bottom the corrosion was practically zero. This occurred in a distillates hydrotreater unit. The pipe material was carbon steel ASME SA-106 Grade B. There was a single wash water injection point too far upstream of the (REAC) system inlet. The long distance existing between the injection point and the condensers in a horizontal pipe section allowed enough residence time for the stream to form a wavy stratified two-phase (gas-liquid) flow with the wash water occupying the bottom part of the pipe and the NH_3/H_2S laden hydrocarbon gases moving faster on top. The flow pattern intermittently maintained the upper surface of the pipe in wet condition while at the same time the surface was subjected to the higher wall shear stress of the much faster vapor phase flowing on the top half of the pipe. There was thus a perfectly uniform wall thinning along the horizontal pipe section upstream of the reactor effluent condensers, including a 90° elbow that also exhibited wall thinning only on the top half. There was no localized and rough corroded surface that could suggest salt deposition on the top half of the pipe. The failure demonstrated the large influence the flow regime could have on the corrosion of a pipe with two-phase flow in NH_4HS corrosive environment. Had the flow regime been single phase, or nonstratified or annular during service, there would be no reason why the corrosion occurred mainly at the top of the pipe, while at the bottom there was no corrosion. Injecting wash water that far upstream of the air coolers created this damaging two-phase flow.

Naphthenic acid corrosion produced iron naphthenates that reacted with H_2S present in the recycle hydrogen and thus produced iron sulfide that precipitates and were trapped in the reactor [85] of a mild hydrocracker unit, resulting in premature reactor plugging. The iron naphthenates were not produced in the hydroprocessing unit itself but came dissolved in the feed from the crude or vacuum unit where the feed stream was produced. There the corrosion rate was not high, less than 0.13 mm/year, but this relatively low corrosion rate occurring in long piping circuit transported enough iron naphthenates to cause this premature reactor plugging. Thus, under these circumstances, although the corrosion rates were relatively low, the piping handling the untreated feed was upgraded to naphthenic acid corrosion resistant steels, S31600 or S31700 steel, not because of excessive wall thinning but to prevent this premature plugging of the reactor.

17.8.3 Catalytic Reformer

The first reactor of a fixed-bed catalytic reforming unit experienced premature plugging in several occasions, detected by increased pressure drop across the reactor. It was found that the reactor was fouled with a blackish fine powder. This powder was strongly magnetic and was identified to consist of mainly iron oxide. The possibility of H_2S corrosion in the upstream equipment and piping was considered; the resulting iron sulfide could decompose into iron oxide during the regeneration process. A filter system was then installed to trap any corrosion product from the feed, but the reactor plugging problem persisted. The problem was attributed to oxidation of 1¼Cr–½Mo steel piping occurring during the regeneration cycles, with possibilities of high-temperature excursions causing further oxidation on the 1¼Cr–½Mo steel surface. The inlet piping to the reactor as well as the large and tall feed/effluent exchanger (often referred to as the Texas Tower) was covered with high-temperature oxide scale that detached relatively easy from the surface. Several oxide scale pieces were seen inside this exchanger having the exact shape of the tube outside surface, together with large quantities of iron oxide fine particles. Although not enough to cause significant wall loss over time, this oxidation occurring over large surface area of the piping and feed/effluent exchanger tubes was able to produce enough oxide scale to plug the reactor. The catalyst was dumped to remove this fine blackish powder; the amount collected was weighed and it varied from 108 to 426 kg. The oxide scale did not necessarily detach from the steel surface during the regeneration but mainly during subsequent operation, which is why it took from 6 to 18 months of operation to see the pressure drop increase from 0.34 to 2.41 bar. At the time, the regeneration process was changed from using only air to oxygen, but whether this change was responsible for the problem could not be accurately determined. Metallographic evidence was found to indicate that the metal temperatures have greatly exceeded the normal temperature levels of the regeneration process. High-temperature excursion during regeneration was thus suspected to have caused this excessive oxidation of the 1¼Cr–½Mo steel.

17.8.4 Furnace Tubes Melting from Inside

In three separate and independent occasions, tube samples were submitted to failure analyses in which the tube showed melting from inside. Metallographic examination of the solidified metal layer or pieces found inside these failed tube showed microstructure similar to gray cast iron, in the case of a carbon steel heater tube, and white iron, in the case of 2¼Cr–1Mo and 9Cr–1Mo steel heater tubes [86]. At first, it seemed inconceivable that melting occurred inside the tubes while on the outside the tube was still solid. The source of heat is located outside the tubes and the temperature across the wall thickness should be the same or slightly higher on the outside than the inside surface of the tubes. This assumption is still valid. What occurred was that the melting point of the steel adjacent to the ID decreased significantly because it was first transformed to austenite and then this austenite absorbed so much carbon from the coke formed inside the tube that it melted and transformed to either cast iron or white iron when solidified.

During normal operation, the metal temperature of ferritic heater tubes should never reach the lower critical temperature. When the flow through the inside of heater tubes is interrupted, due to plugging (e.g., coke) or operational upset (e.g., interrupting the flow), the metal temperature increases significantly and the ferritic steels may then transform to austenite under these very abnormal conditions. At these temperature levels of overheating, the remaining hydrocarbon inside the tubes quickly turned into coke that became the major source of carbon and severe carburization. Carbon solubility in austenite is much greater than in ferrite. Under conditions imposed by an interruption of the flow, the internal pressure in the tubes is absent or fairly low, so none of these tubes ruptured. Once in the austenitic state, the carbon enrichment process occurred fast in the steel, and the increase in carbon content reduced the melting point in a manner similar to that described by the iron-carbon or iron-chromium-carbon equilibrium phase diagrams.

REFERENCES

[1] White, R.A., and Ehmke, E.F., *Materials Selection for Refineries and Associated Facilities*, NACE International, 1991.

[2] Metals Handbook, 9th ed., *Volume 13: Corrosion*, ASM International, Materials Park, 1987.

[3] Garverick, L., Ed., *Corrosion in the Petrochemical Industry*, ASM International, Materials Park, 1994.

[4] Helle, H., *Corrosion Control in Crude Units*, Corrosion Control Nu, 2003.

[5] API Publication 571, 1st ed., *Damage Mechanisms Affecting Fixed Equipment in the Refining Industry*, API Publishing Services, December, 2003.

[6] Merrick, R.D., and Auerbach, T., "Crude Unit Overhead Corrosion Control," Paper No. 96, *CORROSION 1983*, NACE International.

[7] Bagdasarian, A., Feather, J., Hull, B., Stephensen, R., and Strong, R., "Crude Unit Corrosion and Corrosion Control," Paper No. 615, *CORROSION 1996*, NACE International.

[8] Gutzeit, J., *Crude Unit Corrosion Guide: A Complete How-To Manual*, PCC Process Corrosion Consultants, Gulf Breeze, FL, 2006.

[9] Gutzeit, J., "Controlling Crude Unit Overhead Corrosion – Rules of Thumb for Better Crude Desalting," Paper No. 567, *CORROSION 2007*, NACE International.

[10] Technical Committee Report by NACE International Task Group 274, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International Publication 34105, NACE International, August, 2005.

[11] Rechtien, R., and Duggan, G., "Identifying the Impact of Amine Contamination on Crude Units," Paper No. 581, *CORROSION 2006*, NACE International.

[12] Garcia, J.M., and Lordo, S.A., "Chemistry and Impacts of Commonly Used Amine-Based H_2S Scavengers on Crude Unit Towers and Overheads," Paper No. 571, *CORROSION 2006*, NACE International.

[13] NACE International Publication 8X294, *Review of Published Literature on Wet H_2S Cracking of Steels Through 1989*, NACE International, September, 2003.

[14] NACE Standard MR0175/ISO 15156-1, Item No. 21306, 1st ed., *Petroleum and Natural Gas Industries—Materials for Use in H_2S-Containing Environments in Oil and Gas Production*, NACE International, 2001.

[15] NACE Standard MR0103-2007, *Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments*, NACE International, 2007.

[16] Technical Committee Report by NACE International, *Materials and Fabrication Practice for New Pressure Vessels Used in Wet H_2S Refinery Service*, NACE International, 2006.

[17] NACE Standard RP0472-2005, *Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*, NACE International, 2005.

[18] NACE Standard RP0296-2004, *Guidelines for Detection, Repair, and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H_2S Environments*, NACE International, 2004.

[19] API RP 580, *Risk Based Inspection*, 1st ed., API Publishing Services, May, 2002.

[20] Hau, J.L., Ledezma, M., and Yepez, U.A., "Material Damage Implications of Post Weld Heat Treating H_2 Blisters in Carbon Steel," Paper No. 520, *CORROSION 2001*, NACE International.

[21] NACE International Publication 5A171 (2001 revision), *Materials for Receiving, Handling, and Storing Hydrofluoric Acid*, NACE International, 2001.

[22] API Publication 932-A, *A Study of Corrosion in Hydroprocess Reactor Effluent Air Cooler Systems*, API Publishing Services, September, 2002.

[23] Singh, A., Harvey, C., and Piehl, R.L., "Corrosion of Reactor Effluent Air Cooler," Paper No. 490, *CORROSION 1997*, NACE International, 1997.

[24] Horvath, R.J., Cayard, M.S., and Kane, R.D., "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions," Paper No. 576, *CORROSION 2006*, NACE International.

[25] Ehmke, E.F., "Corrosion Correlations with Ammonia and Hydrogen Sulfide in Air Coolers," *Materials Performance*. NACE International, July, 1975, pp. 20–28.

[26] Horvath, R.J., and Lewis, K.R., "Implementation of Best Practices for Water Washes in Hydroprocessing Units," Paper No. 654, *CORROSION 2003*, NACE International.

[27] Toba, K., Ishimoto, H., Murakami, Y., Asotani, T., and Uegaki, T., "A New Approach to Prevent Corrosion of the Reactor Effluent System in HDS Units," Paper No. 653, *CORROSION 2003*, NACE International.

[28] Singh, A., and Harvey, G., "Corrosion Management in Fractionator Feed Preheat Exchangers in Hydroprocessing Units," Paper No. 687, *CORROSION 2000*, NACE International.

[29] Shargay, C.A., Jacobs, G.E., and Price, M.D., "Ammonium Salt Corrosion in Hydrotreating Units Stripper Column Overhead Systems," Paper No. 392, *CORROSION 1999*, NACE International.

[30] Bagdasarian, A.J., and Truax, D.J., "Chloride Stress Corrosion Cracking of Austenitic Stainless Steels in Hydroprocessing Units," Paper No. 501, *CORROSION 1997*, NACE International.

[31] Material Selector for Hazardous Chemicals, MTI Publication MS-4: "Hydrogen Fluoride and Hydrofluoric Acid," *Materials Technology Institute of the Chemical Process Industries, Inc.*, St. Louis, MO, 2003.

[32] Schutt, H.U., "Corrosion Abatement in Sulfuric Acid Alkylation Unit Horizontal Contactors," Paper No. 494, *CORROSION 1997*, NACE International.

[33] NACE International Publication 5A171 (2001 Revision), *Materials for Receiving, Handling, and Storing Hydrofluoric Acid*, NACE International, September, 2001.

[34] Material Selector for Hazardous Chemicals, MTI Publication MS-1, 2nd ed., "Sulfuric Acid," *Materials Technology Institute of the Chemical Process Industries, Inc.*, St. Louis, MO, 2005.

[35] API 570, *Piping Inspection Code*, 2nd ed., API Publishing Services, October, 1998.

[36] API RP 574, *Inspection Practices for Piping System Components*, 2nd ed., API Publishing Services, June, 1998.

[37] NACE International Task Group 174 *Technical Committee Report on Refinery Injection and Process Mixing Points*, NACE International Publication 34101, NACE International, March, 2001.

[38] NACE Standard RP0198-2004, *The Control of Corrosion Under Thermal Insulation and Fireproofing Materials – A Systems Approach*, NACE International, 2004.

[39] McIntyre, D.R., and Dillon, C.P., "MIT Publication No. 15, Guidelines for Preventing Stress Corrosion Cracking in the Chemical Process Industries," *Materials Technology Institute of the Chemical Process Industries, Inc.*, Columbus, OH, March, 1985.

[40] API Technical Report 938-C, *Use of Duplex Stainless Steels in the Oil Refining Industry*, 1st ed., API Publishing Services, May, 2005.

[41] NACE Standard RP0403-2003, *Avoiding Caustic Stress Corrosion Cracking of Carbon Steel Refinery Equipment and Piping*, NACE International, 2003.

[42] Clarke, S., "Stress Corrosion Cracking of Stainless Alloys in Oxygenated Caustic Environments," Paper No. 596, *CORROSION 2000*, NACE International.

[43] API RP 945, *Avoiding Environmental Cracking in Amine Units*, 3rd ed., API Publishing Services, June, 2003.

[44] Kmetz, J.H., and Truax, D.J., "Carbonate Stress Corrosion Cracking of Carbon Steel in Refinery FCC Main Fractionator Overhead Systems," Paper No. 206, *CORROSION 1990*, NACE International.

[45] Milton, D.J., Smalley, C.G., Botto, R.I., Bresnahan, W.T., and Zagrany, B., "FCCU Light Ends Plant Carbonate Stress Corrosion Cracking Experience," Paper No. 564, *CORROSION 2007*, NACE International.

[46] NACE International Task Group 347 *Technical Committee Report on Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters*, NACE International Publication 34108, NACE International.

[47] NACE International Publication 35103, *External Stress Corrosion Cracking of Underground Pipelines*, NACE International, October, 2003.

[48] NACE International Publication 5A192, *Integrity of Equipment in Anhydrous Ammonia Storage and Handling*, NACE International, April, 2004.

[49] Gutzeit, J., "High Temperature Sulfidic Corrosion of Steels," *Process Industries Corrosion—The Theory and Practice*, B.J. Moniz and W.I. Pollock, Eds., NACE International, 1986.

[50] API Publication 581, *Base Resource Document on Risk-Based Inspection*, 1st ed., API Publishing Services, May, 2000.

[51] McConomy, H.F., "High-Temperature Sulfidic Corrosion in Hydrogen Free Environment," presented at the meeting of the Subcommittee on Corrosion during the 28th Midyear Meeting of the American Petroleum Institute's Division of Refining, in Philadelphia, PA, held in May, 1963 (Washington, DC: API).

[52] de Jong, J.P., Dowling, N., Sargent, M., Etheridge, A., Saunders-Tack, A., and Fort, W., "Effect of Mercaptans and Other Organic Sulfur Species on High Temperature Corrosion in Crude and Condensate Distillation Units," Paper No. 565, *CORROSION 2007*, NACE International.

[53] NACE International Publication 34103, Technical Committee Report, Task Group 176 on Prediction Tools for Sulfidic Corrosion: "Overview of Sulfidic Corrosion in Petroleum Refining," NACE International, 2004.

[54] Couper, A.S., and Gorman, J.W., "Computer Correlations to Estimate High Temperature H_2S Corrosion in Refinery Streams," *Materials Protection and Performance*, January, 1971, pp. 31–37.

[55] Derungs, W.A., "Naphthenic Acid Corrosion – An Old Enemy of the Petroleum Industry," Corrosion Information Compilation Series (CICS): Refining Industry: Naphthenic Acid Corrosion, 2001 Update, NACE International.

[56] Babaian-Kibala, E., and Nugent, M.J., "Naphthenic Acid Corrosion Literature Survey," Paper No. 378, *CORROSION 1999*, NACE International.

[57] Gabetta, G., Montanari, L., Mancini, N., and Oddo, G., "Preliminary Results of a Project on Crude Oil Corrosion," Paper No. 644, *CORROSION 2003*, NACE International.

[58] Groysman, A., Brodsky, N., Penner, J., Goldis, A., and Savchenko, N., "Study of Corrosiveness of Acidic Crude Oil and Its Fractions," *Materials Performance*, Vol. 44, No. 4, April, 2005, NACE International, 2005.

[59] Shargay, C., Moore, K., and Colwell, R., "Survey of Materials in Hydrotreater Units Processing High Tan Feeds," Paper No. 573, *CORROSION 2007*, NACE International.

[60] API Publication 941, 6th ed., *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, API Publishing Services, March, 2004.

[61] ANSI/API Standard 530/ISO 13794, *Calculation of Heater Tube Thickness in Petroleum Refineries*, API Publishing Services, January, 2003.

[62] API RP 579-1/ASME FFS-1, June 5, 2007 (API 579 2nd ed.), *Fitness-For-Service*, API Publishing Services.

[63] Hau, J.L., and Seijas, A., "Furnace Tube-Life Assessment as Impacted by the Methodology Used," Paper No. 08547, *CORROSION 2008*, NACE International.

[64] ANSI/API RP 573, 2nd ed., *Inspection of Fired Boilers and Heaters*, API Publishing Services, December, 2002.

[65] Lai, G.Y., *High-Temperature Corrosion of Engineering Alloys*, ASM International, Materials Park, OH, 1990.

[66] Ravestein, M.H., "Metal Dusting in Catalytic Reforming Furnace Tubes," Paper No. 496, *CORROSION 1997*, NACE International.

[67] Jones, R.T., and Baumert, K.L., "Metal Dusting – An Overview of Current Literature," Paper No. 01372, *CORROSION 2001*, NACE International.

[68] Hau, J.L., and Seijas, A., "Sigma Phase Embrittlement of Stainless Steel in FCC Service," Paper No. 06578, *CORROSION 2006*, NACE International.

[69] Duggan, G.G., and Rechtien, R.G., "Application of Ionic Equilibria Process Simulation for Atmospheric Distillation Overhead Systems," Paper No. 586, *CORROSION 1998*, NACE International.

[70] Tebbal, S., Schutt, H., Podlecki, R., and Sudhakar, C., "Analysis and Corrosivity Testing of Eight Crude Oils," Paper No. 636, *CORROSION 2004*, NACE International.

[71] Lee Craig, H. Jr., "Naphthenic Acid Corrosion in the Refinery," Paper No. 333, *CORROSION 1995*, NACE International.

[72] Hau, J.L., Yepez, O., Torres, T., Specht, M.I., "Classifying Crude Oils According to Corrosivity Using the Fe Powder Test," Paper No. 699, *CORROSION 2000*, NACE International.

[73] Kane, R.D., and Cayard, M.S., "A Comprehensive Study on Naphthenic Acid Corrosion," Paper No. 555, *CORROSION 2002*, NACE International.

[74] Smart, N.R., Rance, A.P., and Pritchard, A.M., "Laboratory Investigation of Naphthenic Acid Corrosion Under Flowing Conditions," Paper No. 484, *CORROSION 2002*, NACE International.

[75] Decker, S., Hynes, T., and Buchheim, G., "Safe Operation of a High Temperature Hydrogen Attack Affected DHT Reactor," Paper No. 09339, *CORROSION 2009*, NACE International.

[76] Kimura, K., Ishiguro, T., Hattori, K., Okada, H., Kawano, K., Yamamoto, H., and Sakamoto, K., "Metallurgical Effect on Hydrogen Attack Damage in C-0.5Mo Steels" PVP-Vol. 336. *Structural Integrity, NDE, Risk and Material Performance for Petroleum, Process and Power*, ASME 1996, pp. 8–18.

[77] Petersen, P.R., "The Use of Corrosion Inhibitors in the Refining Industry," Paper No. 594, *CORROSION 1996*, NACE International.

[78] API RP 579-1/ASME FFS-1, June 5, 2007 (API 579 2nd ed.), *Fitness-For-Service*, API Publishing Services.

[79] Cayard, M.S., Kane, R.D., and Cooke, D.L., "An Exploratory Examination of the Effect of SOHIC Damage on the Fracture Resistance of Carbon Steels," Paper No. 525, *CORROSION 1997*, NACE International.

[80] Piehl, R.L., "Survey of Corrosion in Hydrocracker Effluent Air Coolers," *Materials Performance*, January 1976, NACE International, 1976, pp. 15–20.

[81] NACE Standard RP0170-2004, *Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking During Shutdown of Refinery Equipment*, NACE International, 2004.

[82] Nugent, M.N., and Dobis, J.D., "Experience with Naphthenic Acid Corrosion in Low TAN Crudes," Paper No. 577, *CORROSION 1998*, NACE International.

[83] Caceres, M., Brett, C., and Hau, J.L., "Naphthenic Acid Corrosion Experience in the Refinería El Palito Vacuum Unit," 2nd Inspection and Corrosion Workshop, Petróleos de Venezuela, S.A., (PDVSA), Valencia, Venezuela, December 3–5, 1997.

[84] Hopkinson, B.E., and Penuela, L., "Naphthenic Acid Corrosion by Venezuelan Crudes," Paper No. 502, *CORROSION 97*, NACE International.

[85] Rodriguez, H., and Penuela, L., "Experiences with Naphthenic Acid Corrosion in an Extra Heavy Oil Upgrader Facility," Paper No 586, *CORROSION 2006*, NACE International.

[86] Hau, J., "Oil Refining Heater Tube Failures for Internal Melting," *Materials Performance*, Vol. 47, No. 12, NACE International, December, 2008, pp. 60–64.

18

Product Analysis and Quality Control

Pradeep Kumar[1] and N.S. Murthy[1]

18.1 QUALITY MANAGEMENT IN REFINERY AND PETROCHEMICALS—AN OVERVIEW

The hydrocarbon industry is more than a century old, and in the past refineries were built with domestic socioeconomic considerations in mind rather than creating "world-class assets" and competing to achieve the best from the bottom of the barrel. Technology incorporations in the refineries were again to reduce energy consumption or to comply with statutory/clean fuel needs. In bygone days, crude oil refining was confined mostly to fewer processing configurations, stated on a scale of Nelson's complexity factor, with operations largely routine and refiners content with lower margins ($/bbl). With successive oil shocks in the last 4 decades, refiners have been left with no option but to try "newer"/tough crudes, which are mostly sour (high sulfur) or have high acidity and added impurities such as high nitrogen, high metals, high chlorides, etc. These tough crudes, although termed "opportunity crudes," bring in new challenges such as mitigating corrosion, sustaining/enhancing product quality, keeping pace through plant changes to manage process integrity and handle varying yields, controlling pollution/emissions, etc. New secondary processing units were added to the refining configuration to process such tough crudes. In short, manufacturing needs "engineering precision" to monitor and control operations to get the best from any given crude. Operations needs a "knowledge partner" to perform to its full potential and close to its capability. All of these imply a greater emphasis on stream testing/analysis and quality control.

With soaring oil prices and worldwide recession coupled with the need to restrict/reduce greenhouse emissions, there is a paradigm shift taking place in the product mix from refineries. Furthermore, the cyclic nature of the petrochemical business shrinks margins of the integrated refining complex. Hence, the cost of quality is being increasingly brought under focus to improve the bottom line, and to this end an extensive use of online quality measurements and information technology are being leveraged by refiners. A typical block flow diagram of a modern refinery and petrochemical plant is given in Figure 18.1.

Refiners are coming under extreme pressure to evaluate, accept, and process newer feedstocks successfully or with the least effect on plant/process reliability. The key in this is the response time, and as such several advancements are being tried by refiners to shrink the sampling/testing/analysis of feedstock, which is the single largest time-consuming factor. In fact, a few oil majors are investing substantially to reduce crude oil testing duration from months to a few hours under the concept of the "refinery of the future." This is a seamless integration of all functions across supply chain management in which feed/product analysis and quality control will play a pivotal role in decision process and timely interventions are essential to obtain the best from given assets.

Most oil majors have their own research and technology wing to support business improvement plans such as testing of new-generation catalysts; pilot testing of feedstocks to understand/predict the effects in actual operations; engine laboratories to replicate performance of automobile fuels in automobiles with respect to durability, comfort, energy efficiency, and emissions; product application evaluation especially for polymers; and laboratory simulation to assess behaviors such as fouling, coking propensity, compatibility from likely precipitation of asphaltenes, etc. Furthermore, a few leading oil companies are pursuing next-generation technology in the areas of deep hydroprocessing to upgrade residues and tar sand oil; maximize olefins, especially propylene and ethylene; convert C_{10}+ aromatics into *para*-xylene; and recover 2,6-dimethylnaphthalene (DMN) from light-cycle oil for production of plasticizers, etc. All of these green field research techniques need several designs of experiments at a laboratory scale that involve testing, analyses, and quality-control procedures for ensuring technology reproducibility.

Clean fuels and biofuels are yet other dimensions to the refining complexity today. The drives for sustainable mobility and, if needed, smoother changeover of energy sources are equally compelling refiners to adopt best practices in analysis and quality control. The repeatability and reproducibility values are diminishing with the introduction of newer/smarter techniques by leading institutes such as ASTM. Today, refiners are blessed with test methods that can detect at the parts per billion (ppb) level. Most test methods are automated to minimize human errors. Furthermore, nonintrusion techniques are gaining acceptance because of the robustness in analysis over a wide spectrum of quality parameters with inherent precision. Refiners in the last 2 decades have maximized online spectroscopy techniques.

"Quality giveaway," a phrase used widely in refineries, is one of the components of cost of quality. It is the extent of "quality overkill" above the stipulated specification. It depends on the confidence level in product certification that is based on the competency of the laboratory in testing a given product with a high degree of precision and close to accurate values. It is measured in cents per barrel of crude processed and can vary from 2 to 10 cents/bbl depending

---

[1] Reliance Industries Ltd., Gujarat, India

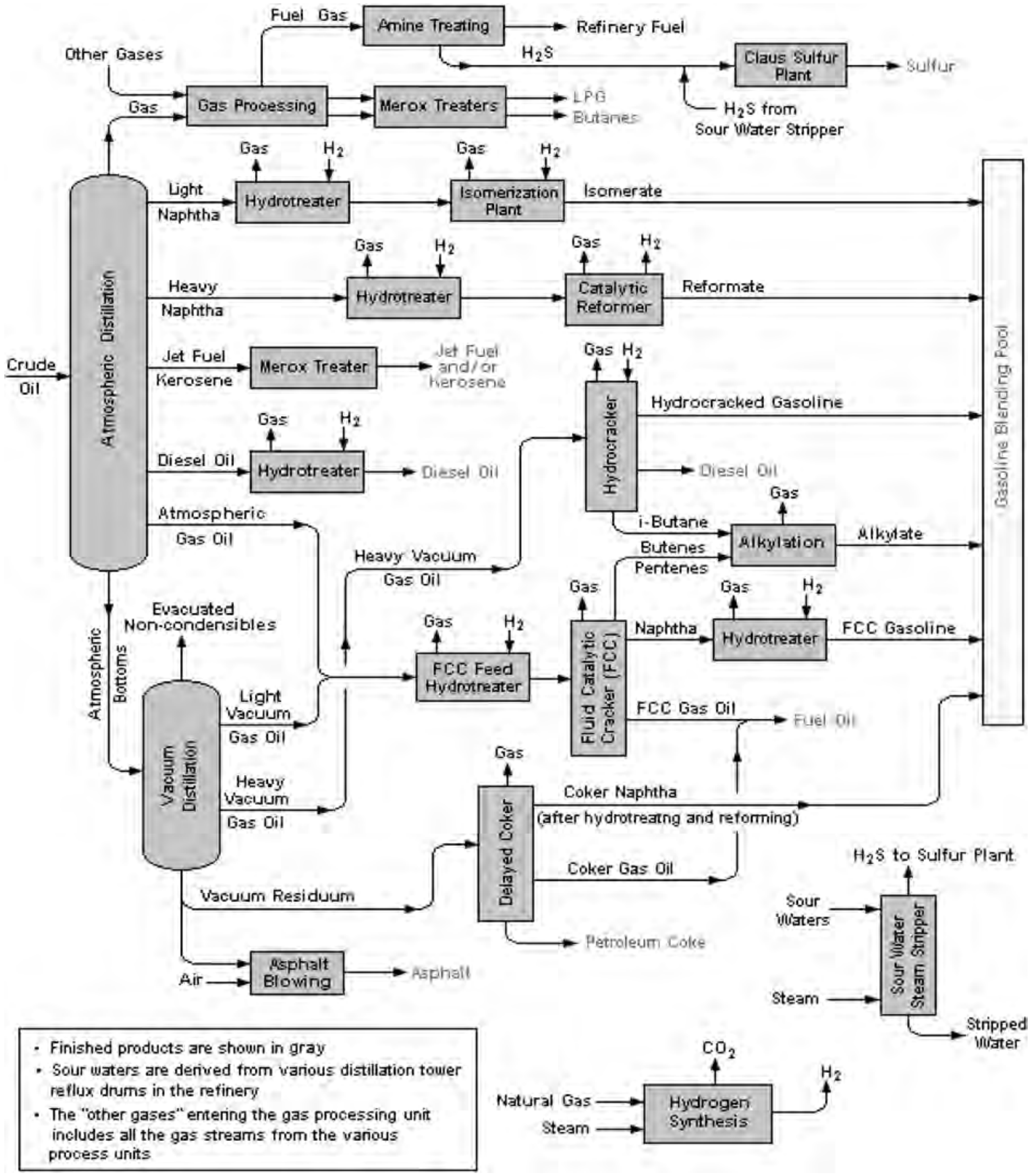


Figure 18.1—Block flow diagram of modern refinery. *Source*: Refinery Block flow from http://en.wikipedia.org/wiki/Refinery.

on the best practices adopted in the field and laboratory for quality measurements and control. Unlike petrochemical products, which are predominantly pure components, petroleum products are a mixture of several hydrocarbons. Hence, to ensure customers, repeatability and reproducibility values are defined for each test method. Refiners stretch their "release specification" of products, which provides their customers confidence so that there is minimal product quality giveaway.

A quality-control laboratory in a pacesetter refinery will have the capability to test crude and products. In most refineries and petrochemicals complexes, the central laboratory operates on a 24/7 basis guiding operations to exploit the asset's capability. The central laboratory undertakes developmental studies in the formulation of "niche products," newer blend recipes, etc. It has become an integral part of the refining and petrochemical operations and also plays an important role in troubleshooting. It renders active support by analyzing trace components, identification of species, diagnosing molecular structures of corrosion products, yield loss, etc. In some refineries the central laboratory undertakes statutory requirements of testing and conforming treated effluent quality, assisting air quality monitoring, validating safe disposal of solid wastes, etc. Furthermore, to ensure customers of product quality, most quality-control laboratories undertake “round-robin” tests of a given sample to assess the performance in accurate testing ability. The time spent on various activities in a modern laboratory is as follows:

- Safety compliance and continual learning—5 %
- Certification of products—30 %
- Customer relations management—5 %
- In-process testing—40 %
- Crude quality tracking and assay generation—10 %
- Operation guide and QMI certification—10 %

In short, the central laboratory facilitates refinery and petrochemical business management to select and buy the “best” (value for the money on crude oil/feedstock purchase), operate assets to the “best,” and make customers feel the “best.” Appendix 18.1 provides a “bird’s-eye” view of a performance comparison of a quality-control laboratory.

18.2 PRODUCT ANALYSIS

Fuel quality is important in today’s competitive markets. Delivery of products to the customer that are free from any contamination or adulteration is the key to maintaining customer confidence and increasing fuel sales. Fuel quality compliance does not stop at the refinery gate where fuel is tested to ensure that manufacturing specifications are met. After manufacture, fuel is moved to bulk storage depots by rail, sea, or pipe line and from there on to services stations by road tankers. At each stage in the distribution chain there is ample opportunity for fuel quality to deviate. Key tests are therefore routinely performed throughout the delivery chain to ensure that product quality is preserved and “fit-for-purpose” product reaches customers.

Refiners today are preparing to meet newer stipulations by way of cleaner fuels and ever-increasingly stringent environmental regulatory requirements. The cost of testing to sustain business can be a double-edged sword. State-of-the-art technology can provide improved measurements but at the same time costs in terms of dollars and staff expertise. However, to create a competitive edge in the market, precise product testing by the business is essential and it has proved to pay rich dividends because of increased awareness by consumers. Clearly, the best analytical technology in a laboratory for product testing supported by online analyzers is necessary in modern times.

Laboratories have been taking a holistic view on modernization to support manufacturing and the market. Analytically, the testing laboratories face new challenges with ever-changing performance goals (raise the bar) to optimize operation and the supply chain. As a result, reduction of quality cost demands better methods with improved precision and detection limits. At a very low level of detection, even sample handling to prevent contamination or loss of the trace analysis has become a concern. For example, with the world migrating to ultralow-level sulfur diesel at less than 10 ppm, the testing ability within accepted criteria is continuously driving the need for new or improved analytical testing methodology.

To control production, analytical methods must be fast, accurate, and reliable. The demand for robust process control to get the best from a given barrel of crude drives the induction of better testing methods in the laboratory or online quality measurements directly in the plant. Further, there are instances when even an alternative method has better reliability and accuracy, because of peer pressure or customer choice, and the given test has to be performed for contractual agreement with the compliance method. For example, a refinery may choose an alternative method over the regulatory method because the alternative method may be more precise or avoid duplication of testing and in the process better assists production control. As an example, a correlative spectroscopic method may provide more precise olefin data in a few minutes than the labor-intensive liquid chromatography ASTM D1319 can in 2 hrs or most automated, time-consuming, multidimensional gas chromatographic techniques. The same correlative analysis might also include benzene, aromatics, oxygenates, and distillation points. ASTM D6708-07 defines how to assess the agreement between two standard test methods that purport to measure the same property of a material and how to determine if a simple linear bias correction can further improve the expected agreement.

From a holistic perspective, product analysis provides proof of a fuel’s performance on use so as to control the expected effect on the environment. Most developed countries are already using ultralow-sulfur fuels and have established work processes to test forecourt fuel samples for parameters influencing exhaust emissions. Hence, the ability for precise testing of fuels is critical to control potential adulteration between refinery and the point of sale.

The process of error-free product testing starts from the initial sample collection, through analysis, to the final reporting and sample retention for checking in case of disputes later. First, a representative sample must be obtained from the process. Care must be taken to prevent loss of lighter components, avoid contamination, and preserve the sample for testing. This sample must then be transported to the laboratory for preparation. For efficiency, a laboratory may break down the sample into smaller portions that can be tested concurrently in different sections.

Once a particular method is chosen, it must be calibrated. For many of the fuel quality parameters (olefins, distillation), gravimetric standards are rarely available and may not be up to the desired requirements. ASTM D6299, standard practice for applying statistical quality assurance to evaluate analytical measurement system performance, provides information for using various statistical tools to monitor and control a measurement system, including how to establish reference materials.

It is good practice to validate the calibration robustness against vagaries seen in sample quality. A change in refinery feedstocks would affect the sample matrix, invalidating the results from a matrix-dependent method.

Although over a dozen test parameters may be monitored during a batch formation through blending of several streams that go into the production of diesel or gasoline, the challenge is compliance with the sulfur specification of less than 10 ppm. Most refiners use online quality measuring instruments (QMIs) for such compliance, and a laboratory plays the role of certifying the QMIs. Successful blending depends on (1) selection of a reliable online analyzer, an appropriate sample tap, and a debugged sample loop that gives stable and connected signals; (2) operators monitoring instantaneous, integrated values, keeping the overall manufacturing targets in mind; (3) regular spot samples analyzed at the refinery laboratory; (4) laboratory specialists performing the analysis and communicating results to operations; and (5) accumulated blending experience and wisdom to interpret the delta (difference of online minus offline values), and after a thorough analysis, determining if actions are needed. With good laboratory statistical quality-control practices in place, the blending process then can be kept on track by statistical process control of these deltas over many blends. In total, with a dedicated team, online analyzers can help the blender face up to the following challenges and successfully add up to the refinery's bottom line by way of

- Real-time information and feedback that permits reduction in re-blends and touch-ups and tighter control for key variables.
- Management of quality giveaway for the specification, which costs the refiners money during blend.
- Accurate and reliable online analyzer performance will build the eventual case for a performance-based measurement system (PBMS).

An effective product testing/analysis program must also ensure a reliable documentation system, which facilitates quality tracking. Most pacesetting organizations deploy LIMS (Laboratory Information Management System). For regulatory compliance, records must be retained for 5 years from the date of creation (40CFR 80.74—a code of federal regulations for housekeeping requirements). There could be special needs requested by customers. Aviation standards require monitoring of the particulate specification at each step in the supply chain (from refinery units to fuel in delivery to aircraft) so as to improve product hygiene. In such cases, records and retention samples need to be maintained by all players (refinery, marketing, common carriers, intermediates, etc). The sample retention requirement for a normal shipment certification sample is 30 days. To preserve sample integrity and prevent loss of light ends, the samples must be sealed and chilled (10°F below ambient temperature).

18.2.1 Product Specification Development and Significance of Analysis

The petroleum industry is a century old, and product specifications have been formulated and continually improved upon with decades of experience. Developments in engine technology, newer processes, emphasis of creating value from waste, newer products especially in the petrochemical field, ecofriendly mandates, higher conversion/yields from a given feed, deeper understanding of raw materials, etc. have facilitated product specification developments. Developments of infrastructure such as the express highway, where speed and stability are the critical requirements, have also added to defining newer specifications such as drivability index, lubricity, etc., in automobile fuels. Further, several calculated parameters such as the calculated carbon aromaticity index, combustion ignition index, Watson K factor, etc., have been put to use to specify product characteristics.

The significance of each of the properties that must be tested under fuel specification is briefly described in Table 18.1. The conventional test methods for each property

TABLE 18.1—Significance and Test Method of Various Product Specifications

Fuel Properties and Significance	Test Methods ASTM/IP
Appearance is visually assessed in a qualitative fail/pass test for cleanliness, to preclude free water, sediments, and suspended matter.	D4176
Total acidity of combined organic and inorganic acids indicates the corrosive potential of fuel to metals. Trace organic acids can affect the water separation properties.	D3242/IP354
Aromatic content relates directly to flame radiation, carbon deposition, and smoke. Also affects swelling of elastomer in the fuel system.	D1319/IP156 D6379/IP436
Hydrogen content contributes to combustion cleanliness and is broadly related to aromatic content.	D3701/IP338
Olefins are unsaturated hydrocarbons that are potential contributors to instability during fuel storage.	D1319/IP156
Total sulfur is controlled because sulfur oxides formed during combustion can cause corrosion to turbine blades.	D4294, D5453/IP336
Mercaptan sulfur compounds are limited because they have a very unpleasant odor and attack certain elastomer material.	D3227/IP342
Doctor test detects the presence of reactive sulfur compounds—alternative method to qualitatively ascertain mercaptan sulfur.	D4952/IP30
Distillation curves define the boiling range, which needs to be appropriate for balanced vaporization of the whole fuel volume.	D86, D2887/IP123
Flash point is related to volatility and therefore affects combustibility. It is a leading factor determining the safety in fuel handling.	D3828, D56/IP170, IP523, IP303
Density must be known for weight-loading calculations because fuel is customarily metered in volumes. Also relates to specific energy.	D1298, D4052/IP365
Vapor pressure is significant for wide cut fuels and indicates venting losses of light ends at altitudes and in hot climates. Also relates to cold starting.	D5191/IP69
Freezing point limits higher molecular-weight hydrocarbons that crystallize at low temperatures; it therefore influences low-temperature pumpability during flight.	D2386/IP16
Viscosity affects fuel pumpability over the operating temperature range and relates to droplet size in sprays produced by burner nozzles.	D445/IP71

TABLE 18.1—Significance and Test Method of Various Product Specifications (Continued)

Fuel Properties and Significance	Test Methods ASTM/IP
Specific energy (net heat of combustion) denotes the amount of heat energy obtainable from a fuel to provide power (value is calculated).	D3338, D4809/IP12, IP355
Smoke point indicates the tendency of a fuel to form soot, which is related to the type of hydrocarbons making up the composition.	D1322/IP57
Naphthalenes are polycyclic hydrocarbons and high in carbon content, exacerbating the problems of carbon formation, flame radiation, and smoke.	D1840
Copper strip corrosion test pass ensures that organic sulfur compounds will not corrode copper components in the fuel system.	D130/IP154
Thermal stability (JFTOT) measurements relate to the amount of deposits formed at high temperature in the engine fuel system.	D3241/IP323
Existent gums are nonvolatile residues left on evaporation of a fuel and serve as a check for contamination within a product distribution system.	D381/IP540
Particulates such as dirt, adsorbent, and rust fines are undesirable and are detected by fine filtration through a membrane filter.	D5452/IP423
Filtration time is measured by the same test procedure as indicated for particulates.	D5452/IP423
Water reaction determines the presence of materials that react with water and affect the stability of the fuel water interface.	D1094/IP289
Water separation (MSEP) index rates the stability of the fuel to release entrained or emulsified water when passed through a fiber glass filter coalescer.	D3948
Electrical conductivity needs to be reasonably in line to specification to dissipate electrostatic charges generated during fuel handling operations so as to prevent fire or explosion hazards.	D2624/IP274
Lubricity (BOCLE) refers to the effectiveness of the lubricating moving parts in engine fuel system components such as pumps and control units where boundary lubrication is a factor in the operation of the component, thus minimizing wear scar diameter.	D5001
Lubricity (SLBOCLE and HFRR) is the ability to reduce friction between solid surfaces in relative motion through a combination of hydrodynamic and boundary lubrication, thus minimizing wear scar diameter.	D6078, D6079
Cloud point of a fuel is a guide to the temperature at which it may clog the filter system and restrict flow; this is increasingly important for fuels used in high-speed diesel engines.	D2500, D3117/IP219
Pour point is an indication of the lowest temperature at which the fuel can be used/pumped.	D97/IP15
Cold filter plugging point (CFPP) indicates the highest temperature at which a given volume of fuel fails to pass through a standardized filtration device in a specified time, thus providing an insight for estimating the lowest temperature at which a fuel will give trouble-free flow in a certain fuel system.	D6317/IP309
Carbon residues are values of a burner fuel that serves as a rough approximation of the tendency of the fuel to form deposits in vaporizing pot- and sleeve-type burners.	D189, D524
Carbon residues (micro method) values of the various petroleum materials serve as an approximation of the tendency of the material to form deposits under degradation conditions and can be useful as a guide in the manufacturing of certain stocks.	D4530
Oxidation stability—distillate fuel oil (accelerated method) values obtained through this test provide a basis for the estimation of storage stability of the middle distillate fuel such as No. 2 fuel oil.	D2274
Oxidation stability—gasoline (induction period method) values obtained through this test provide an indication of the tendency to form gums in storage.	D525
Cetane number (diesel fuel oil) provides a measure of the ignition characteristics of diesel in compression ignition engines.	D613
Research octane number is used by engine manufacturers, petroleum refiners, and marketers as a primary specification measurement related to the matching of fuels and engines.	D2699
Motor octane number is used by engine manufacturers, petroleum refiners, and marketers as a primary specification measurement related to the matching of fuels and engines.	D2700

are shown and do not take into account any extra margin needed to cover handling losses or repeat determinations. The fuel from a nondestructive test (e.g., from the appearance test) can generally be reused for a different test if the sample quantities are limited for conducting product analysis.

18.2.2 Test Method Development

ASTM will not adopt a requirement for a property until a "standard" test method has been developed to measure that property. The test method development process starts with a technical review of the proposed method. Next, an interlaboratory test protocol (round-robin—an oil industry practice followed by Shell, IP, and customers) is conducted in which a common set of samples are sent to a group of laboratories, which independently analyze them. The results of the participating laboratories are compiled and statistically reviewed. If the agreement among the participating laboratories is acceptable, a precision statement is developed that gives the acceptable difference among results obtained by different laboratories on the same sample (reproducibility).

Many of the ASTM test methods were developed from the 1920s until now; however, the test methods that are based on advancement in new technologies are continually being renewed and adopted. To be sure they remain up to date, ASTM requires each test method to be reviewed promptly and reapproved, revised, or cancelled.

ASTM Committee D02 on Petroleum Products and Lubricants meets twice a year—in June and December. The committee, with a current membership of approximately 1500 industry professionals and experts, currently has jurisdiction over 500 standards. These standards play an important role in all aspects relating to the standardization of petroleum products and lubricants.

ASTM Committee D02 consists of the following subcommittees:

1. Property subcommittees, promoting the knowledge and development of test methods for specified properties and standard practice, guides, and terminology.
2. Product subcommittees, promoting the knowledge of the product(s) in the scope. Only product subcommittees may develop specifications and classifications.
3. Coordinating subcommittees, which perform functions that are not covered in the scopes of product and property subcommittees.

D02 Subcommittees meeting December 2007 has reflected the following outcome/changes.

18.2.2.1 PROPERTY SUBCOMMITTEES

- ASTM D909 (Standard Test Method for Knock Characteristics of Aviation Gasoline by the Supercharge Method; F-4 engine) is rewritten to align it with form and style nongeneric equipment guidelines. The method is also updated to include the new engine control equipment that is available and to remove references for parts that are no longer available.
- ASTM D7170 (Standard Test Method for Derived Cetane Number by Fuel Ignition Tester) now includes a full precision statement after the finalization of the round robin. Also, between-method reproducibility (differences between bias-corrected results from ASTM D7170 and Test Method ASTM D613) is defined.
- ASTM D2699 [Standard Test Method for Research Octane Number (RON) of Spark Ignition Engine Fuel] and ASTM D2700 [Standard Test Method for Motor Octane Number (MON) of Spark Ignition Engine Fuel]: Changes have been made and published to allow for the use of automatic octane equipment in conjunction with the standard Cooperative Fuel Research engine to produce a research/motor octane number. The octane analyzer is a fuel delivery system that varies the fuel delivered to the vertical jet to produce a maximal knock intensity reading. ASTM research report RR-D02-1549 has concluded that the octane ratings obtained with the current test procedures and the proposed new autoanalyzer procedure are statistically equivalent.
- Several test methods, i.e., ASTM D482, D1266, D1552, D3348, D5059, D6334, and D6920, including D6299 (Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical System Measurement Performance) and D6792 (Practice for Quality System in Petroleum Products & Lubricating Testing Laboratories) under quality control.
- Significant revisions to ASTM D4294 (Sulfur by ED-XRF) accorded.
- ASTM D5453 (Sulfur by Ultraviolet Fluorescence) has been revised and published as ASTM D5453-08a with the following changes:
  - Added note 3 regarding the working standard.
  - Scope extended to include ethanol and biodiesel fuel blends.
  - Deleted precision information appearing previously against 15.1.1.1 and 15.1.2.1
- New method ASTM D7398 [Test Method for Boiling Range Distribution of Fatty Acid Methyl Esters (FAME) boiling between 100 and 600°C by Gas-Chromatography] introduced.
- New method ASTM D7215 (Standard Test Method for Calculating Flash Points from Simulated Distillation Analysis of Distillate Fuels) introduced.
- New method ASTM D7371 (Standard Test Method for Biodiesel "Fatty Acid Methyl Esters content" in Diesel Using Mid-Infrared Spectroscopy, FTIR-ATR-PLS) introduced.
- ASTM D97 (Pour Point) sections 6.7 and 8.3.2 have been revised and published.
- ASTM D5773 (Cloud Point by Auto Constant Method) sections 7.3, 11.1, 11.2, 11.3, 11.7, and 11.10 have been revised and published.
- New method ASTM D7397 Standard Test Method for Cloud Point of Petroleum Products (Miniaturized Optical Method) introduced.
- ASTM D2533 (Standard Test Method for Vapor-Liquid Ratio of Spark Engine Ignition Fuels) is no longer used and was therefore withdrawn.
- ASTM D445 (Kinematic Viscosity) Grand Design Task Group rewrites the method and precision section to include manual and automatic instruments. Preliminary data do not suggest any acceptable bias between automated and manual data sets.
- ASTM D86 (Atmospheric Distillation) has been revised and published. The main changes are the revision of section 13 with a new precision and bias statement. Other changes include revision to Annex A1 (new precision charts); revision to A4.9; revision to 10.2, 10.3,

and X 2.2.2 (reference correct tables); and revision to note 19.

- A new method is being developed to measure the oxidation stability of gasoline. The method is based on Petrotest's PetroOxy (test method to rapidly reduce testing time for oxygen stability) equipment and received several negatives that will be addressed during the next subcommittee meetings.
- A generic method is being developed to use a particle counter for gasoline.
- A new method is under development for particulate contamination of biodiesel.
- A new practice is being developed that provides information on sampling methods that are useful when validating the performance of process analyzers according to ASTM standard D3764. The new practice also applies to analyzers covered by ASTM D6122.

18.2.2.2 PRODUCT SUBCOMMITTEES

The main topic dealt with keeping the specifications for motor gasoline (ASTM D4814-11b) upto date with state and federal regulations and ensuring that current and relevant test methods are listed. The effect of oxygenates on fuel volatility and vehicle drivability is always under careful scrutiny. To do this effectively, it is crucial that committee members represent the various industries, from fuel suppliers, ethanol producers, supply and distribution, and automotive original equipment manufacturers (OEMs).

Progress on biodiesel continues to generate some positive momentum as work continues against pressure from regulatory agencies. Work on the B5 specification under ASTM D975 remains tabled, and the attempt for a B6-B20 stand-alone specification now moves to D02 level for balloting.

18.2.2.3 COORDINATING SUBCOMMITTEES

The activities of this subcommittee are important in the context of development of standard with respect to product release through QMIs. For ASTM D6299 "Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance," several proposals for change were discussed related to run rules of control charts and expressing precision as standard deviation of the mean in addition to expressing precision as a moving range of two. The main changes are as follows:

- Control charts are based on series of 20 data points instead of 15 data points.
- Run rules are to be treated as mandatory instead of optional.
- One run rule was modified, now saying that nine or more data points falling on the same side of the central line are an indication for an out-of-control situation.
- One new rule was added (i.e., seven data points steadily increasing or decreasing is indicative of an out-of-control situation).

ASTM D6708 "Standard Practice for Statistical Assessment and Improvement of Expected Agreement between Two Test Methods That Purport to Measure the Same Property of a Material: Revision" were approved and published as ASTM D6708-07 with the main updates being a more robust equation for estimating "between-methods" reproducibility and the term "between-method reproducibility" replaces "cross-method" reproducibility.

18.2.3 Comparison of Test Methods

Like ASTM, there are other industry standards in petroleum testing used by various customers in different countries, including test methods by IP (Institute of Petroleum), DIN (Deutsches Institut Fur Normung), ISO (International Organization for Standardization), GOST (Gosstandart of Russia), EN (European), etc. In addition, some of the oil majors and leading process licensors have developed their own proprietary test methods for the purpose of better understanding the refining operations. It is a good practice for pacesetting laboratories and refiners who sell their products anywhere in the world to have a ready comparison table for most test methods with widely used ASTM method. This helps refiners to serve the customers even if the customer-specified test method and associated laboratory equipment are not readily available. On a few occasions it is seen that equivalent test methods may not truly represent customers' needs, and it is worth taking up such issues upfront before entering into a sale agreement. Furthermore, making laboratory personnel aware of intricacies between test methods is vital for preventing postsale clarifications/litigations.

Table 18.2 provides an illustration of test methods typically used in oil industries. Please note that it is not an exhaustive comparison table. However, the most commonly used test methods for fuel products are listed. It is imperative that the laboratories work in tandem with the marketing/sales team to understand the customers' desired test methods and prepare the laboratory testing accordingly.

18.2.4 Accuracy, Repeatability, and Reproducibility in Test Methods

The "terms and definitions" related to test methods are more frequently used to validate the final results. A value that serves as an agreed-upon reference for comparison is derived as:

1. A theoretical or established value that is based on scientific principles;
2. An assigned or certified value that is based on experimental work;
3. A consensus or certified value that is based on collaborative experimental work under the auspices of a scientific/engineering group; and
4. When 1, 2, and 3 are not available, the expectation of (measurable) quantity (i.e., the mean of a specified population of measurements).

- *Accuracy:* The closeness of an agreement between a test result and the accepted reference value. When applied to a set of test results, the term accuracy involves a combination of random components and a common systematic error or bias component.
- *Bias:* The difference between the expectation of the test results and the accepted reference value. Bias is the total systematic error as contrasted to random error.
- *Intermediate precision:* Precision under conditions in between repeatability and reproducibility; most often used for long-term precision in one laboratory and different operators using the same equipment.
- *Precision:* The closeness of agreement between independent test results obtained under stipulated conditions. Precision depends mainly on the distribution of random error and does not relate to the true value or the specified value. Precision is usually expressed in terms of standard deviation.

TABLE 18.2—Product Specifications: Various Test Methods

Tests	Jet A-1 Defense Standard 91-91	Aviation Turbine Fuel D-1655	Diesel EN-590	Diesel D-975	Motor Gasoline EN-228	Motor Gasoline D-4814
Density	D4052	D1298	ISO3675		ISO3675	D1298
	IP365		IP160		IP160	
Flash point	IP170	D56	ISO2719	D93		
		D3828	IP34			
Distillation	IP123	D86	ISO3405	D86	ISO3405	D86
	D86		IP123	D2887	IP123	
Sulfur	IP336	D1266		D5453		D1266
	D4294	D5453		D2622		D5453
	D5453	D3294		D129		D2622
Freeze point	IP16	D2386				
	D2386					
Cloud point			EN23015	D2500		
			IP219			
CFPP			EN116	D6371		
Viscosity	IP71	D445	ISO3104	D445		
	D445		IP71			
Smoke point	IP57	D1322				
	D1322					
Cu corrosion	IP154	D130	ISO2160	D130	ISO2160	D130
	D130		IP154		IP154	
Existing gum	IP540	D381	ISO6246		ISO6246	D381
	D381	IP540	IP131		IP131	
Aromatics	IP156	D1319		D1319	IP156	
	D1319				D1319	
CCR			ISO10370			
			IP398			
CN			EN15195	D613		
			IP498			
Vapor pressure					EN13016	D5191
					IP394	
Oxidation stability					ISO7536	D525
					IP40	
CCI				D976		
Lubricity	D5001			D6079		

- *Repeatability conditions:* Conditions in which independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.
- *Repeatability limits:* The value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be within a probability of 95 %. The symbol is designated by r.
- *Reproducibility conditions:* Conditions in which independent test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

- *Reproducibility limits:* The value less than or equal to which the absolute difference between two test results obtained under reproducibility conditions may be expected to be with a probability of 95 %. The symbol is designated by R.
- *Root mean square error prediction:* This is an accuracy measure and it is expressed in the same unit as the variable y to which it relates. The abbreviation used is RMSEP or RMSP.
- *Standard deviation:* A measure for the deviation from the mean (i.e., it is a precision measure and is the square root of the variance), it is expressed in the same units as the variable y to which it relates. The symbol is designated by σ. The precision of a measurement method can be characterized by several different standard deviations (e.g., the repeatability standard deviation), the reproducibility standard deviation, and the between-day standard deviation.
- *Standard error prediction:* The standard deviation of the prediction residuals (difference between reference value and predicted values); it does not include the bias. The abbreviation used is SEP. (Note that SEP is frequently confused with RMSEP.)
- *Trueness:* The closeness of agreement between a test result and the accepted reference value. The measure of trueness is usually expressed in terms of bias.
- *Variance:* Termed as a measure for precision. Usually the standard deviation, which is the square root of the variance, is used. The symbol is designated by σ^2.

18.2.5 Release Specification of Products

Because all hydrocarbon product testing involves a bit of uncertainty owing to limitations in the methods deployed (in the form of repeatability and reproducibility values of test standards), refiners try to stretch their testing capabilities closer to specification limits within their own laboratory-ascertained repeatability value. Selling the products closer to specification limits improves the bottom line; however, the confidence level in testing products and "releasing" closer to specification limits requires close scrutiny. Many refiners take a conservative approach of releasing products at specification value plus or minus reproducibility limit (depending upon if the specification is the minimum or maximum limit) so that there is the least chance of the product failing/crossing limits at the destination. Other refineries may choose their release specification as the specification value plus or minus repeatability in consultation with their customers. As such, not all specifications are critical to end-use need and hence such "pushing" close to limits can be accepted. Few other refiners perform quarterly weighted average of supplies and ensure that the average value is within the specification limit. In short, the release margin is decided by every refinery and other confidence-building measures such as round-robin tests, visits to customers' premises, arranging a walk-through of facilities by customers, etc., are done to minimize the cost of delivered products.

18.2.6 Laboratory Correlation Programs

Ensuring the quality of test and calibration results requires that laboratories must have quality-control procedures for monitoring the validity of test results and calibrations performed. The resulting data are recorded in such a way that trends are detectable and, where practicable, statistical techniques are applied for reviewing the final results. Therefore participation in interlaboratory comparison or proficiency testing programs is considered important to validate performance of the laboratories.

The laboratory correlation programs in accordance with ISO guide 43 are aimed at helping the participating member laboratories to improve their testing performance in reducing the product quality incidents and being best in class regarding product quality giveaway (QGA). The current benefits of this program are in providing laboratories with a quality assurance tool for measuring and improving the precision of their test results. In turn, this leads to increased confidence in the integrity of product quality data produced by the laboratory. Other benefits include influencing standardization bodies to write more realistic and practical methods and to build in accuracy and quality control into laboratory operations by using well-characterized secondary reference material. However, the potential customers to laboratory correlation program where providing leverage to the efficiency and effectiveness can enhance added values in the product quality management distribution chain. These include production of reference samples for quality measuring instrument (QMI) implementation and application, especially with the more modern applications such as near infrared (NIR) and nuclear magnetic resonance (NMR) that rely on modeling with real and well-characterized reference material.

Testing accuracies with a high degree of precision lead to the minimization of product QGA, which in turn improves the bottom line of the operating units.

Laboratories are considered excellent provided they remain within (±) twice the standard deviation $(R/2.77)^2$ of the prime method over the mean values for each test result calculated from the participating laboratories. In a well-balanced analytical system, z scores should fall outside of the following ranges:

- –2 to +2 in 5 % of instances
- –3 to +3 in 0.3 % of instances.

In short, the correlation program is used as a quality improvement tool to add to the bottom line.

18.2.7 Testing Productivity

A high-performing laboratory is essential if refineries wish to achieve best-in-class status. However, in addition to operating to a high standard with regard to the integrity of test results, it is equally important that the laboratory service is delivered in an efficient and cost-effective manner. Technology pace and ongoing automation has required great effort associated with laboratory benchmarking and overall productivity for better comparison with peers/technical service/consultancy providers with the objective of gaining more insight into the factors that influence laboratory manpower and efficiency.

Broadly speaking, two main factors that determine the manpower in the laboratory are the volume of work (i.e., number of samples, test parameters for routine/nonroutine sample specimen) and the efficiency with which the analytical function is executed. Laboratory automation has resulted in executing unscheduled requirements, such as operational adjustment, test runs, troubleshooting needs, QMI performance check in addition to maintaining in-house compliance,

---

[2] R is reproducibility and R/2.77 is 1σ standard deviation.

etc., with much faster pace and with the limited manpower set for optimized sample schedules around the clock.

In an ideal refinery, all laboratory testing would be scheduled and routine, with minimal check samples and no troubleshooting exercises required. However, in the real world this is far from the case. The percentage of nonroutine analytical requirement may vary from 5 to 30 % of the total testing.

The relatively high manhours per normal shift position may indicate a significant scope for manpower efficiency improvements; on the other hand, inclusion of a high level of overtime hours may exacerbate the situation. It is most likely that high staff numbers in the testing laboratory are mainly due to a high number of samples/nonoptimized schedules being analyzed on a yearly basis rather than just laboratory inefficiency.

The key indicator for the efficiency of the work execution is the number of tests performed per hour, per person; this should demonstrate productivity of the analyst staff when comparing with other laboratories of similar magnitude. Again, this would suggest that the laboratory is not overstaffed compared with the volume of work it has to handle. There is no doubt that laboratory efficiency can be improved by increased automation and adoption of new technologies.

18.2.8 Case Studies from Customer Relations Management

The sayings "the customer is always right," "customer loyalty," etc., are always an integral part of business and are even more critical in this period of low returns and intense competition. It is a reality that users on most occasions have not learned the "best" use of products supplied. It is applicable to any products including fuels from a refinery. On many an occasion there is a tendency to use a same quality product for different end applications and in the process customers do not "see" the money going down with no returns. Although most off-shelf tools on customer relations management (CRM) capture the buying pattern, price sensitivity, just-in-time inventory, payment options, etc., there is hardly any mention or drive on the "right fuel for given end application." With soaring oil prices, it is imperative that the CRM initiatives also probe these aspects and increase value to customers. This can be effectively done through development of "niche" fuels for a given market segment. Few fuel specifications in different parts of the world vary substantially, including the developed world, although the end use is the same. For example, diesel is widely used in internal combustion (IC) engines (automotive and stationary), gas turbines, boilers/furnace, etc. Although diesel for automotive engines needs to be at prime quality with high Cetane, lowest sulfur, better stability, and a higher degree of hygiene, etc., the same are not essential for other applications. In other words, understanding the end application at the customer premises is as important as having an excellent relationship with customers. On several occasions, "challenging" conventional wisdom or out-of-the-box thinking has helped to assess the critical properties in fuels, which could then be optimized within the logistic capabilities.

To illustrate the gains realized through customer interaction, a refinery was supplying the same grade of furnace oil for 10 years that was used as fuel in boilers of various industries and as feedstock to manufacture fertilizers in other industries. Although the carbon/hydrogen ratio is critical to the fertilizer industry, the parameters such as viscosity, caloric value, metals, sulfur, pour point, etc., are of importance to boiler fuels. With poor interactions between refineries and marketing in turn with customers, the same grade of furnace oil was being delivered to both market segments. Because viscosity became the controlling specification, substantial cutter stock (middle distillate such as kerosine, jet fuel, and diesel) was getting diverted to meet specification limits. Subsequently, the refiner started making two grades of furnace oil: one for fertilizer units and another for boiler fuel for industries. This small act alone resulted in a saving of over $7 million per annum by way of cutter-stock saving.

Inviting customers and walking through the quality-control/assurance system provide greater confidence to customers. A transparent approach always delivers results. There are instances of asphaltene control requirements in carbon black feedstock (CBFS). The asphaltenes in CBFS render hard spots in tires, making them vulnerable to developing cracks during runs. In fact, unusual demands make refiners look into "best operating days" in the fluid catalytic cracking process to meet the newer specifications. In short, customers having the requisite knowledge of manufacturing processes by which a given product is made and refiners knowing the critical attributes of a product in its end application are vital to creating value to customers and suppliers.

18.2.9 For Extended Learning in Product Testing

Governments worldwide continue to take action to address the major environmental and human health problems caused by sulfur emissions. For the petroleum industry, this has meant the introduction of stringent legislation to limit the allowed levels of sulfur in automotive fuels. Because these regulations are set to become even more rigorous in the future, accurate and precise measurement of sulfur in petroleum products has never been more important.

Ultralow sulfur diesel (ULSD) is a standard term that describes diesel fuel with significantly lower sulfur content. Petroleum products constitute a significant source of sulfur dioxides (SO_x) in air. As a result, sulfur content has been subject to increasingly challenging controls over the last few decades, resulting on one hand in continuous improvements in hydrotreatment technologies and on the other hand in analytical techniques to assess the effectiveness of the desulfurization processes used.

Such measures have helped in achieving a dramatic reduction in sulfur deposition worldwide—a 71 % decrease in SO_x emissions from 1987 to 2001 was reported by the World Mineral Exchange. In parallel, automobile manufacturers the world over are developing engines with advanced emissions control system that require ultralow sulfur fuels to sustain reliability.

Today, government regulations impose extremely low limits for sulfur in fuel. For example, in the United States, the U.S. Environmental Protection Agency (EPA) has mandated the use of ULSD from the model year 2007. The allowable sulfur content for ULSD in the United States is now set at 15 ppm, down from 500 ppm. The same has been done in Europe, and the sulfur specification in European diesel that was previously less than 50 ppm was lowered to 10 ppm since October 2009. In Asia, many national environmental bodies (e.g., those in Taiwan and Singapore) have adopted the Euro V standard.

Benchtop analytical instrumentation such as energy-dispersive X-ray fluorescence (EDXRF), wavelength-dispersive X-ray fluorescence (WDXRF), and ultraviolet fluorescence measurement technologies, with their increased resolution, detector sensitivity, and precision margins, have provided much relief for measurement of sulfur to the desired level of accuracy in product certification and in satisfying contractual agreement and legislation. The technology is ideal for quality control and to ensure compliance with international norms, including ASTM, IP, ISO, DIN, and EPA. Customized/traceable standards supplied by leading manufacturers and correlation samples in the expected sulfur range assist in making the use of technology more robust and user-friendly.

18.3 QUALITY CONTROL

The process of quality control in a modern refinery/petrochemical complex can adopt either the Six Sigma methodology of DMAIC (Define, Measure, Analyze, Improve, and Control) or the guidelines of total quality management involving steps of PDCA (Plan, Do, Check, and Act). Although both approaches could lead to similar end results, the robustness of the designed process and the set of key performance indicators to monitor the efficiency and effectiveness of the process are the main differentiators between a quality-control program in a world-class organization and the rest. The process of quality control in best-in-class refineries will encompass the facets given in Figure 18.2.

The various elements of the quality-control process are elaborated further for the purpose of giving insight into the salient activities that go beneath. Most IT-savvy refiners and petrochemical units deploy a laboratory information management system (LIMS) to facilitate an effective quality management system. A well-defined and implemented LIMS provides an online audit of sample tracking, test bench occupancy, quality control by way of exceptional reporting, stream quality variations over time, quality traceability of finished products, testing performance of laboratory personnel, tracking of laboratory equipment calibration frequency/bias update records, tracking of stored reference sample, etc. A world-class quality system begins with having a dedicated setup for quality management directly under the head of the complex and is an independent function having single-point accountability to ensure quality to customers. The quality-control cell interacts with all stakeholders through operations, process engineering, planning/scheduling and shipping, the reliability team of inspection and maintenance, statutory bodies, the environmental team, the marketing and customer relations team, etc. The key features of different subsets of the quality-control process are outlined in the following subsections.

18.3.1 Quality-Control Organization

This team in a refinery/petrochemical complex is responsible for providing timely and precise test results, managing laboratory facilities, supporting the manufacturing processes by way of inputs at a fundamental level of basic science, facilitating customers' requirements with product performance features, demonstrating testing methods, participating in national and international forums of specification and test method development, performing product benchmarking, undertaking round-robin tests with peer laboratories,

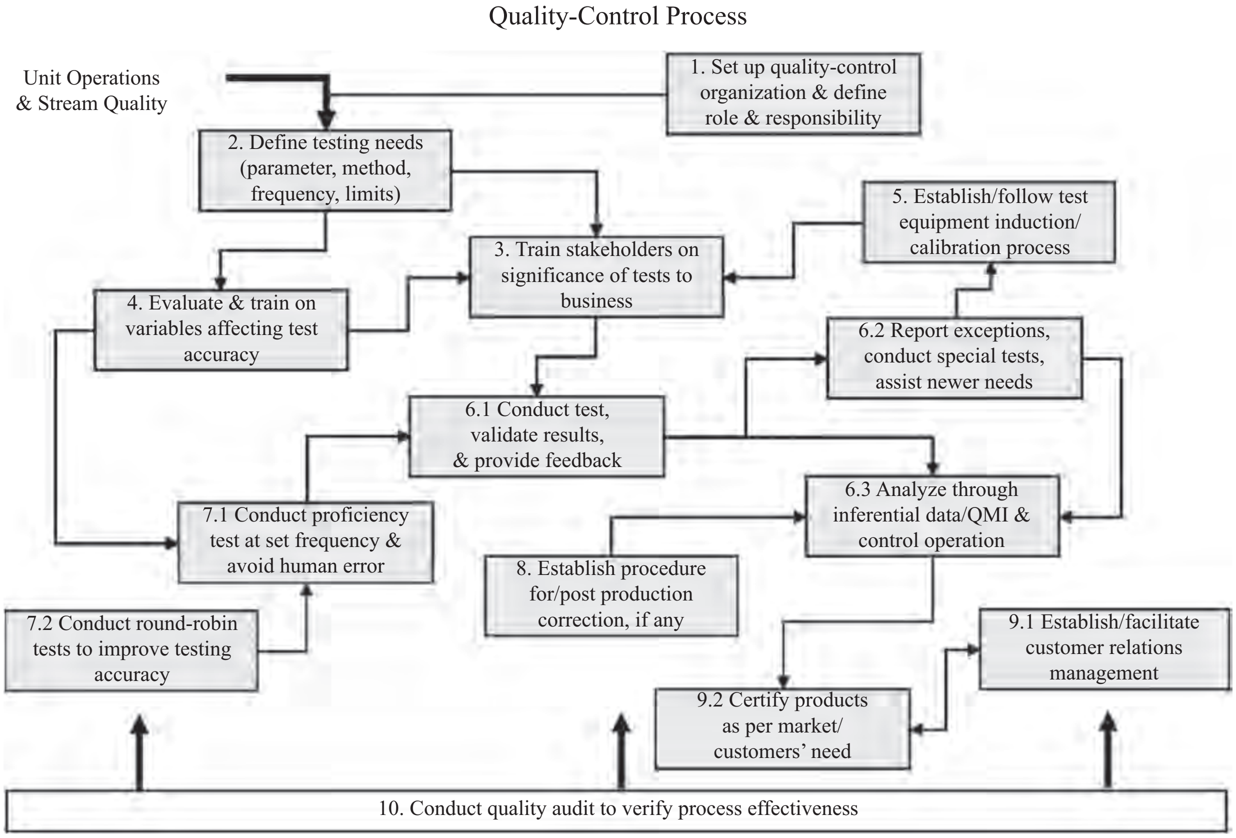


Figure 18.2—Activities involved in quality control in a typical refinery.

developing and being the custodian of modeling, certifying online QMIs, etc. In short, this team does the “overseer” function for the quality value chain across the entire manufacturing process.

Some of the high-level key performance indicators (KPIs) routinely monitored under this segment of the quality-control process are laboratory safety and environmental aspects; customer feedback and redressal; accomplishment rating in industry round-robin tests; implementation status of audit (internal and external) recommendations; LIMS uptime factor, laboratory equipment reliability; personnel productivity and training; market development with respect to competitive performance of products; induction of new tests; initiatives relating to research; improvement in testing and service delivery using quality improvement techniques such as Six Sigma, 5S, and Lean; new crude assays, etc.

Modern laboratories in the refining and petrochemical industry will have the capability to test crude oil, hydrocarbon streams, and products with most international test methods through ASTM, IP, DIN, UOP, ISO, etc. This is essential because different customers have their own unique needs in testing. Furthermore, having a clear understanding of product acceptability criteria by different customers is vital to ensuring the quality of products delivered.

Induction of state-of-the-art QMIs has placed considerable resource demand on ensuring the availability and reliability of a given sophisticated laboratory test appliance. Some of the advanced test equipment that was hitherto only seen in research laboratories but is now being inducted in refining and petrochemical units includes inductively coupled plasma detection, wide-angle X-ray diffraction, gas chromatography-pulsed flame photometric detection, crude true boiling point testing, low oxygenate gas chromatography, hot liquid process simulator, etc. With the incorporation of electronics in laboratory testing, a reliable source of power is another prerequisite. In short, progressive laboratory management has become versatile in dealing with multiple challenges from the supplier (for all inputs) and customer (for all outputs) end to control quality.

18.3.2 Testing Needs Identification and Acceptance

Quality control begins with having an in-depth knowledge of the refining/petrochemical manufacturing processes, listing measurement parameters that are “critical to quality” (here quality is in wider spectrum and is inclusive of stream specifications, processing units’ efficiency and effectiveness, KPIs, and people supporting the unit operation/maintenance/rendering services), and assessing Cp—the process capability in statistical terms of control variables so as to achieve business objectives throughout the lifecycle of the manufacturing complex. Further, defining the interaction through testing needs, test methods to be adopted, frequency of testing, data archiving, control limits, sample conditioning, etc., between manufacturing and laboratory services takes into consideration past experience both within and elsewhere for the similar unit operation. An illustration of statistical means to establish the optimal and effective testing needs for any given manufacturing unit is given in Figure 18.3.

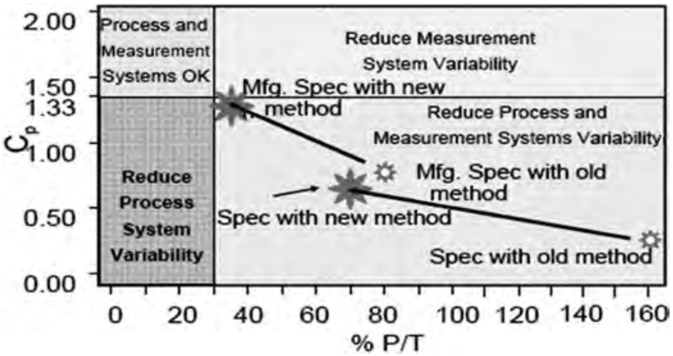


Figure 18.3—Process capability assessment through measures of precision/tolerance [1].

Mfg. Spec, manufacturing specification for any given measurement parameter; Cp, the process capability, is calculated from measurement of mean, LSL/USL (lower specification and upper specification limits), and standard deviation of the measured parameter; P, precision of measuring instrument being used to measure the parameter; T, tolerance of measured value within which the process is to be operated and controlled i.e. within LSL/USL.

$$C_{pk} = \min\left(\frac{\text{USL}-\mu}{3\sigma},\frac{\mu-\text{LSL}}{3\sigma}\right)$$

where μ = the mean of the process

σ = the standard deviation of the process

Defining test needs, setting up minimal and maximal limits, etc., requires considerable expertise from operations, laboratory services, process engineering, licensor inputs, factors likely to affect plant reliability, etc. There will be a tendency to state “overkill” on the requirements in the initial setting-up phase, which can be tailored to optimum by addition of new requirements and reducing the frequency of testing on the basis of steady-state operation. In other words, testing needs identification and implementation will be dynamic and calls for periodic review (at least once every 6 months) to keep the business needs focused.

Tracking the quality of crude oil is another important activity of a laboratory because 90 % of refiner input cost is only on purchased crude. Every refiner attempts to widen the crude choice so that there is adequate flexibility to exploit the delta in crude price between low and high API crudes. Because crude wells do get depleted, there are variations between batches supplied. When the actual API of supplied crude goes down from that used at the time of selection/purchase, there is a substantial penalty. Hence, refiners either update the crude database once every 2–3 years with the latest assays or track quality so as to take up with the supplier to appropriately protect refining margins. There are several test parameters [such as recovery at 1050°F, total sulfur, total acid number, bottom sediment and water (BS&W), etc.] that are tracked for each lot of supply, which is then compared with an assay database for the extent of variation and subsequent resolution/claims, if any, with suppliers.

Reliability is another “watch word” repeatedly brought under focus in refinery and petrochemical plants. The extent of degradation of the unit operations requiring periodic downtime to repair/correct/replace equipment, pipelines, machines, etc., to bring back to “fit for purpose” is critical to monitor to avoid incidents. Here again, the material science team under inspection as well as conditioning monitoring engineers for rotary equipment play a pivotal role in assigning laboratory test supports in consultation with process engineering team and operations.

Most petroleum products are a blend of different streams. The planning and scheduling department that oversees the day to day intake and offtake movements in consultation with a logistics and inventory management team set up laboratory testing needs. At times when a common dispatch line is used, monitoring of the interaction between successive products being transshipped will also be critical to avoid quality degradation/product failures at load points. Hence, laboratory management undertakes a comprehensive testing requirement study, evaluates the past results for optimizing the load, and gets the acceptance of stakeholders to ensure quality control.

The bottom line for effective quality control is the need for collating an adequate understanding of refining/petrochemical processing schemes by a laboratory management team so as to deliver precise test results to its internal/external customers.

18.3.3 Significance of Testing to Business [2]

It is imperative that laboratory personnel are given an orientation to the effect of testing on business. It is one of the best practices to develop a business environment in laboratories because delays/errors in testing could cost the organization millions of dollars. Throughout the petroleum business, products are sold in volume, and the sensitivity of a volumetric correction factor involves representative sampling, accuracy of density determination, and reporting by the laboratory. Similarly, the BS&W test on crude, especially heavier crudes (with API less than 15), is tedious and could lead to errors, which can result in lower value realization from crude being processed. Further, with the cleaner fuel campaign around the world, there is price parity that is based on the sulfur levels of diesel. Hence, determination of sulfur by most modern methods is critical to business. Examples of other quality parameters of products that are linked to price are the research and/motor octane numbers of gasoline, the viscosity of fuel oil, the Bureau of Mines correlation index of CBFS, the viscosity index of lube base stocks, the purity level of petrochemical products, the total paraffins of naphtha, etc.

Appendix 18.2 provides an illustration of improvements of repeatability (r) and the reproducibility (R) of some of the tests important to business. In fact, test standards are continually updated by global standards agencies such as ASTM, IP, etc. The scientific community works in liaison with laboratory tests equipment manufacturers and conducts tests with newer generation methods, and r and R values are captured to verify the test robustness before acceptance.

As can be seen from Appendix 18.2, the quality of measurements has improved over the years with the incorporation of newer and better test methods. This improved quality has benefited suppliers and customers. At the suppliers' (refiners) end, lower r and R in a test method help to improve the bottom line by way of reduced QGA in sale and the "correct" value for the money paid in crude purchased. Refiners have their own in-house program to evaluate the extent of quality overkill in supplies such as cents per barrel of product/unit of measure in a given specification. For example, refiners typically incur erosion of margins when there is QGA in products dispatched, as given in Appendix 18.3.

Improvement in the accuracy of quality measurements will also benefit the customers in terms of "true value" on the assured quality of products, avoiding complaints and even at times litigations, allocating useful time to work with suppliers for obtaining a higher degree of quality consistency in product delivered, etc. Because "zero tolerance" on product quality is a business imperative, laboratory personnel also need to be aware of the commercial implications.

18.3.4 Parameters Affecting Testing Accuracy—6M Methodology

Because testing effectiveness is very critical to quality control, most businesses look for factors that could lead to errors in testing. To approach the identification of parameters that influence testing, one of the best tools is the Ishikawa cause-and-effect matrix or 6M methodology. An illustration of potential causes that could result in testing error is given in Figure 18.4. Setting up proper control plans for each of the subgroups through mother nature, man, machine, measurement, method, and material and effective training of stakeholders in the quality testing process will enable an error-free testing, in other words, quality control.

On the basis of the complexity of manufacturing units and implications/consequences of test errors, each organization can prioritize the mitigation measures from the causes as indicated in Figure 18.4. Getting the quality system accredited to ISO 7025 is another effective way of ensuring testing effectiveness. Refiners perform round-robin tests on a common sample to assess the extent of deviation among laboratories, and this will assist laboratory management in setting the corrective plans. A few companies participate in Deming or Malcolm Baldrige award programs as testimony to exhibit the precision in product testing leading to lasting customer satisfaction.

18.3.5 Test Equipment Induction and Calibration

Most modern laboratories are designed and constructed keeping safety and workflow for better productivity in mind. Sample entry, segregation, conditioning, sequence of testing (destructive and nonintrusive), archiving of samples to comply with contractual obligations, and safe disposal of used samples follow a preset path in laboratories. Because the laboratory environment should be conducive for better productivity, the quality management team emphasizes good layout of laboratory testing equipment, incorporation of a 5S concept right from the design stage, adherence of ambient air quality in testing areas, well-defined sample container movement, display of supercritical test equipment operating/calibrating procedures as a ready reference, online tracking of samples, data warehousing, environmentally friendly disposal of laboratory wastes, fire prevention and proofing features, emergency safe exit, etc.

Each country sets its own standards/codes and best practices for safety in petroleum laboratories. Hence, any new tests being introduced go through a systematic protocol of series of actions to be taken through space assessment, power and utility requirements, sample conditioning need, reference sample, post-test cleanup, LIMS connectivity, failure modes and effects analysis to handle potential incidents,

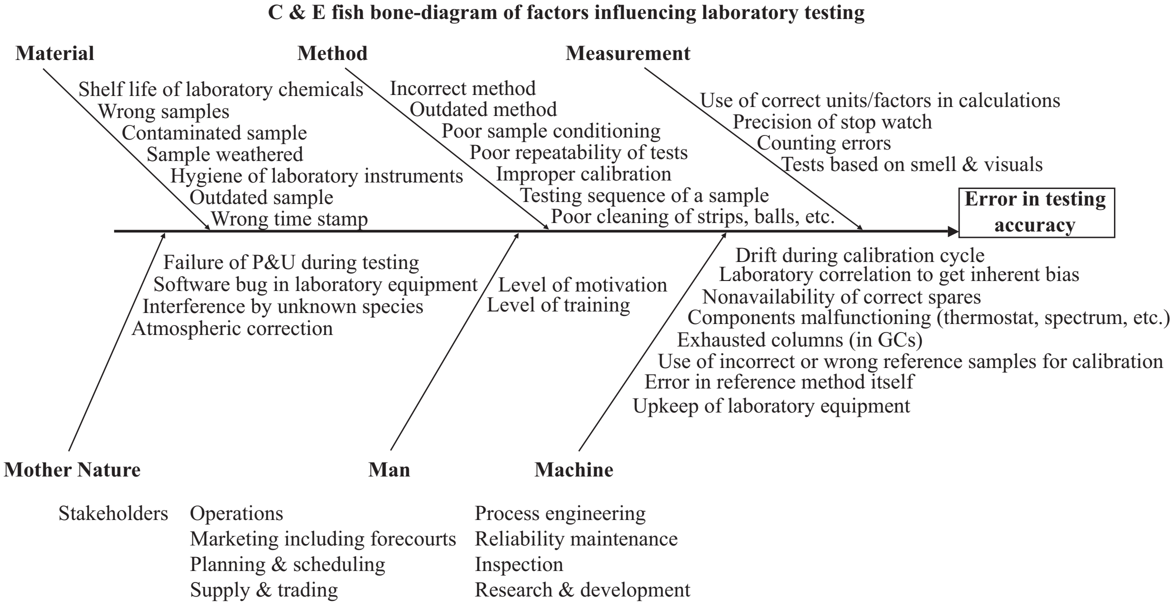


Figure 18.4—Potential error possibility in quality testing.

operating spares and consumables, customer confidence enhancement plan, setting up calibration frequency, statutory clearances, if any, etc. In short, every activity in a laboratory has a bearing on quality control and it is done after a good conceptualization starting from "critical to quality." It is again a best practice to have an operating manual written by users so that the nitty-gritty in effective use of test equipment is well documented and consistently used.

With regard to calibration of any test equipment, some of the traits of a good laboratory are display of acceptance criteria (normally it is within ±1 standard deviation) and trends of past calibration just over the test equipment, time stamp of the next calibration due, having master/reference laboratory instruments wherever applicable to calibrate the rest, assisting calibration by proven/skilled laboratory professionals, tracking of calibration status, etc. Depending on the manufacturing process needs (wherein the test is being performed), the calibration frequency can be optimized.

18.3.6 Testing, Validating, Reporting, and Ensuring Quality Control

Apart from standard calibration of test equipment, a few pacesetting laboratories have a system of validation of test results through an inferential method of manufacturing plant data. It is a routine practice in hydrocarbon industries to correlate the operating parameters with laboratory data and formulate a statistical equation to predict stream critical properties such as density, distillation/cutpoints, key component strength, sulfur, freezing point, flash point, etc. [3] Online computing has grown versatile with the enormous capability in servers and a greater understanding of process dynamics. Validation of laboratory tests has become an integral part of the checks before making changes in plant conditions. Refiners and petrochemical units are exploiting advancements in process automation and taking it to the next level of real-time process simulation and monitoring using a model-based approach. These models predict for a given feed the properties of product streams under varying operating conditions. Thus, laboratory tests are validated and feedback is provided. It is a common practice to retest through a check sample for correctness of the tests.

To obtain precise validation, it is imperative that the time of the sample is correlated with the then operating conditions of the unit with due adjustment to process lag in the system. The concept of using a barcode has become the boon to quality control because exact timing of sample collection can be placed, setting aside potential human error in the validation of laboratory tests. Further, the new-generation LIMS has the provision to "lock" test results entering into the LIMS database out of "calibration overdue" instruments. These are some of the ways to ensure better validation of test results.

Some refineries extensively use online QMIs/analyzers; even product certification and dispatch is conducted based on such instruments. In such a setup, the role of the laboratory is predominantly to move from certification of products to certification of QMIs. Here again the principles of good upkeep, calibration of QMIs, performance auditing, etc., are followed rigorously to ensure quality control.

18.3.7 Proficiency Tests and Round-Robin Evaluation

Proficiency tests and round-robin evaluation are the two critical parameters required for quality control and have been dealt with in great detail in the previous section. Because the strength of any process is determined by its weakest link, laboratory personnel proficiency in testing "accurate" on a sustained basis is very important for assuring internal and external customers on quality inputs. Compliance with ISO 17025 systems will assist development of the required overall proficiency of a laboratory team. Few refiners have a technical services agreement with some of the oil majors, which again shall facilitate laboratory productivity, a key to quality control. In addition, participating in national and international forums on test development, continuous update of testing capability with new-generation methods, interaction with test equipment vendors, refresher courses, etc., are some of the traits used by pacesetting laboratories to stay ahead and provide impeccable services in quality control.

18.3.8 Quality Cost

The quality cost is critical to the hydrocarbon business and every refiner tries to reduce the delivered cost to customers. Quality cost is one such component and it can typically vary from 2 to 25 cents/bbl of crude processed. The elements of quality cost are reblending, reprocessing, downgrading to a lower-value product, yield realized versus potential planned, QGA or quality overkill, in-process inventory due to delays in batch formation/certification time, rework, pilferage, evaporation loss, underfreighting, discounted offer to customer due to being off specification in one or more parameters, and product return from customer.

Pacesetter refining companies monitor each and every batch to minimize quality cost and undertake several initiatives for performance improvement. Some of the exemplary work done by refiners to reduce quality cost are online blending and certification, deployment of Lean Sigma to streamline the certification process, use of the Kano model[3] in creating "value" to customers for the given product; performing quality chain audits to preempt failure potential and take proactive actions such as additional field tests, inferential predictions, product quality tracking across the delivery chain, etc.

The quality cost with respect to yield versus potential is routinely assessed, and a variance report is critically monitored for bridging the gap. This is often one of the major elements in the overall cost of quality. Leading refinery houses use model-based software tools to verify the plant behavior and take appropriate corrective measures. In short, the pacesetting quality-control program that is to sustain the business also encompasses quality cost aspects so as to reduce the delivered cost of products supplied to customers.

18.3.9 Customer Relations Management

Although the importance of CRM and a couple of case studies have been already dealt with in previous chapters, the different facets of CRM are outlined here. An effective CRM program begins with customer enrollment and continues until the supplier and customer are engaged in business transactions. Every business process for its effective deployment requires KPIs that are measurable and well understood by each stakeholder of the process. Because quality control is the primary focus, customer engagement relating to it is dealt with specifically. A pacesetting organization first prioritizes customer engagement considering aspects such as the degree of importance to business volume; competitor strength in making inroads into its own customers; alternatives available to the customers (e.g., a gas turbine can be run on different fuels starting from natural gas, naphtha, kerosine, diesel, light cycle oil, etc.); criticality of product quality to the customers' business, and the size of sale volume per transaction, which helps to optimize logistics cost. Furthermore, defining the product specification parameters critical to quality, agreed test methods to measure quality norms, sequencing of product upliftment, in-transit quality-control needs, tracking of quality over time, complaint handling procedure, etc., are well documented as part of the agreed-upon business transaction.

It is normally the onus of the supplier to ensure quality delivered right up to the customers' premises. In other words, the best practice is to ensure quality until the door of the customer. In short, effective CRM will also alert product quality practitioners to look at systemic failures and thus improve the overall business.

A modern quality management system will comprise documented quality policy, quality control in the manufacturing process, product safety features and handling practices, customer engagement practices, laboratory accreditation process, etc. Although no business house could afford conflicts with customers, having a quality complaint-handling procedure as part of a quality management system is essential and is shared with customers. The main objectives of a complaints procedure are to satisfy the customer and not to prove them wrong. However, there are instances of no real problem, and a simple education in testing procedures has resolved many conflicts. Further, increased processing of opportunity crudes in the refining diet, use of chemicals for enhanced oil recovery in oil fields, handling of different products in similar containers to optimize shipping cost, etc., add to contaminants in products (even at parts-per-million levels), which requires newer ways to mitigate complaints.

Additionally, complaints do not relate only to the specification; many complaints relate to understanding different parameters of the specifications. Hence, it is imperative that the frontline staff are provided with adequate information on the product features, inputs on frequently asked questions, product manufacturing process, in-process quality control, and the quality management system in place to ensure and protect the customer's interests.

An effective CRM program must include visits to the customer site as required, and potential actions should be taken to resolve the problem in one visit. Frequent visits to resolve a problem project a poor image of the technical problem-solving ability of the organization. Samples should only be taken for evaluation as a last resort. The taking of samples adds complexities and a certain degree of uncertainty associated with the interpretation of results. Where the complaint relates purely to a measured quality or quantity, consideration must be given for application of ISO4259, a complaint resolution procedure. One of the best practices is to regularly review complaints and, when necessary, use tripartite (manufacturing including laboratory personnel, marketing, and the customer) investigation to avoid recurring failures. The customer is generally not interested in internal changes or corrective actions taken, but they should be reassured that the incident will not occur again. In short, refiners and petrochemical manufacturing teams have much to learn through effective customer engagement.

18.3.10 Quality Audit

A quality audit is one of the provisions in the quality management system to assure the management on a proactive basis of the effectiveness of the internal processes delivering value to customers. Typically, the audit scope covers each and every element of the quality delivery chain starting from the formulation of an agreed-upon specification between the supplier and customer with appropriate test methods, internal checks and balances to produce and deliver on-grade quality products all of the time, interaction with customers

---

[3] The Kano model is a theory of product development and customer satisfaction developed in the 1980s by Professor Noriaki Kano that classifies customer preferences into five categories: attractive, one-dimensional, must-be, indifferent, and reverse.

on a preset cycle to enhance value in the business transactions, prearranged visits between the two, training and refresher courses, participating in round-robin tests with peer laboratories and lesson deployment from feedback, conflict resolution methodology, etc. Further, the quality audit must examine the understanding of the importance of quality control and its implications at a grass-root level of production. The audit should also look into the effectiveness in handling customers' complaints. Pacesetting organizations conduct two to three quality audits to assure management of the overall excellence in quality delivery.

ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to the following, for without their help and encouragement, documenting this chapter could not be accomplished: Reliance Jamnagar Refinery management for sharing excerpts from the internal quality management processes and best practices in product analysis and quality control, the Six Sigma team at Jamnagar for having given the cause-and-effect matrix on potential error in product testing, and fellow colleagues with the Jamnagar quality-control/assurance team who helped in the preparation of this document.

REFERENCES

[1] Published literature downloaded from internet on typical refinery block flow diagram, Six Sigma lessons (Cp Vs % P/T chart).
[2] Rand, S.J., ASTM MNL 1, 8th Ed., *Significance of Tests for Petroleum Products,* West Conshohocken, PA, 2010.
[3] Hydrocarbon Processing Magazine, www.HydrocarbonProcessing.com.

APPENDIXES

APPENDIX 18.1—Performance Comparison of Quality-Control Laboratories

	Categorization of Quality-Control Laboratory		
Attributes	**Good**	**Pacesetter**	**World Class**
Number of tests per hour per person	2–3	3.5	4+
Test precision in standard deviation[a]	~	<1σ	<1σ
Support to operations on product quality/ certification	Limited feed-forward inputs	+ Build blend models	+ Migrate to QMI certification
Quality management system	ISO9001, 17025	+ Track PQ through LIMS	+ Mostly automated laboratory
Compliance to specification	Participate in round-robin tests	+ Take customer care program	+ use Kano model to add spec
Product certification time	~	2–3σ	4+σ
LIMS uptime	~	99+	100

[a] The standard deviation represents 1 divided by 2.77 of reproducibility
i.e., 1s = R/2.77

APPENDIX 18.2—Illustration on Test Method Precision Improvement

				Repeatability		Reproducibility	
Product/Test	**Specification**	**Year Published**	**Method**	**r**	**%**	**R**	**%**
Jet/sulfur	0.3 % wt max				–		–
		2003	D4294	±0.014		±0.043	
Diesel/sulfur	50 ppm max	2006	D3120	±4.3	–	±26.1	–
		2008	D5453	±2.2	49	±19.1	27
Diesel/Cetane index	46 min				–		–
		2004	D4737	±0.3		±0.7	
Gasoline/benzene	1 % vol max				–		–
		2007	D3606	±0.04		±0.18	
Naphtha/total paraffin	74 % wt min	2003	D6293	±0.97	–	±3.9	–
		2004	D5443	±0.55	43	±1.46	63
Crude oil/density	As ° API				–		–
		1999	D1298	±0.2		±0.5	

APPENDIX 18.3—Typical Cost of Quality Giveaway

Attributes	Unit	U.S. Cents/bbl/ Unit Change
Diesel cloud	deg C	30.5
Diesel of 50 ppm sulfur	ppm	6.2
Diesel 10 ppm sulfur	ppm	98.6
Diesel CFPP	deg C	0.8
Diesel CN	Number	6.6
Diesel T 95 % (50 ppm)	%	52.5

The data presented above can vary between refineries because they depend on refining configuration and delivered cost of crude oil.

19

Fuel Blending Technology and Management

Suresh S. Agrawal[1]

19.1 INTRODUCTION

A typical crude oil refinery produces 100 or more different product grades, and only a few of them are sold directly as they are produced by the various process units. Most of the products sold by a refinery are the blended products made by mixing several refinery intermediate products to meet the end-user specifications and demands. Refineries earn as much as 60% of their revenues from the blended products. Examples of blended products are gasoline (Mogas), diesel (middle distillate), fuel oil, jet fuel, bitumen, etc. In fact, a refinery produces approximately 65–85% of its end products by blending 6–12 components or stocks of different monetary and quality values to meet 6–10 end-product specifications. Figure 19.1 shows that a barrel of oil generates products that constitute approximately 40–50% gasoline, 20–25% diesel, 5–10% fuel oil, and the remaining of other light- and heavy-end products.

These blended products are made in "offsite" areas of the refinery and hence are a part of offsite operations, compared with process units, which are a part of "onsite" operations. As simple as it may seem, the blending operation is technically complex; time-consuming; manpower intensive; and, last but not the least, can affect the refinery's bottom line because of inefficient operation, excessive quality giveaways, reblends of products to meet the specifications, poor quality and inventory data, and lack of coordination between the planned and actual blend lifting schedule.

This chapter is devoted entirely to all aspects of fuel blending and will discuss blending configurations; blend models; and integration of blending equipment, software, hardware, and analyzers, etc., from the design consideration points of view. The chapter will also discuss the economic justification of a blending project and methodology to assess the current state of blending operations and successful phase-wise implementation of a blending project.

19.2 OVERVIEW AND FUNDAMENTALS

19.2.1 Modes of Blending

There are two types of blending operations, usually referred to as sequential blending and inline blending, in the refining industry. Inline blending is further divided into batch blending and run-down blending. Unfortunately, these terms are used interchangeably in the industry; therefore, we will clarify them here because they will be used repeatedly throughout this chapter. In sequential blending, components are blended one at a time, whereas inline blending simultaneously mixes all components. Batch blending is referred to as blending in which the sources of components are tanks, and run-down blending mixes the components coming directly from process units. It is also possible to operate blending in a hybrid mode, for example, combining run-down blending with component tanks to debottleneck the limiting constraints on one or two components. Examples of batch blending are gasoline, fuel oil, and bitumen, whereas kerosine and diesel blending are usually done in run-down blending mode.

Sequential blending is time-consuming, manually operated, and often results into reblends or quality giveaways. Batch blending, if properly designed and operated, can be very flexible, efficient, and improves refinery profitability. On the other hand, run-down blending is a continuous process and can be very interactive, complex, and less flexible in terms of the manipulation of component ratios. Table 19.1 shows the detailed comparison of sequential, batch blending, and run-down blending.

Figures 19.2 and 19.3 show examples of inline batch blending (tank to tank) for gasoline and multiheader run-down blending (process units to tanks) for distillate or diesel fuels.

19.2.2 Fuel Properties

Although the properties of petroleum products are discussed in detail in an earlier chapter, we will just list the major properties of fuels in this chapter for the sake of completeness.

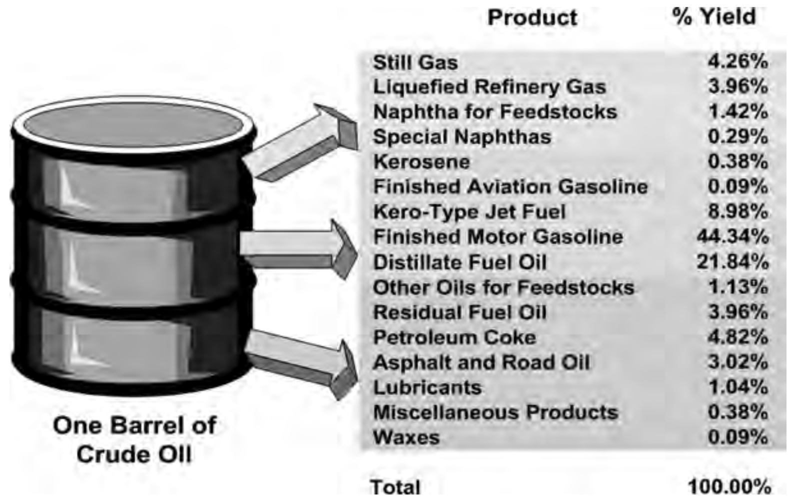
19.2.2.1 GASOLINE FUELS

This section discusses the major properties of gasoline fuels and their effect on gasoline engine performance and emission considerations.

- *Octane number:* A measure of a fuel's resistance to an abnormal combustion condition called knocking that is determined by a simple mixture of *n*-heptane and *iso*octane. For example, a 90–10% mixture of *iso*octane and *n*-heptane has an octane number of 90, and any gasoline fuel knocking at the same compression ratio has the same octane value. The antiknocking property is represented by three numbers: RON (research octane number), MON (motor octane number), and PON (pump octane number). RON measures performance at normal road conditions, MON is indicative of high-speed performance, and PON is the arithmetic average of RON and MON. PON is also sometimes referred as AKI (antiknocking index) or RDOI (Road Octane Index).
- *RVP (Reid vapor pressure):* A measure of the vapor pressure that fuel exerts at 100°F and can pressure up a gas tank in summer at high temperature and can boil in an open container and create air pollution problems. In winter, it must have minimum value for proper fuel vapor pressure.

---

[1] Offsite Management Systems, LLC, Sugar Land, Texas, USA



Product	% Yield
Still Gas	4.26%
Liquefied Refinery Gas	3.96%
Naphtha for Feedstocks	1.42%
Special Naphthas	0.29%
Kerosene	0.38%
Finished Aviation Gasoline	0.09%
Kero-Type Jet Fuel	8.98%
Finished Motor Gasoline	44.34%
Distillate Fuel Oil	21.84%
Other Oils for Feedstocks	1.13%
Residual Fuel Oil	3.96%
Petroleum Coke	4.82%
Asphalt and Road Oil	3.02%
Lubricants	1.04%
Miscellaneous Products	0.38%
Waxes	0.09%
Total	100.00%

Figure 19.1—Representative product distribution from a barrel of oil. *Source:* Reproduced with permission from [1].

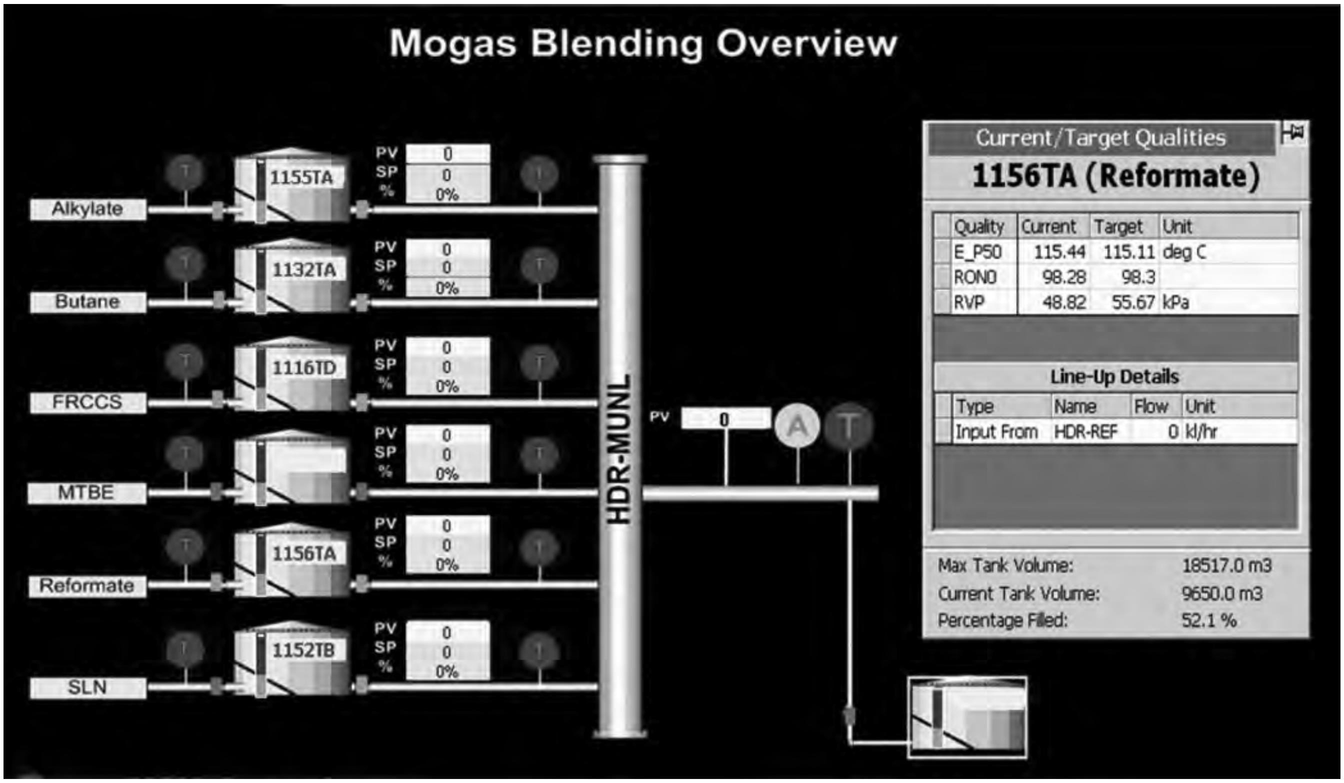
- *Distillation points:* The ASTM distillation point curve governs the ease of starting, warm-up, mileage economy, and performance. The distillation point curve values are different for common vehicles versus high-speed racing cars.
- *Sulfur:* This signifies the importance of vehicle emissions for lower air pollution of sulfur dioxide (SO_2) by burning sulfur (S) and also affects the emissions of carbon monoxide (CO), hydrocarbons (HCs), and oxides of nitrogen (NO_x).
- *Aromatics and olefins:* Although they are desirable for their octane value, they lead to engine deposits and increased emissions of ozone, forming HCs and toxic and carcinogenic benzene in the exhaust.

19.2.2.2 DIESEL FUELS

- *Flash point:* The minimum temperature at which the fuel will ignite; its minimum requirement is essential for proper safety and handling.
- *Low-temperature operability:* Two properties—cloud point and cold filter plugging point (CFPP)—characterize the operability of diesel fuel. Cloud point is more important for a refinery's quality-control test, and CFPP is for the low-temperature performance of an engine without plugging its filters.
- *Cetane number/cetane index:* The relative measure of delay in engine starting, rough operation, noise, and exhaust smoke. Engines operate better with higher

TABLE 19.1 COMPARISON OF VARIOUS BLENDING CONFIGURATIONS

Design Aspect	Gasoline	Diesel	Kerosene	Fuel Oil
Mode of blending	Sequential or inline batch	Sequential, inline batch, or run-down	Sequential, inline batch, or run-down	Sequential, inline batch, or run-down
Multiheader blending configurations	Rarely	Single grade (inline batch), multiproducts (run-down blending)	Multiproducts (run-down blending)	Single grade (inline batch), multiproducts (not common)
Typical numbers and types of components	6–10 (naphtha, reformate, FCC, HDS, isomerate, alkylate, butane, isopentane, Merox, MTBE, etc.)	6–8 (CDU middle distillates, hydrocracking streams)	3–4 (CDU kerosine, hydrocracker kerosine, light diesel)	4–6 (light cycle oil, slurry, base fuel oil, etc.)
Types of products	Regular (78–82 RON), premium (83-90), super premium (91–98)	Light and heavy diesel, marine diesel, low- and high-sulfur diesel	Aviation fuels (Jet, JP)	LSFO, HSFO, Marine FO, bunker FO
Number and types of specifications	RON, MON, RDOI, RVP, distillation points (10%, 30%, 50%, 70%, 90%), sulfur, API gravity, aromatics, olefins, benzene, TO_x, NO_x, VOCs	Cetane index, pour point, cloud point, freeze point, flash point, sulfur, viscosity, 90% distillation point, CFPP, API gravity, aniline point	Freeze point, flash point	Viscosity, API gravity, sulfur, flash point, pour point
End uses	Cars, small vehicles	Commercial vehicles, construction equipment	Aviation industry	Boiler, furnaces, ships



Current/Target Qualities

1156TA (Reformate)

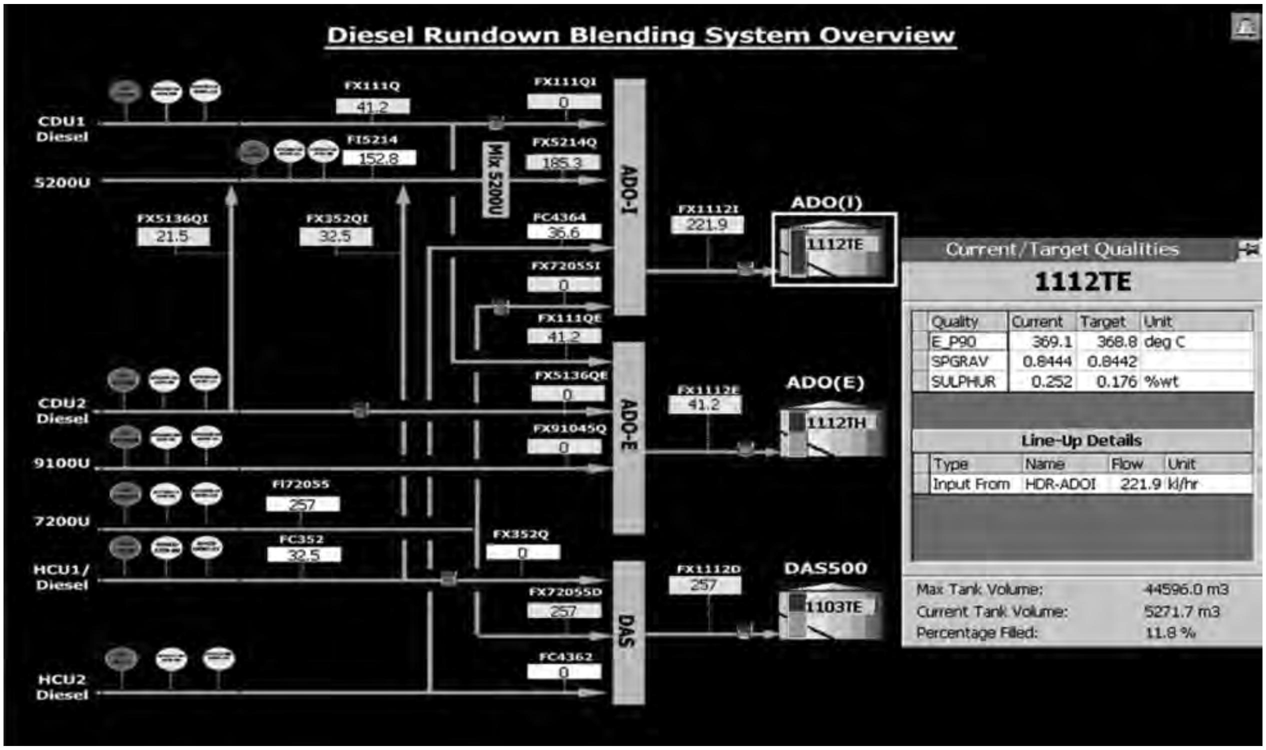
Quality	Current	Target	Unit
E_P50	115.44	115.11	deg C
RON0	98.28	98.3	
RVP	48.82	55.67	kPa

Line-Up Details

Type	Name	Flow	Unit
Input From	HDR-REF	0	kl/hr

Max Tank Volume: 18517.0 m3
Current Tank Volume: 9650.0 m3
Percentage Filled: 52.1 %

Figure 19.2—Inline gasoline batch blender. *Source:* Reproduced with permission from [1].



Current/Target Qualities

1112TE

Quality	Current	Target	Unit
E_P90	369.1	368.8	deg C
SPGRAV	0.8444	0.8442	
SULPHUR	0.252	0.176	%wt

Line-Up Details

Type	Name	Flow	Unit
Input From	HDR-ADOI	221.9	kl/hr

Max Tank Volume: 44596.0 m3
Current Tank Volume: 5271.7 m3
Percentage Filled: 11.8 %

Figure 19.3—Multiheader distillate run-down blender. *Source:* Reproduced with permission from [1].

cetane number. The cetane index is another indication of what the base cetane number represents.

- *Sulfur:* Important for reducing the particulate matter and toxic gas in the exhaust emissions.
- *Distillation:* The ASTM distillation curve measures the range of temperatures over which the fuel will turn to vapor. It indicates the lower toxic emissions at idling conditions and better engine performance at driving conditions.

There are also other important properties such as kinematic viscosity, ash content, water and sediment, lubricity, detergency, etc., that are included in fuel specifications.

19.2.3 Typical Fuel Specifications

Fuel specifications have evolved and tightened over the last several years in the United States and around the world to cut down on toxic gas emissions to minimize the damage to the environment we all live in. The biggest changes in the fuels specifications are the elimination of lead and methyl tertiary butyl ether (MTBE) and reduction in sulfur contents and toxic emissions around the world.

The discussion and the history of the evolutions and current specifications around the world is a chapter in itself. In this chapter we will discuss major fuel properties and their typical specifications.

19.2.3.1 GASOLINE FUEL

Figure 19.4 shows the typical minimum/maximum range of specifications for gasoline fuels.

19.2.3.2 DIESEL FUEL

Figure 19.5 shows the typical minimum/maximum range of specifications for diesel fuels.

19.2.4 Fuel Additives

Additives are soluble chemicals mixed with fuel to enhance certain performance characteristics or to provide characteristics not inherent in the fuel. They are typically derived from petroleum-based raw materials and their function and chemistry are highly specialized. They produce the desired effect at the parts-per-million concentration range (1 ppm is 0.0001 mass percent or 1 mg/kg). The following subsections describe the classifications of fuel additives.

Specification	Unit	Minimum	Maximum	Range
RON		X		83-98
MON		x		76-85
(MON+RON)/2, min		**Calculated**		84-96
Density @ 15°C	kg/m^3			710-780
Reid Vapor Pressure @ 37.8°C	kPa		x	35-100
IBP	°C	x		
T10	°C		x	50-70
T50	°C	x	x	70-120
T90	°C	x	x	150-190
FBP	°C		x	190-225
Drivability Index		**Calculated**		20-50
E70	% vol	**Specified only in few countries**		
E100	% vol			
E150	% vol			
E180	% vol			
E300	% vol			
Lead	g/l		x	0-0.0026
Sulfur	ppm		x	10-1000
Phosphorous	g/l		x	0-0.0004
Benzene	% vol		x	0-3.5
Aromatics	% vol		x	25-60
Olefins	% vol		x	10-45
Oxygen	% vol		x	0-3.5

Figure 19.4—Typical gasoline specifications.

Specification	Unit	Minimum	Maximum	Range
API Gravity		x	x	33-44
Flash Point	°C	x		35-55
CFPP	°C			309
T10	°C			190-225
T50	°C			425-530
T90	°C		x	260-330
Cetane Number		x		43-55
Cetane Index		x		40-45
Sulphur	ppm		x	15-5000
Viscosity	cST @40 °C	x	x	1.3-4.5
Lubricity	Microns			520
PNA	wt%			**3.5**
Nitrogen	ppm			500
ASH	% Mass		x	0.01-0.03

Figure 19.5—Typical diesel fuel specifications.

19.2.4.1 GASOLINE ADDITIVES

- *Oxidation inhibitors (antioxidants are aromatic amines and hindered phenols):* Prevent formation of gums by stopping gasoline's reaction with oxygen.
- *Corrosion inhibitors (carboxylic acids and carboxylates):* Prevent corrosion of tanks and pipelines by water.
- *Metal deactivators (chelating agents):* Prevent active metal ions from catalyzing gasoline oxidation.
- *Demulsifiers:* Polyglycol derivatives that prevent gasoline water emulsion in the high shear field of a centrifugal pump.
- *Antiknock compounds:* Tetraethyl lead or methylcyclopentadienyl manganese tricarbonyl no longer used.
- *Deposit-control additives:* Protect carburetor and fuel-injection system.
- *Anti-icing additives:* Used to avoid icing on aircraft exteriors.
- *Dyes:* Used to distinguish product grades.
- *Markers:* Added to gasoline to track its movement through the supply chain.
- *Drag reducers:* Reduce the pumping cost.

19.2.4.2 DIESEL ADDITIVES

- *Cold-flow improver:* This additive lowers the CFPP and pour point temperatures to avoid blocking filters. The additive has a lower wax content similar to heating oil and similar products and works by changing the size and shape of wax crystals. Cold-flow improvers do not change the cloud point.
- *Detergents:* Keep fuel injectors clean.
- *Cetane improver:* Improves cold temperature and idling of engines and boosts the cetane nonlinearly higher for low-cetane diesel fuels and lower for higher-cetane-number diesel fuels.
- *Thermal stability improver:* Improves the fuel's resistance to form particles as it circulates from tank to engine and back again. Such particles clog filters and injectors.

- *Lubricity improver:* Low-sulfur fuel has less lubricity or lubricating property and absorbs water more readily, and water is an abrasive. Untreated fuel often causes excessive wear on fuel pumps and injector tips.

19.3 BLEND MODELS

19.3.1 Linear Blend Models

Let us assume that we want to blend three components, X_1, X_2, and X_3, with qualities Q_1, Q_2, and Q_3 to make a product of quality Q_B. A simple mathematical equation will determine the quality of the final blend.

$$Q_B = X_1 * Q_1 + X_2 * Q_2 + X_3 * Q_3 \qquad (19.1)$$

Because the qualities (Q_i) of the components are known, one can use a simple calculator or Excel spreadsheet to estimate the recipe fraction (X_i) of the components to produce the specified quality of the blend product. This is called the linear blend model and can be safely used for fuel qualities such as API gravity, sulfur, aromatics, olefins, benzene, bromine number, oxygen, etc. The recipe fraction (X_i) can be either volumetric or weight depending on the property. However, equation 19.1 cannot be used for other qualities such as octane numbers (RON/MON), RVP, distillation points, pour point, flash point, freeze points, cloud point, cetane number, CFPP, etc., for the following reasons:

- Qualities are highly nonlinear in nature and do not produce acceptable results. However, the blended qualities of components depend only on some nonlinear function of the same quality (e.g., RVP, pour point, flash point, freeze point, cetane number, etc.).
- Blended qualities of components may depend on the same qualities of other components (e.g., pour point, flash point, freeze point, etc.).
- Components are highly interactive; that is, their effective qualities in the blend change and depend on the same and other qualities of other components present in the blend. For example, octane numbers (RON/MON) depend on the olefin, aromatic, and benzene contents of all of the other components in the pool.

19.3.2 Nonlinear Blend Models

19.3.2.1 TYPE 1 NONLINEAR BLEND MODELS

This type of model linearizes the component qualities using an index method. The indexed quality then can be blended linearly using equation 19.1 and converted back to quality by using reverse transformation. An example of this is RVP, as shown in equation 19.2.

$$RVPI_i = RVP_i^x \qquad (19.2)$$

Component and heel RVP values, along with the product specifications, are first transformed to blending indices (RVP_i) using a user-supplied exponential factor (x) obtained by nonlinear regression of historical refinery blend data. The component and heel indices are blended volumetrically and then transformed back to yield a predicted RVP for the blend:

$$RVP_B = \left[\sum_{i=1}^{n} v_i RVPI_i\right]^{\frac{1}{x}} \qquad (19.3)$$

where:
v_i = volumetric fraction of component i, and
n = number of components in the mixture.

The exponential factor is very specific to each refinery and component type and is usually obtained by nonlinear regression of historical blend data.

19.3.2.2 TYPE 2 NONLINEAR BLEND MODELS

This type of model is a further extension of the type 1 model. It depends on the range of the same quality of other components present in the blend before its transformation into a linearized index. Cloud, flash, and freeze points are examples of type 2 nonlinear models and are illustrated below for cloud point blending calculations as published by Ethyl Corporation in 1981 [2]. Cloud point is predicted using a scaling algorithm to prevent the generation of index values that would be otherwise difficult to manage by the solver.

$$Scale = \left[\frac{MinQuality + 273}{0.5^x} + \frac{MaxQuality + 273}{0.5^x}\right](0.5) \qquad (19.4)$$

where:
MinQuality is the lowest quality found in the component pool, *MaxQuality* is the highest quality found in the component pool, and X is the user-supplied exponent from the nonlinear regression of the refinery data.

A blending index for each stock (IDX_i) is calculated from component and heel quality values. The user defines the exponent (x), which is obtained by the nonlinear regression of the historical blend data.

$$IDX_i = \left[\frac{(Quality_i + 273)}{Scale}\right]^{(1/x)} \qquad (19.5)$$

Next, index values are combined volumetrically to yield a predicted indexed quality value for the blend (IDX_B).

$$IDX_B = \sum_{i=1}^{n} v_i IDX_i \qquad (19.6)$$

Finally, this value is transformed back to yield a predicted quality value of the blend.

$$Quality_B = (IDX_B)^x (Scale) - 273 \qquad (19.7)$$

Please note that the temperature value for the flash, cloud, and freeze points used in the above type 2 blend models is in degrees Celsius. If degrees Fahrenheit are desired as the temperature units, then replace the factor 273 by 460 for their conversion to the absolute temperature units.

Another example of a type 2 blending model is the calculation of the ASTM D86 distillation points by the ethyl equation [2]:

$$D86_{XB} = \sum_{i=1}^{n} v_i BV_{xi} \qquad (19.8)$$

where:
$D86_{XB}$ = predicted temperature at a given point X,
BV_{xi} = temperature blending value of component, i, at a desired point X, calculated based on the Ethyl S-curve model:

$$\begin{aligned} BV_{xi} &= C0_x + C1_x A_i + C2_x A_i^2 + C3_x A_i^3 + C4_x A_i G_i \\ &\quad + C5_x \frac{G_i}{A_i} + C6_x \frac{G_i}{A_i^2} + C7_x G_i \end{aligned} \qquad (19.9)$$

where
A_i = the average boiling point (based on the selected VABP method) of component i (°F or C),
G_i = component i ASTM severity (T90–T10) (°F or C), and
$C0_x$–$C7_x$ = coefficients for each included D86 distillation point that are regressed from the historical blend data to customize for a specific refinery.

The volumetric average boiling point (VABP) is calculated by the ASTM or Texaco method as follows:

$$\text{ASTM:} \quad VABP_B = \frac{T10 + 2(T50) + T90}{4} \tag{19.10}$$

$$\text{Texaco:} \quad VABP_B = \frac{T10 + T30 + T50 + T70 + T90}{5} \tag{19.11}$$

19.3.2.3 TYPE 3 NONLINEAR MODELS

This type of model is the most complex and does not fall into the above categories because the models are highly interactive in nature, dependent on other qualities of the components in the pool, and are very difficult to solve by ordinary methods such as a calculator or simple Excel calculations.

The generalized equation of this type of nonlinear model consists of two parts: a linear term and a nonlinear term to represent the interaction between components and their qualities in the pool, as shown in equation 19.12.

$$\begin{aligned} Qb{,}1 &= X1 * Q1{,}1 + X2 * Q2{,}1 + X3 * Q3{,}1 \\ &\quad + \ldots\ldots\ldots Xn * Qm{,}n + f(X1{,}X2{,}X3{,}{,}\ldots\ldots Xn{,} \\ &\quad Q1{,}1{,}Q1{,}2{,}\ Q1{,}n{,}\ldots\ldots\ldots Qm{,}1{,}Qm{,}2{,}\ Qm{,}n) \end{aligned} \tag{19.12}$$

The entire effort in the design and implementation of a blending system centers around how to best estimate the second nonlinear term, a nonlinear function of the component mixture and its qualities, in equation 19.12 because it depends on the specific refinery and its component pool mixture for fuel blending. We will later discuss various methods to estimate this nonlinear term to use in the blending equations.

An example of the type 3 blending model is the octane numbers (RON/MON) and is illustrated in equation 19.13 for RON:

$$\begin{aligned} RON_B &= \sum_{i=1}^{n} v_i RON_i \\ &+ A\left[\sum_{i=1}^{n} v_i RON_i^2 - \left(\sum_{i=1}^{n} v_i RON_i * \sum_{i=1}^{n} v_i RON_i\right)\right] \\ &+ B\left[\sum_{i=1}^{n} v_i Olef_i^2 - \left(\sum_{i=1}^{n} v_i Olef_i * \sum_{i=1}^{n} v_i Olef_i\right)\right] \\ &+ C\left[\left[\sum_{i=1}^{n} v_i Sat_i^2 - \left(\sum_{i=1}^{n} v_i Sat_i * \sum_{i=1}^{n} v_i Sat_i\right)\right]\right]^2 \\ &+ D\left[\sum_{i=1}^{n} v_i \left(RON_i * Olef_i\right) - \left(\sum_{i=1}^{n} v_i RON_i * \sum_{i=1}^{n} v_i Olef_i\right)\right] \end{aligned} \tag{19.13}$$

where constants A, B, C, and D are given by Ethyl Corporation [2] as
A = 0.003361,
B = 0.001138,
C = 0.003932, and
D = 0.006761.

In equation 19.13, the RON of the blended product depends nonlinearly on the RON and the olefin and saturates contents of the components in the pool. The constants A, B, C, and D depend on the types of product grades (e.g., regular, midgrade, and premium), are given by Ethyl Corporation [2], and can be used with a bias term in equation 19.13 to customize for a specific refinery. Alternatively, the constants can also be obtained by regression of historical blend data for the same type of blend grades.

Similar and more complex equations involving additional aromatic contents of the components in the pool also exist in the literature and are developed by individual refineries and used in their blending system. However, it is outside of the scope of this chapter to discuss in detail all existing nonlinear blend models for the gasoline octane.

There are also other variations of the blend nonlinear models that do not fall in any of the above three types because they are in the form of dependency of the final blend qualities. Examples are illustrated as follows:

- Volatility index

$$VLI_B = 114.6 - 4.1(RVP_B) + 0.2(T10_B) + 0.17(T50_B) \tag{19.14}$$

- Reformulated gasoline equations

$$\begin{aligned} TOX &= \sim a + b * O_2 + c * S + d * RVP + e * E200 \\ &\quad + f * E300 + g * Ar + h * Ole + i * Bz \end{aligned} \tag{19.15}$$

$$\begin{aligned} NO_X &= \sim j + k * O_2 + l * S + m * RVP + n * E200 \\ &\quad + o * E300 + p * Ar + q * Ole + r * Bz \end{aligned} \tag{19.16}$$

$$\begin{aligned} VOC &= \sim s + t * O_2 + u * S + v * RVP + w * E200 \\ &\quad + x * E300 + y * Ar + z * Ole + aa * Bz \end{aligned} \tag{19.17}$$

Please note that the equations 19.1–19.17 mentioned in this chapter are only for illustration purposes and should not be taken as absolute correlations; hence, they should be used with caution for your refinery only after consultation with a blending consultant.

19.3.3 Effects of Nonlinearity on Blend Quality

The effects of nonlinearity due to interaction of components are illustrated in the penalization and bonus of the blend octane using a two-component system. Let us examine the effect of blending fluid catalytic cracking (FCC) (RON = 91) and reformate (RON = 94) by mixing them in varying proportions as shown in Figure 19.6. In this example, the blend octane is penalized between 0.10 and 0.30 RON depending on the composition of the mixture.

On the other hand, if we examine a mixture of FCC (RON = 91) and isopentane (RON = 90), we observe an octane bonus of 0.10–1.6 RON, again depending on the mixture composition (Figure 19.7).

We will discuss later how to estimate the octane bonus or penalty for any combination of components in the blend component pool.

19.3.4 Methods to Handle Blend Nonlinearity

We discussed earlier that nonlinearity of the components can severely affect the blend octane for gasoline blends and must be properly accounted for to minimize the effect on the refinery bottom line. In this section, we will discuss

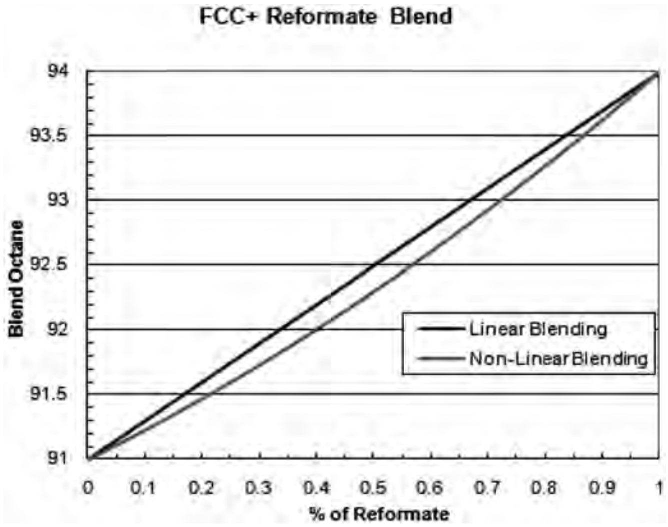


Figure 19.6—Penalty of octane for FCC + reformate blend.

various methods and their pros and cons to effectively tackle the blend nonlinearity. The nonlinearity of the fuel blends can be handled by the following methods.

19.3.4.1 LUMPED BIAS

This method introduces a bias term to the linear calculation of blend quality as follows:

$$Q_{b,j} = \sum_{i=1}^{n} x_i q_{i,j} \pm B_j \qquad \text{for} \quad j = 1 \ldots n \qquad (19.18)$$

The advantages of this approach are that it is simple and easily calculated using a calculator or an Excel spreadsheet. It is valid for simpler and nearly linear qualities. However, the bias term B_j is not constant and varies with product grade and component mixture, which makes it difficult to maintain a database of the bias term for a wide spectrum of blend composition and qualities. Figure 19.8 shows typical ranges of blend model bias for gasoline blends for 1 month of blends and marks the variation between blend batches and blend grades due to severe blend nonlinearity and interactions.

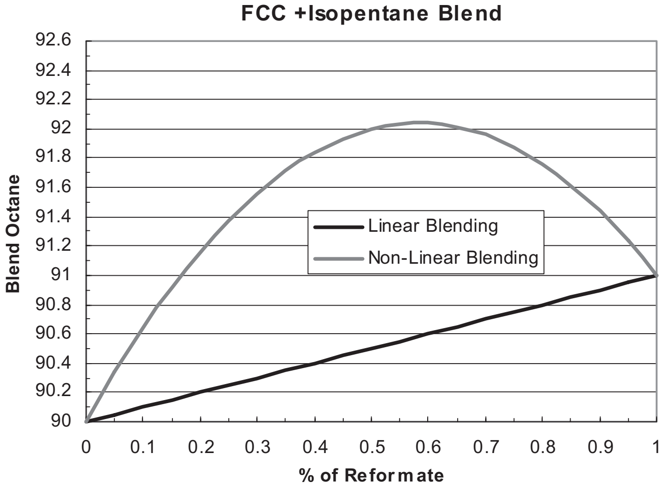


Figure 19.7—Bonus of blend octane for FCC+ isopentane. *Source:* Reproduced with permission from [1].

19.3.4.2 BLENDING VALUES (INDEX)

In this approach, the component qualities are replaced by blending values of indexes to account for the nonlinearity and component interaction to simulate type 2 blend model non-linearity. This is shown in equation 19.19:

$$Q_{b,j} = \sum_{i=1}^{n} X_i BV_{i,j} \pm B_j \qquad (19.19)$$

where:

$BV_{i,j}$ = blend values (index) of component i for quality j and

B_j = average bias for quality j and is a function of product grade.

The blending values are again nonlinear and must be calculated by representative equation 19.20 for octane (RON).

$$\begin{aligned} BlendBV_j = {} & RON_j \\ & + A\left(Arom_j - \sum_{i=1}^{n} v_i Arom_i\right)^2 \\ & + B\left(Olef_j - \sum_{i=1}^{n} v_i Olef_i\right)^2 \\ & + C\left(RON_j - \sum_{i=1}^{n} v_i RON_i\right)\left[\left(RON_j - MON_j\right) - \sum_{i=1}^{n} v_i RM\Delta_i\right] \\ & + D\left(Arom_j - \sum_{i=1}^{n} v_i Arom_i\right)\left(Olef_j - \sum_{i=1}^{n} v_i Olef_i\right) \end{aligned} \qquad (19.20)$$

where A, B, C, and D are given in equation 19.20 or can be regressed constants for the specific refinery from historical blend data, and

$RM\Delta_i$ = difference between RON and MON.

This approach is closer to reality with the same complexity as the original equation 19.13. However, equation 19.20 makes it easier to program and calculate in linear programs or an Excel spreadsheet, but the blend values again depend on the pool composition. Because the blend nonlinearity is taken care of in the blending values, the bias term in equation 19.19 is not as variable as the one in equation 19.18.

19.3.4.3 DUPONT INTERACTION COEFFICIENTS

In this method, the nonlinear term in equation 19.13 is replaced by a binary interaction coefficient originally developed by DuPont Corporation in 1981 as follows:

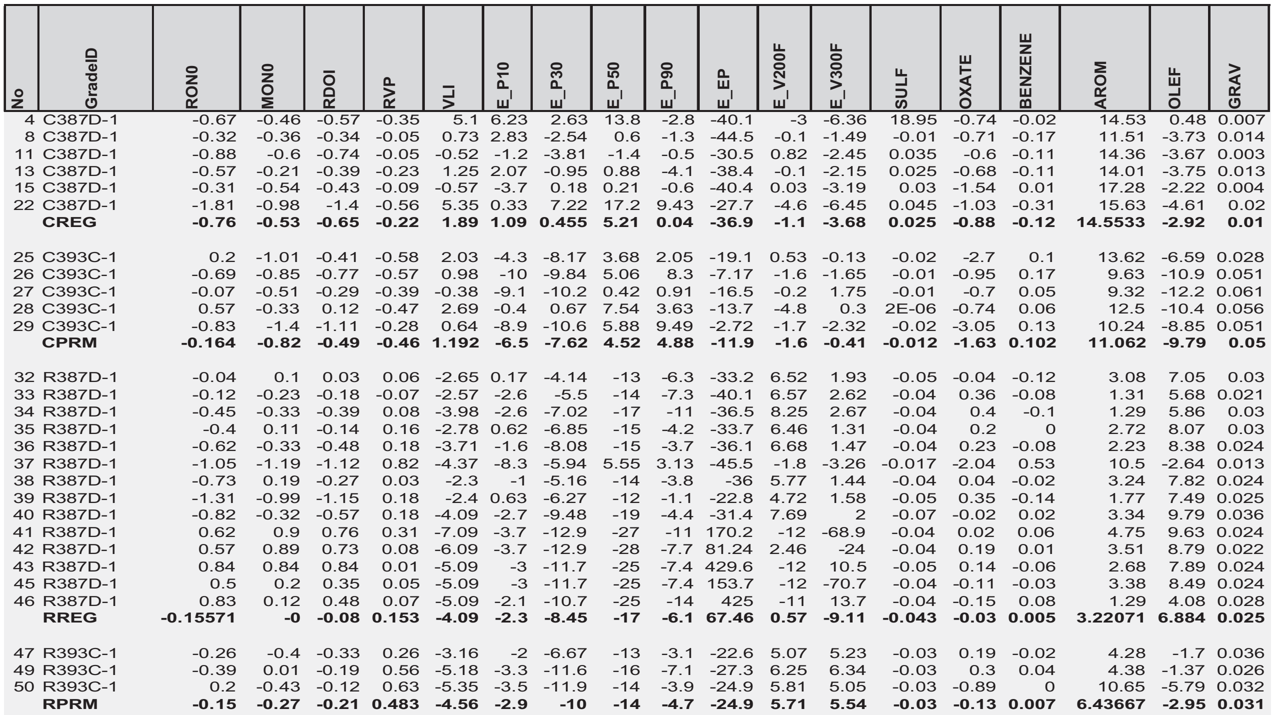
$$Q_{b,j} = \sum_{i=1}^{n} x_i q_{i,j} + \frac{\sum_{i=1}^{n}\sum_{i=1}^{n} b_{ij} x_j}{2} \qquad (19.21)$$

for all i and j, where $i \neq j$ and $b_{ij} = b_{ji}$

This approach is easy to program and calculated in an Excel spreadsheet because it is noniterative. The interaction coefficients b_{ij} and b_{ji} are independent of blend composition. However, they must be determined separately using the 50/50% mixture method.

19.3.4.3.1 50%/50% Mixture Method

1. Collect a minimum of 5 gal of each stock.
2. Measure the RON/MON of each component in the laboratory.



No	GradeID	RON0	MON0	RDOI	RVP	VLI	E_P10	E_P30	E_P50	E_P90	E_EP	E_V200F	E_V300F	SULF	OXATE	BENZENE	AROM	OLEF	GRAV
4	C387D-1	-0.67	-0.46	-0.57	-0.35	5.1	6.23	2.63	13.8	-2.8	-40.1	-3	-6.36	18.95	-0.74	-0.02	14.53	0.48	0.007
8	C387D-1	-0.32	-0.36	-0.34	-0.05	0.73	2.83	-2.54	0.6	-1.3	-44.5	-0.1	-1.49	-0.01	-0.71	-0.17	11.51	-3.73	0.014
11	C387D-1	-0.88	-0.6	-0.74	-0.05	-0.52	-1.2	-3.81	-1.4	-0.5	-30.5	0.82	-2.45	0.035	-0.6	-0.11	14.36	-3.67	0.003
13	C387D-1	-0.57	-0.21	-0.39	-0.23	1.25	2.07	-0.95	0.88	-4.1	-38.4	-0.1	-2.15	0.025	-0.68	-0.11	14.01	-3.75	0.013
15	C387D-1	-0.31	-0.54	-0.43	-0.09	-0.57	-3.7	0.18	0.21	-0.6	-40.4	0.03	-3.19	0.03	-1.54	0.01	17.28	-2.22	0.004
22	C387D-1	-1.81	-0.98	-1.4	-0.56	5.35	0.33	7.22	17.2	9.43	-27.7	-4.6	-6.45	0.045	-1.03	-0.31	15.63	-4.61	0.02
	CREG	**-0.76**	**-0.53**	**-0.65**	**-0.22**	**1.89**	**1.09**	**0.455**	**5.21**	**0.04**	**-36.9**	**-1.1**	**-3.68**	**0.025**	**-0.88**	**-0.12**	**14.5533**	**-2.92**	**0.01**
25	C393C-1	0.2	-1.01	-0.41	-0.58	2.03	-4.3	-8.17	3.68	2.05	-19.1	0.53	-0.13	-0.02	-2.7	0.1	13.62	-6.59	0.028
26	C393C-1	-0.69	-0.85	-0.77	-0.57	0.98	-10	-9.84	5.06	8.3	-7.17	-1.6	-1.65	-0.01	-0.95	0.17	9.63	-10.9	0.051
27	C393C-1	-0.07	-0.51	-0.29	-0.39	-0.38	-9.1	-10.2	0.42	0.91	-16.5	-0.2	1.75	-0.01	-0.7	0.05	9.32	-12.2	0.061
28	C393C-1	0.57	-0.33	0.12	-0.47	2.69	-0.4	0.67	7.54	3.63	-13.7	-4.8	0.3	2E-06	-0.74	0.06	12.5	-10.4	0.056
29	C393C-1	-0.83	-1.4	-1.11	-0.28	0.64	-8.9	-10.6	5.88	9.49	-2.72	-1.7	-2.32	-0.02	-3.05	0.13	10.24	-8.85	0.051
	CPRM	**-0.164**	**-0.82**	**-0.49**	**-0.46**	**1.192**	**-6.5**	**-7.62**	**4.52**	**4.88**	**-11.9**	**-1.6**	**-0.41**	**-0.012**	**-1.63**	**0.102**	**11.062**	**-9.79**	**0.05**
32	R387D-1	-0.04	0.1	0.03	0.06	-2.65	0.17	-4.14	-13	-6.3	-33.2	6.52	1.93	-0.05	-0.04	-0.12	3.08	7.05	0.03
33	R387D-1	-0.12	-0.23	-0.18	-0.07	-2.57	-2.6	-5.5	-14	-7.3	-40.1	6.57	2.62	-0.04	0.36	-0.08	1.31	5.68	0.021
34	R387D-1	-0.45	-0.33	-0.39	0.08	-3.98	-2.6	-7.02	-17	-11	-36.5	8.25	2.67	-0.04	0.4	-0.1	1.29	5.86	0.03
35	R387D-1	-0.4	0.11	-0.14	0.16	-2.78	0.62	-6.85	-15	-4.2	-33.7	6.46	1.31	-0.04	0.2	0	2.72	8.07	0.03
36	R387D-1	-0.62	-0.33	-0.48	0.18	-3.71	-1.6	-8.08	-15	-3.7	-36.1	6.68	1.47	-0.04	0.23	-0.08	2.23	8.38	0.024
37	R387D-1	-1.05	-1.19	-1.12	0.82	-4.37	-8.3	-5.94	5.55	3.13	-45.5	-1.8	-3.26	-0.017	-2.04	0.53	10.5	-2.64	0.013
38	R387D-1	-0.73	0.19	-0.27	0.03	-2.3	-1	-5.16	-14	-3.8	-36	5.77	1.44	-0.04	0.04	-0.02	3.24	7.82	0.024
39	R387D-1	-1.31	-0.99	-1.15	0.18	-2.4	0.63	-6.27	-12	-1.1	-22.8	4.72	1.58	-0.05	0.35	-0.14	1.77	7.49	0.025
40	R387D-1	-0.82	-0.32	-0.57	0.18	-4.09	-2.7	-9.48	-19	-4.4	-31.4	7.69	2	-0.07	-0.02	0.02	3.34	9.79	0.036
41	R387D-1	0.62	0.9	0.76	0.31	-7.09	-3.7	-12.9	-27	-11	170.2	-12	-68.9	-0.04	0.02	0.06	4.75	9.63	0.024
42	R387D-1	0.57	0.89	0.73	0.08	-6.09	-3.7	-12.9	-28	-7.7	81.24	2.46	-24	-0.04	0.19	0.01	3.51	8.79	0.022
43	R387D-1	0.84	0.84	0.84	0.01	-5.09	-3	-11.7	-25	-7.4	429.6	-12	10.5	-0.05	0.14	-0.06	2.68	7.89	0.024
45	R387D-1	0.5	0.2	0.35	0.05	-5.09	-3	-11.7	-25	-7.4	153.7	-12	-70.7	-0.04	-0.11	-0.03	3.38	8.49	0.024
46	R387D-1	0.83	0.12	0.48	0.07	-5.09	-2.1	-10.7	-25	-14	425	-11	13.7	-0.04	-0.15	0.08	1.29	4.08	0.028
	RREG	**-0.15571**	**-0**	**-0.08**	**0.153**	**-4.09**	**-2.3**	**-8.45**	**-17**	**-6.1**	**67.46**	**0.57**	**-9.11**	**-0.043**	**-0.03**	**0.005**	**3.22071**	**6.884**	**0.025**
47	R393C-1	-0.26	-0.4	-0.33	0.26	-3.16	-2	-6.67	-13	-3.1	-22.6	5.07	5.23	-0.03	0.19	-0.02	4.28	-1.7	0.036
49	R393C-1	-0.39	0.01	-0.19	0.56	-5.18	-3.3	-11.6	-16	-7.1	-27.3	6.25	6.34	-0.03	0.3	0.04	4.38	-1.37	0.026
50	R393C-1	0.2	-0.43	-0.12	0.63	-5.35	-3.5	-11.9	-14	-3.9	-24.9	5.81	5.05	-0.03	-0.89	0	10.65	-5.79	0.032
	RPRM	**-0.15**	**-0.27**	**-0.21**	**0.483**	**-4.56**	**-2.9**	**-10**	**-14**	**-4.7**	**-24.9**	**5.71**	**5.54**	**-0.03**	**-0.13**	**0.007**	**6.43667**	**-2.95**	**0.031**

Figure 19.8—Example of blending model bias variation for 1 month of blends. *Source:* Reproduced with permission from [1].

3. Make a 50/50% mixture of all pairs of components. For example, for six-component blends, there should be 15 such pairs at one set of process conditions and they must be made so as to cover all component quality variations for at least the high and low ranges of process conditions. For each pair of components, there would be three RON measurements by laboratory analysis—in total 42 (6+15 RON, 6+15 MON) measurements for both RON and MON at one process condition.
4. Measure the RON/MON of each mixture by the same means as the component octane.
5. Calculate the interaction coefficient as follows:

$$B_{12,j} = \frac{Q_j - 0.50 * (q_{1,j} + q_{2,j})}{0.25} \qquad (19.22)$$

6. The interaction coefficients are not constant and depend on process changes. Hence, they cannot be trusted for all blends.
7. Typically, blend components are collected over 3 month's period to represent all process conditions. There will be 420 RON/MON measurements for just 10 process conditions and it is not enough at times.
8. It is very expensive and time-consuming to analyze component and blend mixture octane of 500+ samples and update the coefficients; most refineries do so only once approximately every 5 years.

19.3.4.3.2 Example of Interaction Coefficient Values

Figure 19.9 shows the typical set of analyzed values of RON by laboratory analysis, and Figure 19.10 shows the calculated values of the DuPont interaction coefficient for all pairs of the component. The values in the figure can be simply calculated in an Excel spreadsheet using equation 19.22.

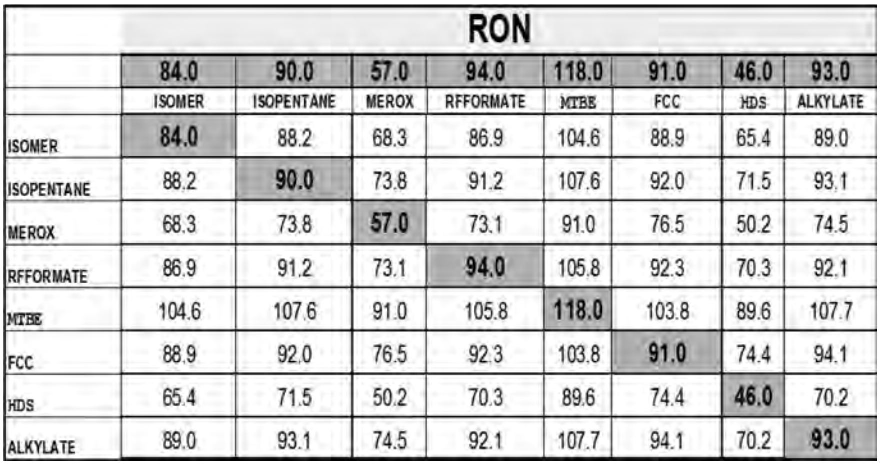
Equation 19.21 can be further extended to include a bias term to account for other inaccuracies (discussed in Section 19.3.4.1).

19.3.4.4 SPECTRUM-BASED BLENDING INDICES

Blending indices for gasoline and diesel blending can also be computed by using their near-infrared (NIR) spectrum [3]. The method uses the entire spectrum of a sample rather than its individual properties as in conventional index calculation methods. Although this method offers more accurate results and faster availability of index calculations, it requires complex and proprietary spectrum blending models, a huge spectrum database, and an extensive set of samples to build the database. The advantages are that this method can be used for all fuel blending (e.g., gasoline, diesel, biodiesel, ethanol blending, etc.). The detailed discussion of this method is outside of the scope of this chapter, and the reader should refer to the paper by Lambert in the www.eptq.com online journal [3].

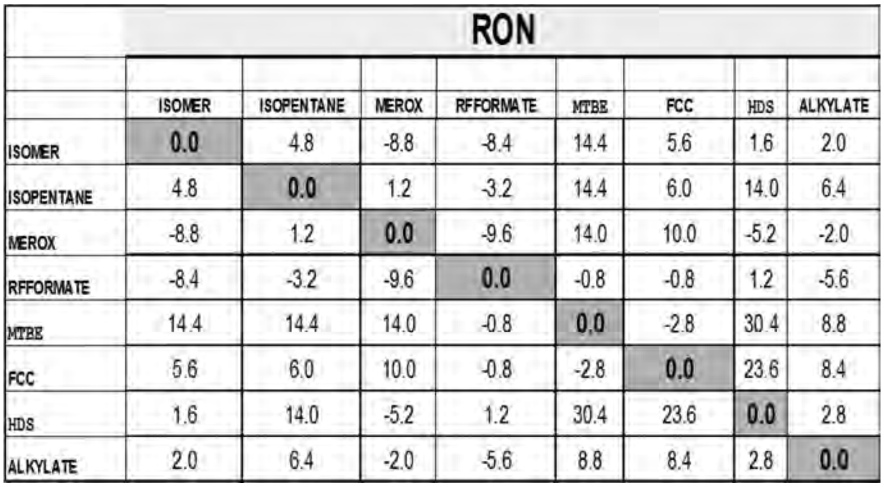
19.3.5 Control Matrix of Qualities

We discussed in earlier sections that blend nonlinearity in the blend model arises from the fact that blend quality not only depends on the component composition and their qualities but also on their interaction with other components in the pool. Figure 19.11 shows the quality dependence of qualities for the gasoline blends, and their relationships are reflected in the blend nonlinear models.



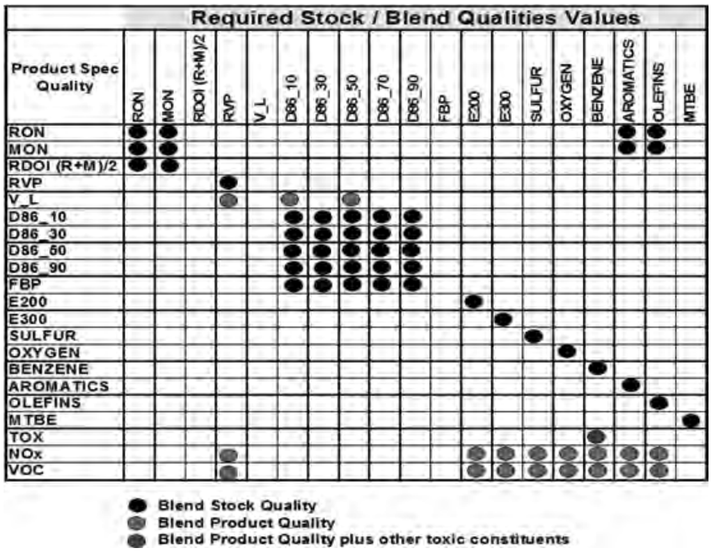
RON								
	84.0	90.0	57.0	94.0	118.0	91.0	46.0	93.0
	ISOMER	ISOPENTANE	MEROX	RFFORMATE	MTBE	FCC	HDS	ALKYLATE
ISOMER	84.0	88.2	68.3	86.9	104.6	88.9	65.4	89.0
ISOPENTANE	88.2	90.0	73.8	91.2	107.6	92.0	71.5	93.1
MEROX	68.3	73.8	57.0	73.1	91.0	76.5	50.2	74.5
RFFORMATE	86.9	91.2	73.1	94.0	105.8	92.3	70.3	92.1
MTBE	104.6	107.6	91.0	105.8	118.0	103.8	89.6	107.7
FCC	88.9	92.0	76.5	92.3	103.8	91.0	74.4	94.1
HDS	65.4	71.5	50.2	70.3	89.6	74.4	46.0	70.2
ALKYLATE	89.0	93.1	74.5	92.1	107.7	94.1	70.2	93.0

Figure 19.9—Typical octane values of blend components. *Source:* Reproduced with permission from [1].



RON								
	ISOMER	ISOPENTANE	MEROX	RFFORMATE	MTBE	FCC	HDS	ALKYLATE
ISOMER	0.0	4.8	-8.8	-8.4	14.4	5.6	1.6	2.0
ISOPENTANE	4.8	0.0	1.2	-3.2	14.4	6.0	14.0	6.4
MEROX	-8.8	1.2	0.0	-9.6	14.0	10.0	-5.2	-2.0
RFFORMATE	-8.4	-3.2	-9.6	0.0	-0.8	-0.8	1.2	-5.6
MTBE	14.4	14.4	14.0	-0.8	0.0	-2.8	30.4	8.8
FCC	5.6	6.0	10.0	-0.8	-2.8	0.0	23.6	8.4
HDS	1.6	14.0	-5.2	1.2	30.4	23.6	0.0	2.8
ALKYLATE	2.0	6.4	-2.0	-5.6	8.8	8.4	2.8	0.0

Figure 19.10—Calculated DuPont interaction coefficients from values in Figure 19.9. *Source:* Reproduced with permission from [1].



Required Stock / Blend Qualities Values																			
Product Spec Quality	RON	MON	RDOI (R+M)/2	RVP	V_L	D86_10	D86_30	D86_50	D86_70	D86_90	FBP	E200	E300	SULFUR	OXYGEN	BENZENE	AROMATICS	OLEFINS	MTBE
RON	●	●															●	●	
MON	●	●															●	●	
RDOI (R+M)/2	●	●																	
RVP				●															
V_L				◎		◎		◎											
D86_10						●	●	●	●	●									
D86_30						●	●	●	●	●									
D86_60						●	●	●	●	●									
D86_90						●	●	●	●	●									
FBP						●	●	●	●	●									
E200												●							
E300													●						
SULFUR														●					
OXYGEN															●				
BENZENE																●			
AROMATICS																	●		
OLEFINS																		●	
MTBE																			●
TOX																◍			
NOx				◍								◍	◍	◍	◍	◍	◍	◍	
VOC				◍								◍	◍	◍	◍	◍	◍	◍	

● Blend Stock Quality
◎ Blend Product Quality
◍ Blend Product Quality plus other toxic constituents

Figure 19.11—Quality dependence matrix for components and blends. *Source:* Reproduced with permission from [1].

19.4 RECIPE OPTIMIZATION

The economic objectives of fuel blending operations are

- Blends should be on specifications with minimal quality giveaway and should have no violations in any circumstances.
- Reblends should be minimal for off-spec blends.
- Blends should be produced with minimal cost.

This section examines the methodology to achieve the above blending objectives.

19.4.1 Control and Manipulated Blend Variables

Let us re-examine the generalized blend equation as follows:

$$Q_b^s = \sum_{i=1}^{n} X_i K_i f_i (X_1, X_2 X_3 \ldots X_n, Q_1, Q_2, Q_3 \ldots\ldots Q_n) \quad (19.23)$$

where:

$K_i = 1$ if blended by volume,

otherwise $\frac{1}{\text{Density}}$ of component if blended by weight, and

Q_b^S = Blended Specification.

In the above equation $\boldsymbol{X_i}$ are the **manipulated variables** because they are changed or manipulated to achieve the target blend specification, $\boldsymbol{Q_b^s}$ (controlled variable). If the blend is a three-component system, then it can be solved deterministically for three qualities. However, in reality, a blending system has more unknown variables than the known variables and hence it cannot generate an unique solution. We will next discuss how to solve equations with more controlled variables (qualities + slack) than the manipulated variables (composition).

19.4.2 Slack Variables

Let us examine a three-component blending system to control three blend qualities (RON, RVP, and 50% distillation point) with minimum and maximum specifications using nonlinear blending equations with DuPont coefficients.

- Minimum specifications

$$\begin{aligned} Q^s_{b,RON} < {} & x_1 {*} q_{1,RON} + x_2 {*} q_{2,RON} + x_3 {*} q_{3,RON} \\ & + \beta_{12} {*} x_1 {*} x_2 + \beta_{13} {*} x_1 {*} x_3 + \beta_{23} {*} x_2 {*} x_3 + \varphi_1 \end{aligned} \quad (19.24)$$

- Maximum specifications

$$\begin{aligned} Q^s_{b,RVP} > {} & x_1 {*} q_{1,RVP} + x_2 {*} q_{2,RVP} + x_3 {*} q_{3,RVP} \\ & + \beta_{12} {*} x_1 {*} x_2 + \beta_{13} {*} x_1 {*} x_3 + \beta_{23} {*} x_2 {*} x_3 + \varphi_2 \end{aligned} \quad (19.25)$$

- Maximum specifications

$$\begin{aligned} Q^s_{b,50\%} > {} & x_1 {*} q_{1,50\%} + x_2 {*} q_{2,50\%} + x_3 {*} q_{3,50\%} + \beta_{12} {*} x_1 {*} x_2 \\ & + \beta_{13} {*} x_1 {*} x_3 + \beta_{23} {*} x_2 {*} x_3 + \varphi_3 \end{aligned} \quad (19.26)$$

where:

φ_1, φ_2, φ_3 = model biases.

Now, equations 19.24–19.26 cannot be solved uniquely because of inequalities in the equation. Hence, we will introduce slack variables in the above equations to convert them to equalities and also use the blending values for nonlinearity to make the equations easier to handle. The transformed equations are as follows:

$$\begin{aligned} Q^s_{b,RON} = {} & x_1 * q^v_{1,RON} + x_2 * q^v_{2,RON} + x_3 * q^v_{3,RON} \\ & + \varphi_1 - G_{b,RON} + V_{b,RON} \end{aligned} \quad (19.27)$$

$$\begin{aligned} Q^s_{b,RVP} = {} & x_1 * q^v_{1,RVP} + x_2 * q^v_{2,RVP} + x_3 * q^v_{3,RVP} \\ & + \varphi_2 + G_{b,RVP} - V_{b,RVP} \end{aligned} \quad (19.28)$$

$$\begin{aligned} Q^s_{b,50\%} = {} & x_1 * q^v_{1,50\%} + x_2 * q^v_{2,50\%} + x_3 * q^v_{3,50\%} \\ & + \varphi_3 + G_{b,50\%} - V_{b,50\%} \end{aligned} \quad (19.29)$$

where:

$q^v_{i,j}$ = blend values for component *i* and quality *j*,
$G_{b,j}$ = giveaway slack variable for quality *j*, and
$V_{b,j}$ = violation slack variable for quality *j*.

Now we have three equations and nine unknowns (X_1, X_2, and X_3 plus giveaway and violation slack variables). Equations 19.27–19.29 have multiple possible solutions as follows, and we must define an additional criterion to select

$$\begin{aligned} Q_s^j = {} & \left\{ \sum_i X_i^1 * K_i * f_i \left(X_i^1, \ldots\ldots., X_n^1, Q_i^j, \ldots\ldots. Q_n^j .. \right) \right\}, \\ & \left\{ \sum_i X_i^2 * K_i * f_j \left(X_i^2, \ldots\ldots., X_n^2, Q_i^j, \ldots\ldots. Q_n^j .. \right) \right\}, \\ & \left\{ \sum_i X_i^m * K_i * f_j \left(X_i^m, \ldots\ldots., X_n^m, Q_i^j, \ldots\ldots. Q_n^j .. \right) \right\} \end{aligned} \quad (19.30)$$

19.4.3 Objective Function

We introduce an additional criterion in equation 19.30 to select a feasible solution subject to minimal quality giveaway from specifications or maximal blend profit. The condition is stated as

$$Q_s^j = Optimum \left\{ \sum_i X_i^1 * K_i * f_j \left(X_i^1, \ldots\ldots., X_n^1, Q_i^j, \ldots\ldots. Q_n^j .. \right) \right\} \quad (19.31)$$

subject to maximal profit on blend $\left(P^b - \sum_{i=1}^{n} X_i * C_i \right)$ or minimal quality giveaway $\left(Q_s^j - Q_b^j \right)$, where P^b is the sale price of the blend product and C_i is the cost of component *i*.

Now, the monetary cost of a component is not easy to compute in a refinery and is practically not used. Instead, a blending value is computed for components on the basis of their RON and RVP values relative to the blend product. It is outside of the scope of this chapter to discuss the methodology and equations to calculate component blending values for the cost of components.

The above objective function is a simpler form of the basic terms of optimization. In reality, there are other factors considered in a refining blending system to optimize the recipe. An example of additional terms used in the formation of an objective function is shown in Figure 19.12. The objective function would then be as follows:

$$\text{Objective function} = \text{A} - \text{B} + \text{C} - \text{D} - \text{E} - \text{F} - \text{G} - \text{H} - \text{I} - \text{J} \quad (19.32)$$

Figure 19.12 explains the definitions of each of the terms listed in equation 19.32.

		Applicable for the optimization of	
Term	**Description**	**Maximum Profit**	**Minimum Giveaway**
A	Values of Products	**Yes**	**Yes**
B	Cost of all Stocks	**Yes**	
C	Value of Closing Stock Inventory	**Yes**	
D	Cost of Antiknock Compound	**Yes**	
E	Cost of Cetane Improver **	**Yes**	
F	Cost of Distress Buying	**Yes**	**Yes**
G	Cost or Value of Distress Selling	**Yes**	**Yes**
H	Cost of Distress Quality Buying or Selling	**Yes**	**Yes**
I	Penalty Cost for Deviation from Preferred Recipe	**Yes**	**Yes**
J	Quality Giveaway Cost and Violation Penalty Cost		**Yes**
** For distillate blending only			

Figure 19.12—Additional terms in the objective function. *Source:* Reproduced with permission from [1].

Distress buying and selling costs are used to buy or sell components to ease the infeasible solution due to shortage or excess of component inventories. Typically, the distress buying cost is higher than the component cost (or blending value cost) and the selling cost is less than the component cost (or blending value cost) to facilitate arriving at an optimal blend recipe solution. The objective function in Figure 19.12 has typical cost factors and can be modified to include other expensive additives. The violation penalty costs are usually higher by many-fold and are used in the relative importance of quality violation. For example, RON cannot be violated and hence may be given a violation penalty factor of 10,000 with a penalty factor of 8,000 for RVP and so on and so forth. Typically, offline optimization by a planner or blend engineer is done based on profit whereas online optimization focuses on the minimization of quality giveaways. Since the cost of components are not accurately available, their relative blending values are used in the profit function.

19.4.4 Optimization Algorithms

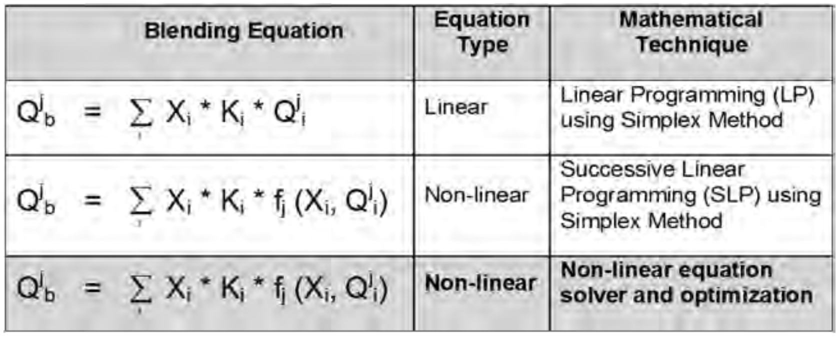
The system of equations discussed in earlier sections can be solved by any of the three mathematical techniques on the basis of the nature of the blend equations used. Figure 19.13 shows a summary of blend equations and mathematical techniques.

Nonlinear blend equations can be solved by successive linear programming (SLP) or a true nonlinear solver. However, SLP is a sampler technique because it involves iteratively executing the linear programming (LP) algorithm until the solution converges, but it requires custom programming over the commercial LP algorithm. The implementation of SLP in commercial LP programs usually requires interface to it, if feasible and tools are available from the vendor, or it creates a wrapper around the algorithm to repeatedly solve the LP matrix until the nonlinear qualities and blend recipe converge.

19.5 DESIGN OF A TYPICAL BLENDING SYSTEM

In this section we will discuss design considerations for a typical blending system and will focus mostly on a gasoline blender because it is the most complex blender in a refinery [4,5]. A typical blending system has the following ten automation islands, in addition to design configuration of blending configuration:

1. Tank farm
2. Automatic tank gaging system
3. Laboratory analysis
4. Field equipment and instrumentation
5. Fuel additives
6. Quality analysis and measurements
7. Advanced blend control, optimization, planning, and scheduling



Blending Equation	Equation Type	Mathematical Technique
$Q^j_b = \sum_i X_i * K_i * Q^j_i$	Linear	Linear Programming (LP) using Simplex Method
$Q^j_b = \sum_i X_i * K_i * f_j(X_i, Q^j_i)$	Non-linear	Successive Linear Programming (SLP) using Simplex Method
$Q^j_b = \sum_i X_i * K_i * f_j(X_i, Q^j_i)$	**Non-linear**	**Non-linear equation solver and optimization**

Figure 19.13—Mathematical techniques used for blend equation. *Source:* Reproduced with permission from [1].

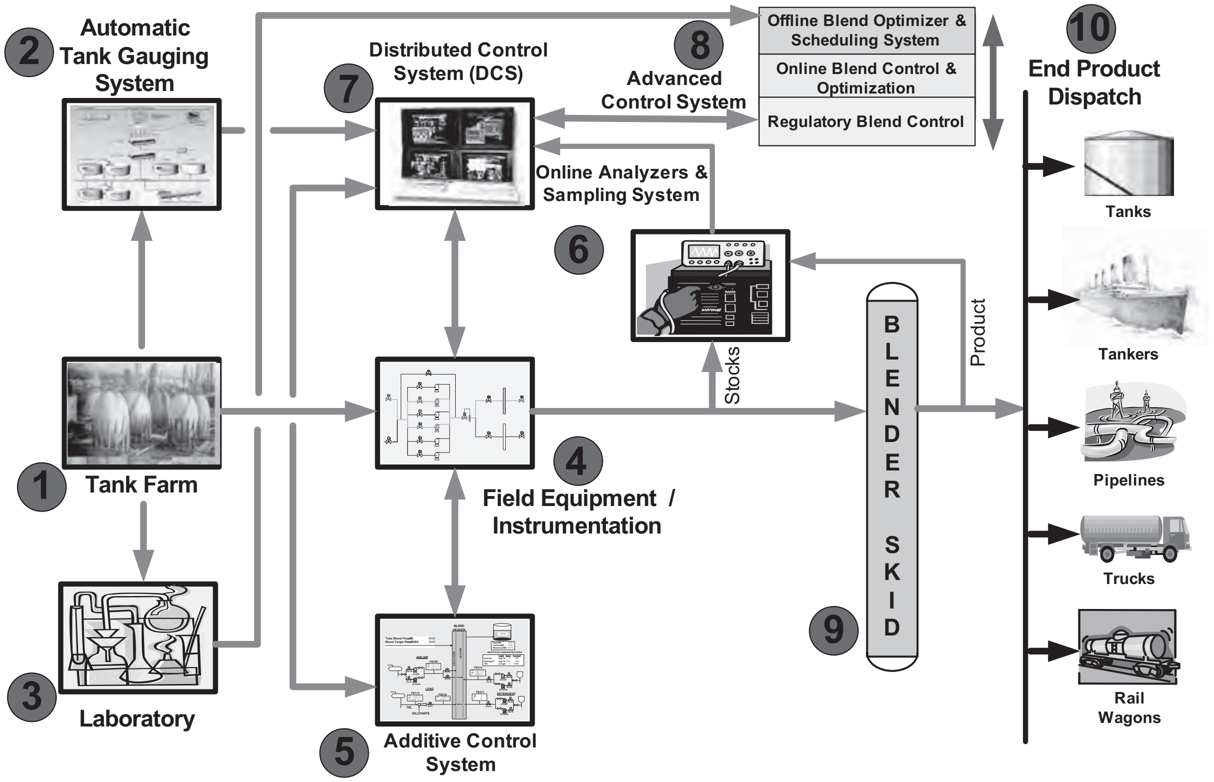


Figure 19.14—Automation islands of a typical blending system. *Source:* Reproduced with permission from [1].

8. Computer system
9. Blend header
10. End-product dispatch

Figure 19.14 shows all automation components of a typical gasoline blending system, and we will discuss the design considerations for each one of them in detail in the following sections.

19.5.1 Blending Configuration

A fuel blending system is configured in many ways, depending on the source, destination, product type, refinery configuration, degree of complexity, and expected flexibility to operate and optimize. Table 19.2 shows the types of blending configurations used in a typical refinery.

The extent of optimization is defined as the ability and freedom to manipulate the component recipe to arrive at the final product specifications. In general, inline batch blending configurations are less complex and more flexible in blend optimization, but they have the disadvantages of increased tankage requirement and large product inventory buildup. On the other hand, run-down blending requires more instrumentation, is limited in optimization flexibility, and is affected by process swings; it has the advantages of low inventory buildup. A limited extent of optimization for inline and run-down blending to ships and pipelines means that a refinery does not get a second chance to correct the giveaway of violated products because the product moves out quickly (pipeline) or is difficult to access (ships).

19.5.2 Tank Farm

A blending tank farm consists of tanks for components and products and is configured in many ways. Blending tank farms offer inherent pros and cons:

- *Single versus paired blend stock tanks:* Each component can have a single tank, paired tanks, or a hybrid combination of single and paired tanks for some of the components. The paired component tanks are the preferred design consideration because it offers flexibility in the planning process, constant tank quality during blending, and stable recipe control.

TABLE 19.2—Blending System Configuration

Mode	Source	Destination	Product Type	Degree of Complexity	Extent of Optimization
Inline batch	Tank	Tank	Gasoline, diesel, fuel oils	Fair	Excellent
Inline batch	Tank	Pipeline or Ship	Gasoline, diesel, fuel oil	High	Limited
Run-down	Units	Tank	Diesel, kerosene, jet fuels	Fair	Average
Run-down	Units	Pipeline or Ship	Diesel, kerosene, jet fuels	High	Limited

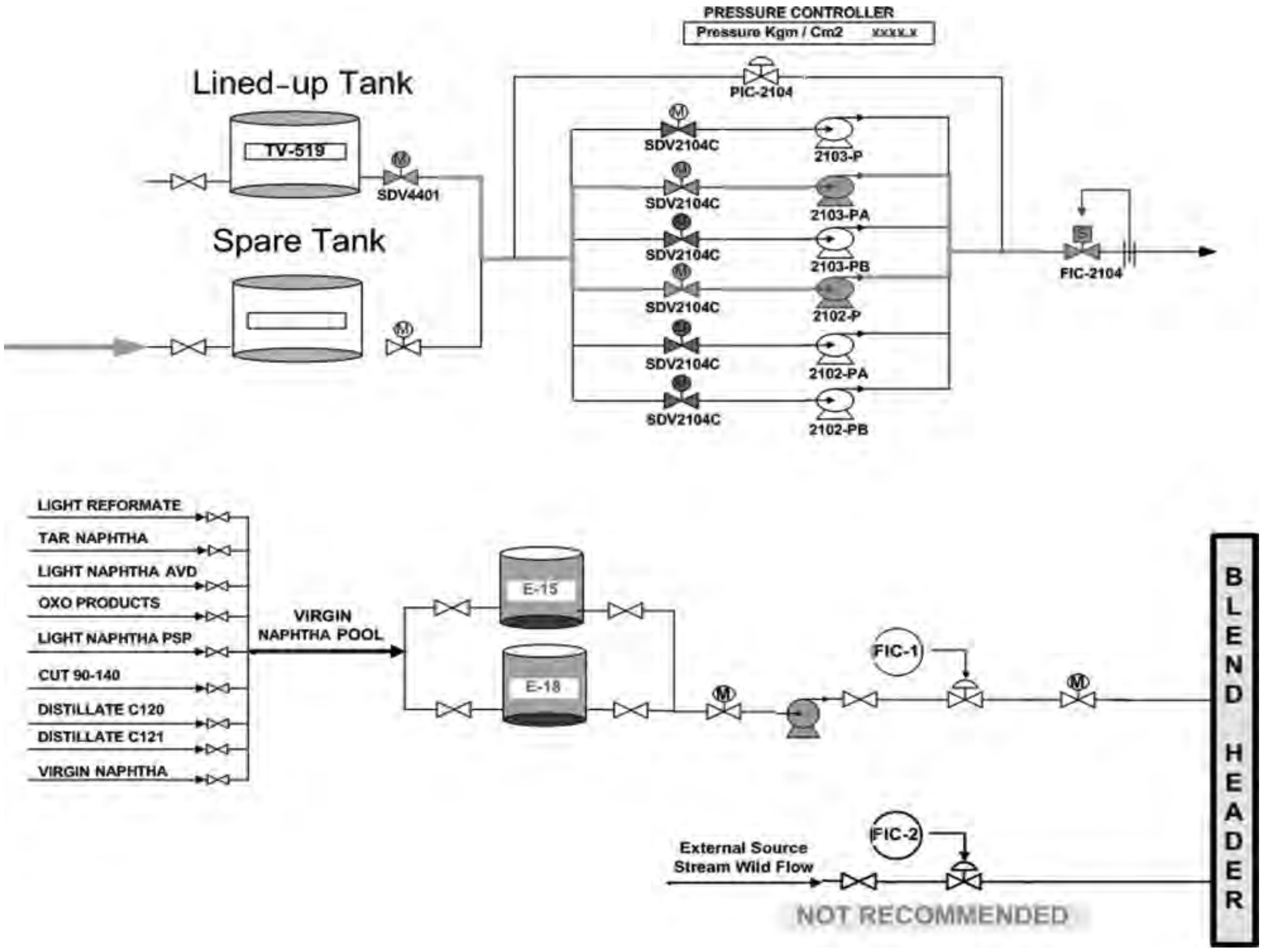


Figure 19.15—Recommended stock tank configuration for a blending system. *Source:* Reproduced with permission from [1].

- *Running versus closed stock tanks:* Running stock tanks receive feed from the units while they feed the blending system. This mode of operation continuously changes the quality of the stock tank and thus affects the blend control and optimization downstream of the stock tank. On the other hand, closed stock tanks do not receive the feed while blending and hence their qualities do not change, remaining the same as those used in the blend planning of the blend recipe, thus minimizing the effect on the blend control system.
- *Stream pooling and wild flows:* Some refineries have multiple streams of low quality, a wild stream from external sources, or both. If these streams are fed directly to the blender, the blend control is erratic and surely ends up in huge quality giveaway or reblends. Hence, it is a good design practice to pool all of these wild and low-quality streams into an existing stock tank with components of comparable qualities. The stream pooling has a risk of quality stratification if the component qualities are quite different. The best possible way to avoid quality stratification is to install a mixture in the tank to homogenize the tank content.
- *Stock tanks versus control loops:* It is not uncommon in refineries for the number of stock tanks to be more than the number of control loops. This results in continuous swapping of the stock tanks based on blend recipe and thus causes a loss of production, quality degradation, and less optimal final blend quality. This can be avoided by using stream pooling as discussed above to rebalance the stock tanks versus control loops.

Figure 19.15 shows the recommended design considerations for configuring stock tanks and pooling of wild and low-quality streams.

It is absolutely necessary to install an automatic tank gaging system (ATGS) for all blend stock and product tanks to monitor the tank inventory in real time for the blending system. Because this topic is dealt with in great detail in Chapter 20 on tank farm management, it will not be discussed in this chapter to avoid duplication.

19.5.3 Field Equipment and Instrumentation

It is very important at the design stage of a new blending system that appropriate instrumentation is provided for a fully automatic blending operation. This fact is sometimes ignored by the refineries to minimize the cost of the blending system by not allocating adequate funds for the field equipment and instrumentation. Table 19.3 shows the design recommendation of various instruments to install for a fully automatic system.

Figure 19.16 shows the locations of all required/optional instruments in a typical blending system.

TABLE 19.3—Location and Requirements of Instruments in a Blending System

Equipment	Location	Manual Valves	Motor-Operated Valve	Pressure Controller	Flow Controller	Flow Meter
Stock tanks	Inlet	Required	Optional			
	Outlet		Required			
Pumps	Inlet		Required			
	Outlet			Required		
Control loop					Required	Required
Header	Inlet		Required			
	Outlet					
Product tanks	Inlet		Required			
	Outlet	Required				

19.5.4 Quality Analysis and Measurements

The qualities of stock and products must be known before, during, and after the completion of a blending batch in real time, offline analysis, or both. The qualities in a blending system are made available by any one or all of the following methods:

- Laboratory analysis
- Online analyzer
- Model-based prediction

19.5.4.1 LABORATORY ANALYSIS OF STOCK AND PRODUCT QUALITIES

Figure 19.17 shows the traditional methods of quality estimation by laboratory analysis samples (S) for stock, product tanks, header qualities, and online analyzers (A) after the blend header to measure blended qualities. The blend models used in the blending system also predict the qualities at the header and final product qualities. Another chapter (18—"Product Analysis and Quality Control") in this manual covers the test methods for laboratory analysis.

19.5.4.2 ONLINE ANALYSIS OF STOCK AND HEADER QUALITIES

Blend qualities of stock tanks and the blend header are analyzed by online analyzers using the following strategy:

- *Discrete analyzers:* RVP and sulfur are analyzed by discrete analyzers in conjunction with a multiplexer and multistream sampling system. Discrete analyzers measure only one quality of one stream at a time.
- *Integrated analyzers:* These include spectrum-based analyzers such as NIR or nuclear magnetic resonance (NMR) to simultaneously analyze multiple qualities.

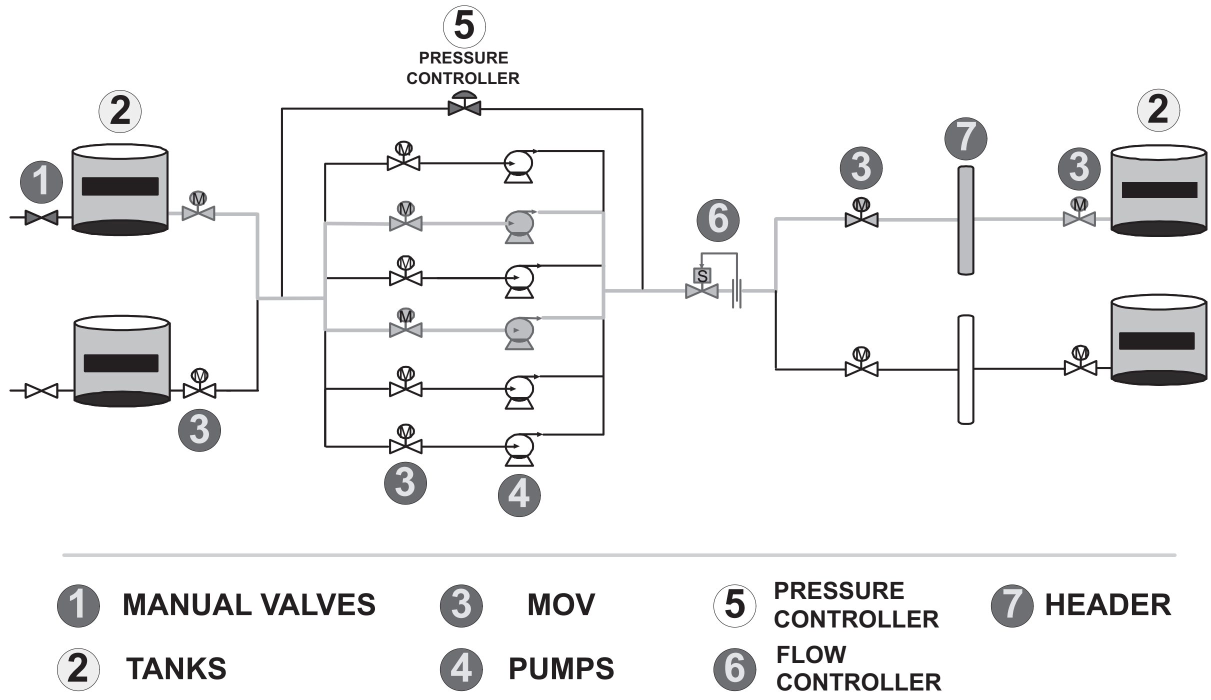


Figure 19.16—Recommended instrumentation for an automatic blending system. *Source:* Reproduced with permission from [1].

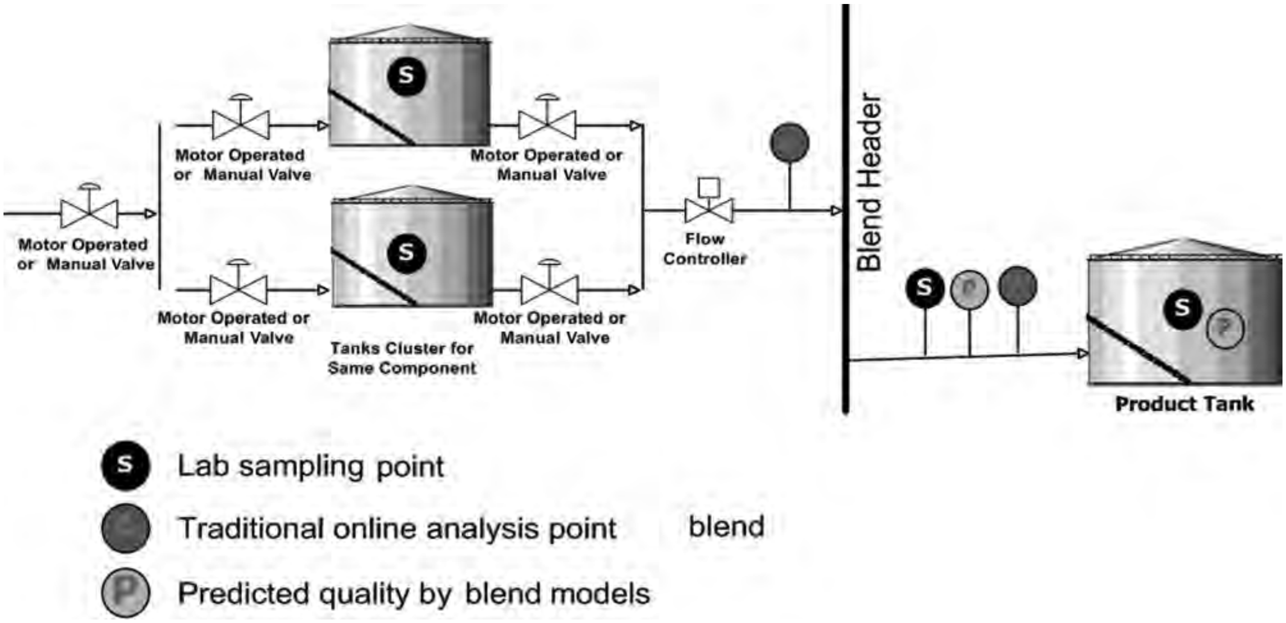


Figure 19.17—Method of quality estimation in the blending system. *Source:* Reproduced with permission from [1].

Qualities such as octane (RON, MON), RVP, distillation points, olefins, aromatics, benzene, and many more can be analyzed by a single integrated analyzer, thus saving huge expenditures for discrete blending analyzers. Chromatography or a similar technology-based analyzer for multiple distillation points is another example of an integrated analyzer.

- *Multiplexed sampling system:* Although discrete and integrated analyzers sample one stream at a time, their usability is enhanced by using a multiplexed multistream sampling system. This strategy samples component tank exit streams and a blend header at slow and fast pace, respectively, and sends them to the set of analyzers for analysis. In this way, all streams are analyzed online by one set of analyzers. Stock tank exit streams are usually sampled at a slow frequency of 20–30 min/stream, and a blend header in fast loop mode is sampled at a frequency of approximately 2–3 min/sample. This is because stock tank qualities change slowly compared with the blend header qualities. On the other hand, blend control and optimization depend mainly on the blend header quality in most blending systems.

Figure 19.18 shows a typical blending system design for online analyzers and a multiplexed multistream sampling system.

19.5.4.3 MODEL-BASED TANK QUALITY MEASUREMENT

Quality measurements by laboratory analysis and online analysis using integrated analyzers with a multiplexed sampling system as described earlier have the following inherent disadvantages:

- Laboratory analyses for blend tanks are manpower-intensive ($3–4 million/year for a 300 KB/day refinery with 44 blend tanks), slow in turnaround period (6–8 h), and are not suitable for running stock tanks and offline/online blend recipe optimization applications.
- On the other hand, integrated analyzers require extensive efforts and expertise to develop NIR/NMR models for a specific refinery under a range of process conditions.
- The usability of integrated online analyzers is limited because they are activated only during blend runs (10–12 h/day) and remain dormant the rest of the time. They also require 20–40 min of line-up and a sample stabilization period, thus losing initial blend quality information.
- Tank qualities are not available to the refinery planner in time for recipe planning because they depend on laboratory analysis. This may result in quality giveaways or reblends if stock tanks are running during blending.

A recent development has eliminated some of the disadvantages of laboratory and online analysis by installing an external tank quality tracking system (software) and repositioning the online analyzers at the inlet points of the stock tanks rather than traditional tank exit points [6]. Figure 19.19 shows the functionality of the online tank quality tracking system in conjunction with alternate placement of online analyzers. The advantages of this technology are

- It reduces the laboratory analysis load by 40–50% for blend tanks and the cost by an average of $0.5—1 million/year [7].
- Tank qualities are available 24 × 7 to all online/offline applications.
- Online analyzers are a larger percentage of the time and hence give a better return on investment (ROI).
- The software contains more than 70 nonlinear quality models and can also be used for nonblend tanks.
- Process units upstream of blend tanks can use this online tank quality information for feedback control purposes.
- It seamlessly integrates with existing and future blending control system software from any third-party vendors.
- It has been demonstrated to save refineries $2–2.5 million/year to minimize quality giveaways for a run-down blending system without an online control system in place [6].

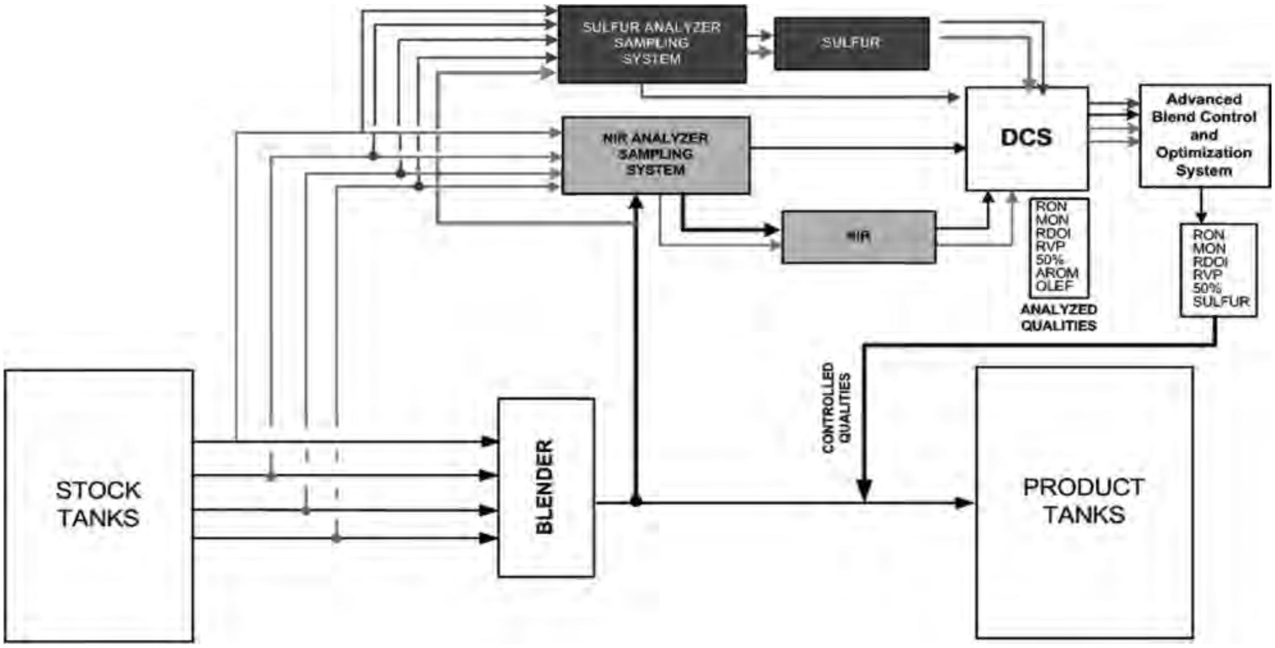


Figure 19.18—Online analysis system with a multiplexer for a typical blending system. *Source:* Reproduced with permission from [1].

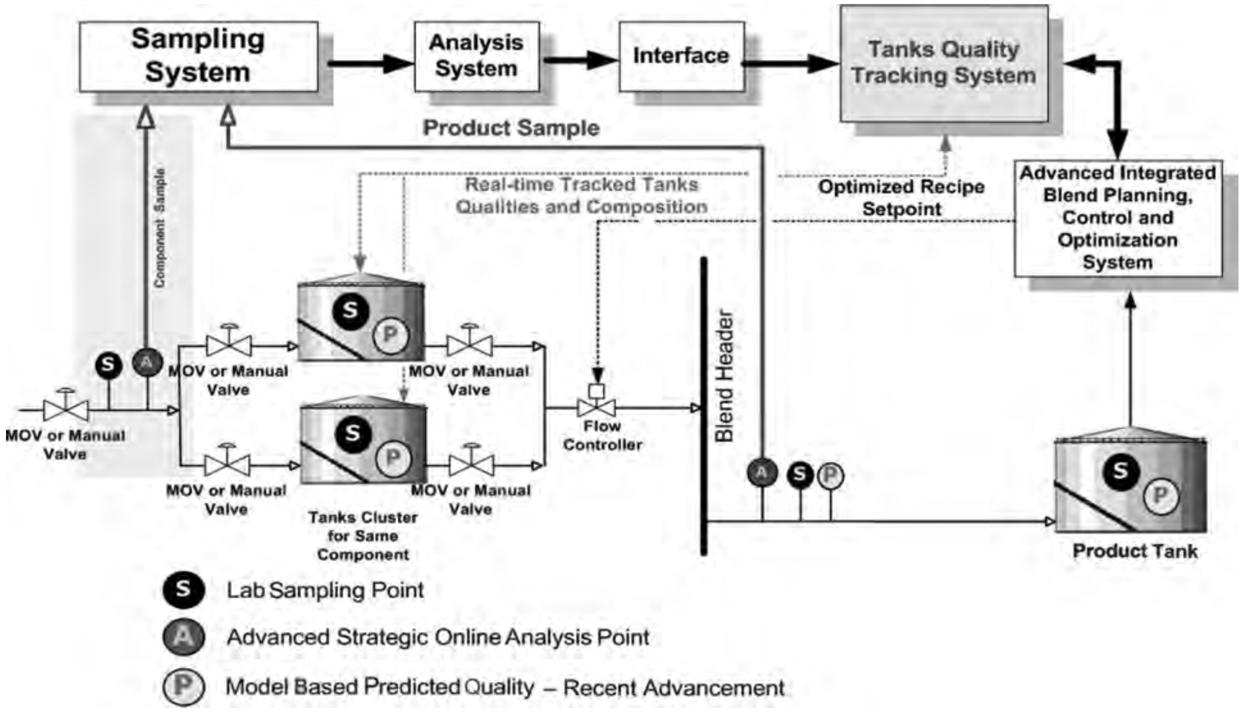


Figure 19.19—Model-based tank quality tracking system with strategic placement of analyzers. *Source:* Reproduced with permission from [1].

19.5.5 Advanced Blend Control, Optimization, Planning, and Scheduling

In this section, we will discuss the different layers and components of an advanced blend control, optimization, planning, and scheduling system. A most modern and fully automated blending system consists of the following three tiers:

1. Regular blend control;
2. Online blend control and optimization; and
3. Offsite blend optimization, planning, and scheduling.

We will discuss in the next sections that the first level of distributed control system (DCS)-based regulatory control is absolutely required for the safe operation of a blending system, and the third level to optimize the recipe in an offline mode is recommended for minimizing quality giveaway and reblends. The second level of online blend control is optional and may not be required at all on the basis of a refinery's blending configuration.

19.5.5.1 REGULATORY BLEND CONTROL

Almost any modern refinery of reasonable capacity (>100 kb/day) has implemented a DCS- or programmable logic controller (PLC)-based regulatory blend control system for an inline blender. However, there are still some refineries in the world that practice manual sequential (one tank at a time) blending operations.

The main objectives of DCS-based regulator blend control system are

- Control the initial blend recipe as downloaded by the planner,
- Minimize the quality giveaways by monitoring the blend header by a set of discrete online analyzers (RON is measured by cooperative fuel research [CFR] knock engines),
- Provide blend trim control to adjust the final tank quality for violation or excessive quality giveaways, and
- Safe blending operations.

A refinery normally implements many more features in the DCS-based regulatory control system. However, it is outside of the scope of this chapter to discuss all of these features here. Figure 19.20 shows a system diagram with online analyzers for a DCS regulatory control system.

The limitations of the regulatory blend control are

- It cannot use feedback from analyzers to adjust the recipe.
- It cannot handle changes in the component tank qualities.
- It can only use recipe as downloaded by the planner and cannot adjust it to meet final specifications.

19.5.5.2 OFFLINE BLEND OPTIMIZATION AND PLANNING

The next step in blend control evolution was to implement some sort of recipe optimization, initially using Excel's GRG2 algorithm, and download the recipe to DCS online or manually via e-mail and phone to the blend operator or both. The refinery planner or blend engineer in some cases would gather the last tank qualities from the laboratory and optimize the recipe on the basis of the desired specifications and blend batch size. This was initially successful for linear blend models. It was later upgraded to a more sophisticated offline optimizer by third-party vendors incorporating nonlinear models and many other desirable features. Figure 19.21 shows a two-tier blend system with a regulatory blend control and offline blend optimizer.

However, the recipe so planned and optimized is only good if the component tank qualities do not change during the actual blend execution. This was never the case for running tanks. Hence, the planner's initial recipe deviated from the final version on the basis of how severe the component tank quality changed during blend and what kind of blend models were used in GRG2 or third-party software.

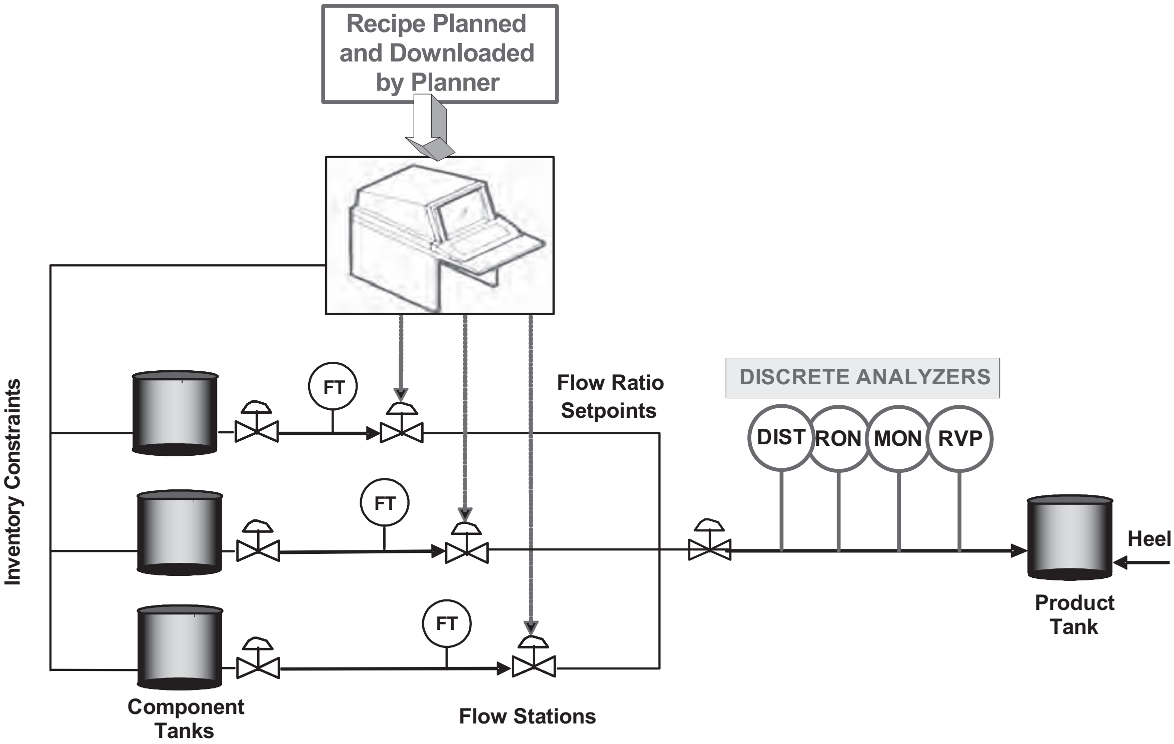


Figure 19.20—DCS-based regulatory blend control system. *Source:* Reproduced with permission from [1].

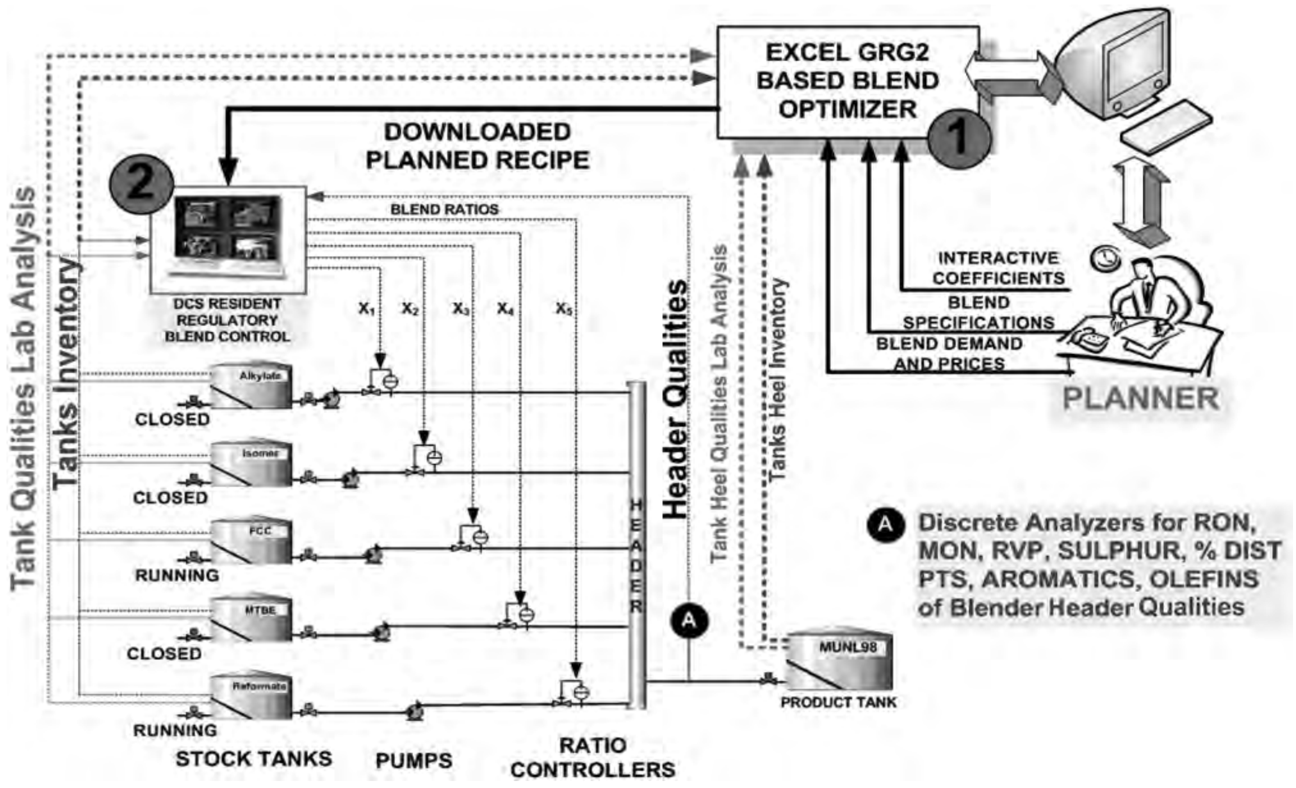


Figure 19.21—Two-tier blending system with regulatory blend control and offline optimizer. *Source:* Reproduced with permission from [1].

The combination of all of these inherent disadvantages in this two-tier system either resulted in quality giveaway or violation. A refinery cannot sell the products with off-specs, but they can accept the reasonable quality giveaways to sell the product.

19.5.5.3 ONLINE BLEND CONTROL AND OPTIMIZATION

Because the blend stock qualities were invariably changing because of limited closed tanks, they were not available in time to plan for recipe optimization. The final recipe deviated from the initial planner's recipe, which was optimized to meet the target specifications. Therefore, it is almost necessary to implement another tier of online blend control between the regulatory blend control and offline optimizer to solve these problems.

However, the traditional implementation of online blend control in which the online analyzers are installed at the tank exit did not help the planner because they had to rely on the laboratory analysis of tank qualities before recipe optimization. Also, the expensive set of integrated NIR/NMR analyzers is not used at all for 40–50% of the time.

Figure 19.22 shows the design of a blending system with a tank quality tracking system and strategic placement of online analyzers to solve the above-mentioned problem. This design consideration takes the tank quality integration function out of the online optimizer module and shifts it to the tank quality tracking system for consistency of blend models throughout the blend system modules.

19.5.5.4 BLEND PLANNING AND SCHEDULING

The blending planning process in a refinery starts from a corporate planner and ends with a blend optimization engineer in a specific refinery. The planning period is approximately 3–6 months at the corporate level and 1–3 days at the specific refinery for blend executions. The planning process also breaks down the multiple product-grade market forecast (A, B, C) total for 3 months in a long-range plan, breaks down multiple grade batches (B1, B2, B3) in a medium-range plan, and further breaks down into single blend batches such as B11, B12, B13...B21, B22, B23, etc., in short-range plans.

A refinery planner makes a plan for 15-to 30-day blending batches and uses a rollover scheme as shown Figure 19.23 to move the next day's blend recipe to the current recipe. For example, 30 days is broken into a single blend's plan for the next 7 days, an aggregate blend batch plan for the next 7 days, and then an aggregate blend production plan for the next 15 days. As the blend quality and market information become more accurate from the next day's blend to the 30th day's blend, the rollover process moves the blend plan accordingly.

19.5.6 *Computer System*

A blending system computer system consists of three main components: the DCS, the advanced control system, and software/hardware interfaces with plant equipment/signals and a third-party system. This is a very challenging and time-consuming task, and their seamless integration plays a very important role in the overall success of the blending project.

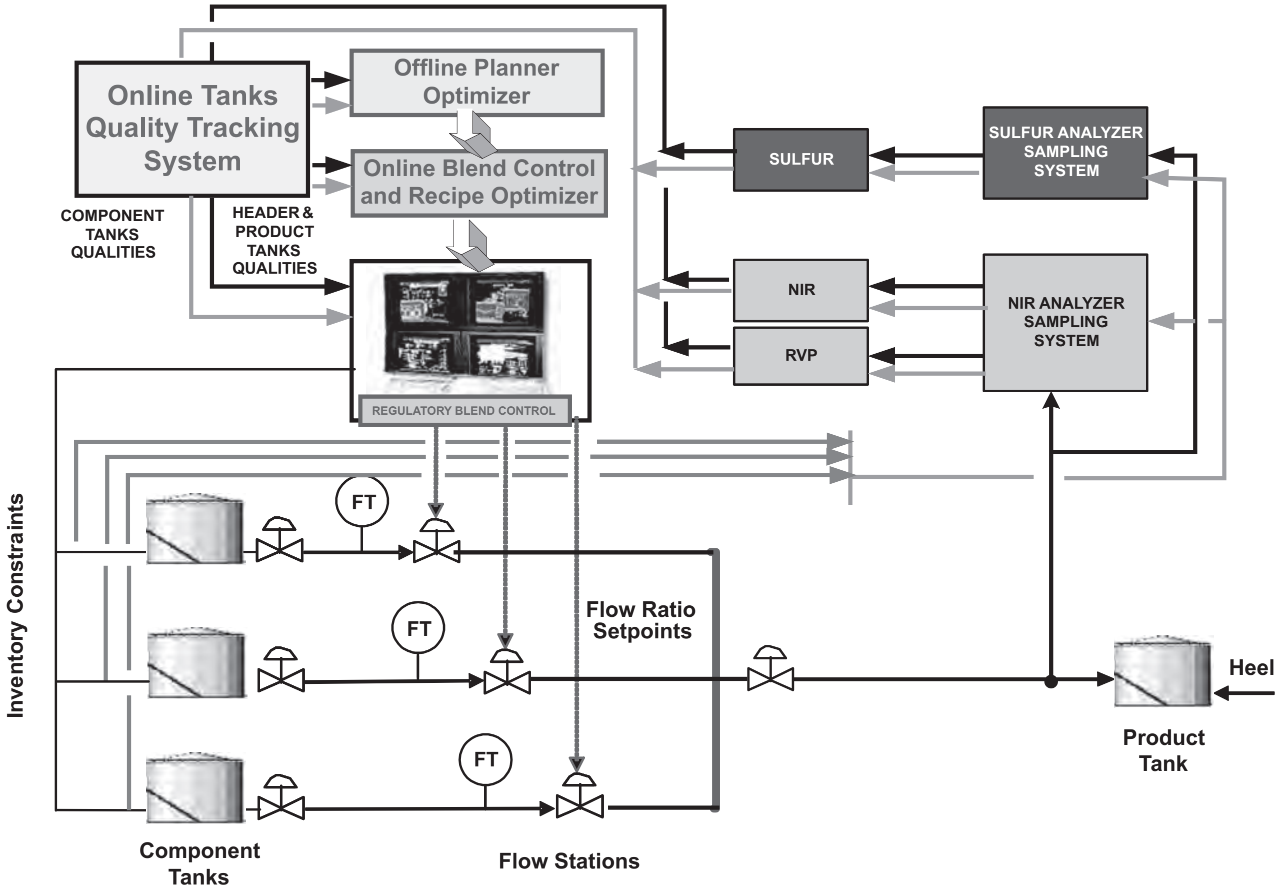


Figure 19.22—Recommended design of a blending system on the basis of recent developments. *Source:* Reproduced with permission from [1].

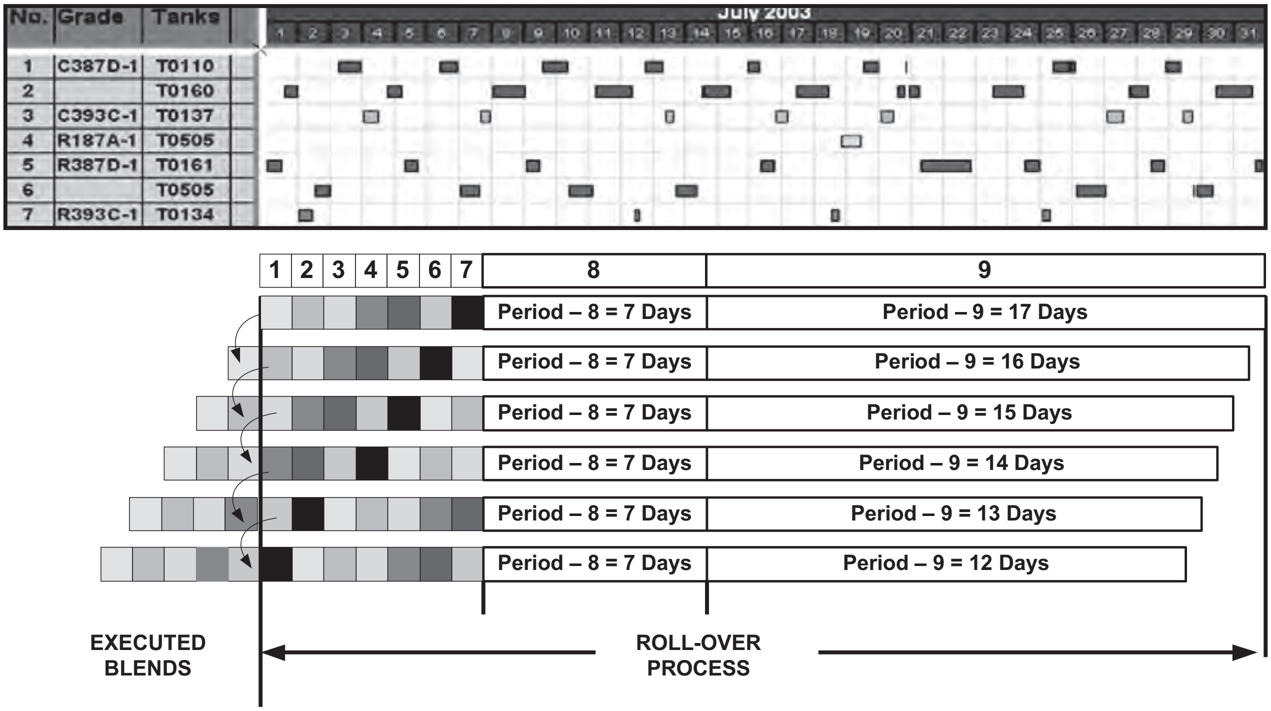


Figure 19.23—Thirty-day blend rollover planning process. *Source:* Reproduced with permission from [1].

19.5.6.1 DISTRIBUTED CONTROL SYSTEM

In earlier sections, we discussed that tier 1 blend control is resident in a DCS and absolutely required for safe operation and recipe control of inline or a sequential blending system. Although the operational philosophy of the regulator blend control is the same, their implementation varies from DCS to DCS and must be specifically designed, developed, and customized for each refinery.

19.5.6.2 ADVANCED CONTROL COMPUTER SYSTEM

A blending control system is typically implemented on high-end PCs using client-server architecture and consists of the following components in the technology set, although it may vary slightly from the system provider and DCS vendor:

- Expert system objects;
- Web link/ActiveX links;
- Oracle/SQL server database;
- Windows server and workstations;
- Integrated Fortran/C/C++ modules for specific functionality/computations;
- Nonlinear optimizer, CPLEX™, Minos™;
- Nonlinear integer scheduling algorithm;
- Integrated third-party ActiveX controls; and
- DCS/process database bridges.

Figure 19.24 shows a typical blending system client-server architecture.

19.5.6.3 INTERFACES

In addition to the DCS and advanced control system, the implementation of a blend system requires many interfaces between plant data and third-party software and databases for challenging system integration. Examples of these required interfaces are

- Process and systems interface with plant database and instruments signals;
- Offline blend optimizer interfaces;
- Tank quality tracking system interfaces;
- Online blend control interfaces;
- Offline/online blender interfaces;
- Oil movement interfaces, including a tank farm and gaging system.

19.5.7 Blend Headers

A blend header is simply a piece of pipe that is connected to all pipelines carrying the blend component streams before feeding to the product tank. The main purpose of the blender is to provide a turbulent mixing of all component streams for a homogeneous mixture. A blending system can be configured either as a single blender (gasoline, diesel, and fuel oils) or multiheaders for run-down distillate or kerosine blending. Another example of a multiheader blending header system is crude and naphtha blending.

A blending system with a single blend header is very flexible to operate and efficient to control and optimize the recipe. On the other hand, multiheader blending systems

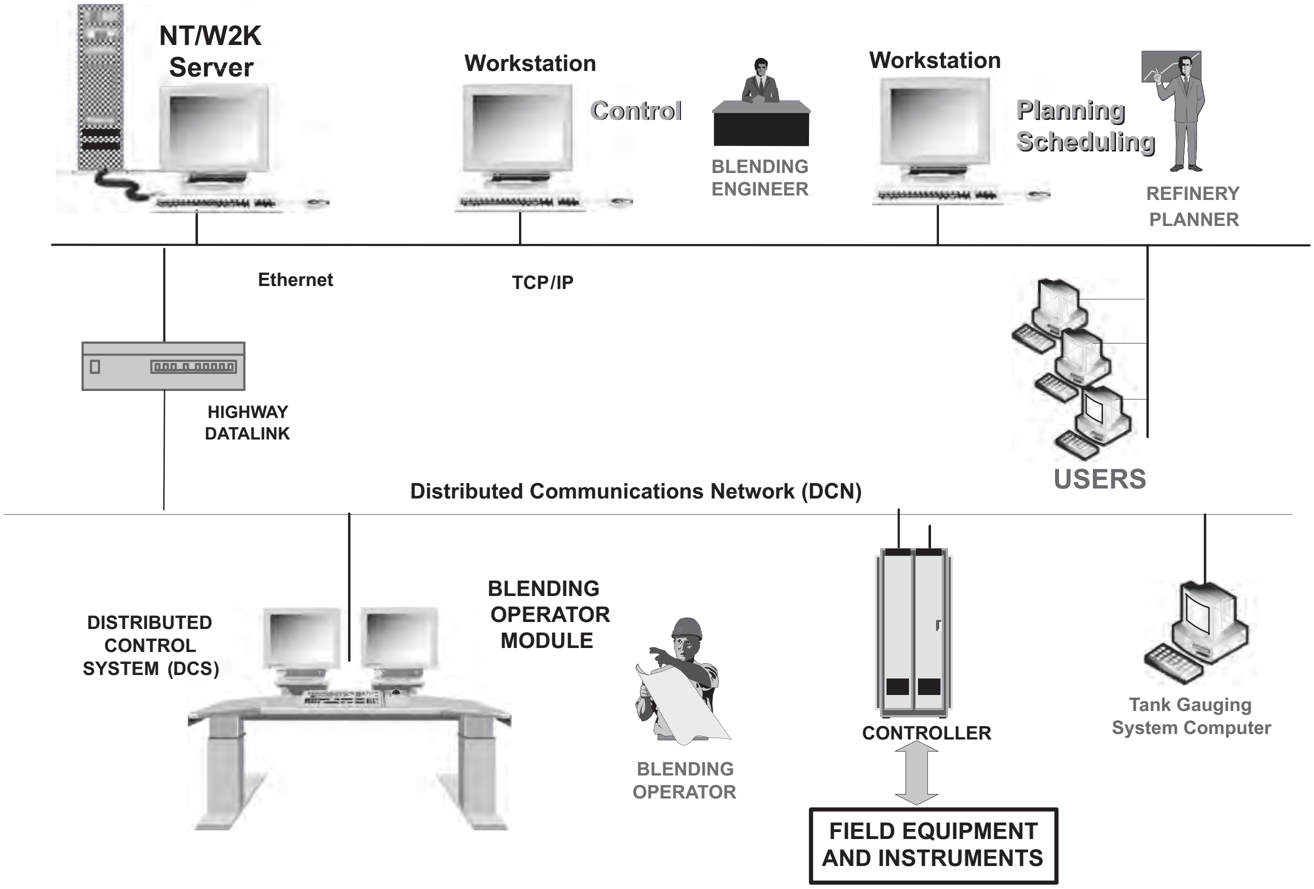


Figure 19.24—Typical system architecture for a blending system. *Source:* Reproduced with permission from [1].

are difficult to operate and less flexible to control and optimize because the recipe of multiple products simultaneously interacts with all available streams. A component recipe has process restrictions in a multiheader system and cannot drastically be changed by the online optimizer.

Design consideration for a blend header involves length, diameter, pressure, order of components connecting points, mode of connection (vertical, horizontal or both) and distance between two connection points. The discussion of this is outside of scope of this chapter.

19.5.8 End-Product Dispatch

The blend product can be blended into a product tank, tanker, ship, and bunker or directly into a pipeline. The design of a blending system is different depending on the product destination.

- Tank-to-tank blending
  - The final product tank quality can be readjusted by reblending for excessive quality giveaways or violations before dispatch to customers.
  - The online control and optimization is focused on the final blend tank, taking into account the blend header quality as measured by the online analyzers.
  - The final product tank is recirculated for 2–4 h to make it homogeneous before its dispatch.
- Tank-to-ship/pipeline/tanker/bunker blending
  - The final product tank quality cannot be readjusted but must be certified for meeting the specification. Quality giveaways must be ignored.
  - The online control and optimization is focused on the blend header quality to blend it to specification and must be certified online using NIR/NMR analyzers.

19.6 DATA RECONCILIATION

Data reconciliation is a methodology to rationalize the difference between "ideal" and "real" data by minimizing or closing the gaps between them. In this section, we will first identify all sources of error in the blending system and then discuss how to estimate those errors (or bias) for feedback corrections.

19.6.1 Sources of Error

The discussion in the previous section focused on the blend models and illustrated that the nonlinearity in the blending phenomenon can drastically affect the refinery bottom line; hence, we discussed methods to effectively handle the nonlinearity. However, the errors in the blend prediction are not limited to the nonlinearity of the blend model alone but also to additional sources of errors, as shown in Figure 19.25.

The sources of errors as identified in Figure 19.25 are defined as follows:

1. Analyzer transport lag,
2. Analyzer dead time lag,
3. Analyzer dynamic lag,
4. Analyzer measurement inaccuracy,
5. Stream and tank sampling errors,
6. Laboratory analysis repeatability and reproducibility,
7. Inaccuracy in quality correlation,
8. Inaccuracy in blending method,
9. Flow measurement, and
10. Product tank prediction bias.

19.6.2 Estimation of Biases

The next approach would be to estimate the corrections in the above sources of error, which is accomplished by defining lumped bias parameters as follows:

$$B_j = \varnothing_l + \varnothing_a + \varnothing_m + \varnothing_t \tag{19.33}$$

where:

B_j = lumped blend quality bias,
$\varnothing_l$ = laboratory analysis bias,
$\varnothing_a$ = online analyzer bias,
$\varnothing_m$ = model prediction bias, and
$\varnothing_t$ = tank quality bias.

The parameters in equation 19.33 can be estimated in a systematic order by analyzing the historical data of online analysis, the laboratory analysis of streams, and the final tank quality and model prediction. Figure 19.26 shows the

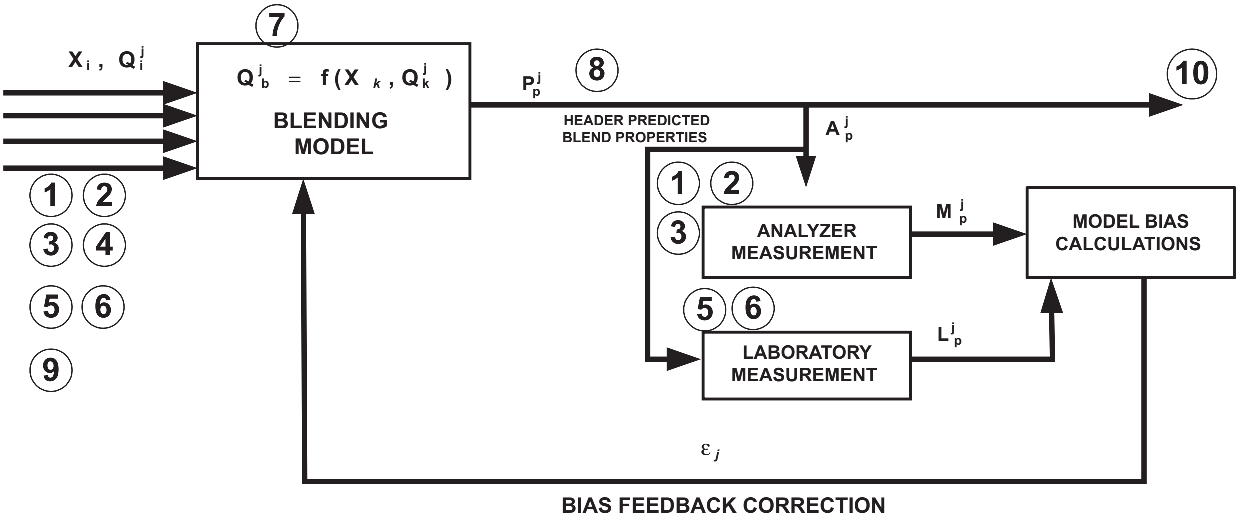


Figure 19.25—Sources of errors in a blending system. *Source:* Reproduced with permission from [1].

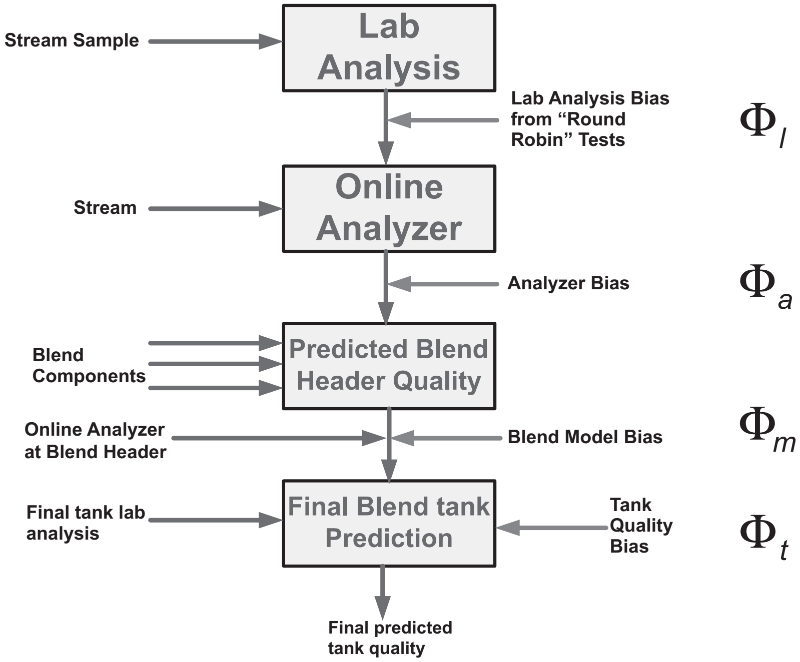


Figure 19.26—Information flow for the calculation of various blending biases. *Source:* Reproduced with permission from [1].

information flow diagram for the calculation of the above parameters.

The analyzer as shown in Figure 19.26 is estimated by comparing the measured online analyzer value with the laboratory sample analysis at the same instance. This analyzer bias along with other techniques such as using a last good value corrects the analyzer value online.

19.7 JUSTIFICATION AND IMPLEMENTATION OF A BLENDING PROJECT

In earlier sections of this chapter, we basically discussed all aspects of the blending technology. In this section we will discuss how to assess the current state of a refinery's blending system; how to perform data analysis for the economic justification; and, if justified, how to successfully implement and manage a blending upgrade or revamp blending project.

19.7.1 Economical Benefits

Let us illustrate the economical importance of blending operations in a refinery by considering the effect of the profit margin of blended fuels. We will consider only gasoline fuels here for simplicity.

Let us assume that an efficient blending operation saves \$0.01/gal of gasoline. For a 100-kbbl/day refinery, producing 50% gasoline will save

$$\begin{gathered}\$\text{Profits/year} = 100{,}000\ \text{bbl/day} \times 42\ \text{gal/bbl} \\ \times\ 0.50\ \text{gal gasoline/gal crude} \times \$0.01\text{/gal gasoline} \\ \times\ 365\ \text{days/year} = \$7.665\ \text{million (U.S.)/year}\end{gathered}$$

Savings from blending automation and optimization is typically an average of 2–3 cents/gal of gasoline. It is well documented that efficient blending operations can achieve a savings of approximately \$100,000 (U.S.)/batch of 100 kbbl. The payback period for full automation and optimized blending operations is approximately 12–18 months, maximum. On a conservative scale, benefits from the automated blending system are in the range of \$10–12 million/year. Figure 19.27 shows the source of these benefits for batch and run-down inline blending systems.

19.7.2 Where and How to Start

There is no universal answer to this question because it depends on the current state of the refinery's blending system and the approach needed to reach the final state, a fully automated blending system. There are in general four states of the refinery's blending operation status:

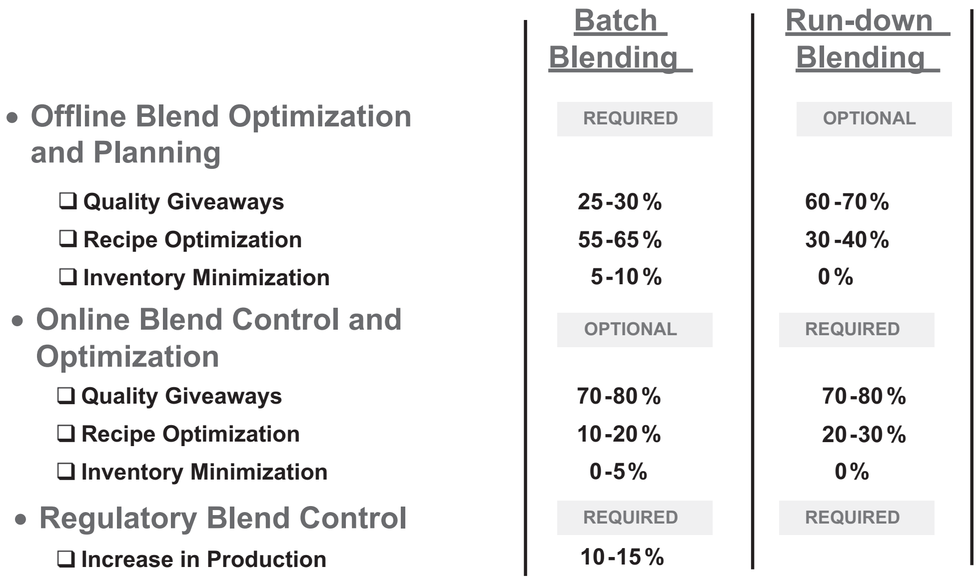
1. Negligible or few installed automation components.
2. Most field automation is installed but there is still manual blending.
3. Inline blending only and no advanced blend control.
4. Full automation but outdated offline/online advanced control.

Figure 19.28 shows the recommended paths and durations on the basis of the current state of the plant's blending operations.

19.7.3 Identifications and State of the Automation Areas

The next step in the blending project justification would be to identify and assess the state of the automation areas in the blending operations. The author of this chapter has developed a proprietary methodology to assess the state of the blending system in a refinery that is discussed briefly in this section. This methodology defines the following two indices:

1. *Automation effectiveness index:* This measures the state of field equipment, infrastructure, computer hardware and software, etc., against the ideal industry standard,



	Batch Blending	Run-down Blending
• Offline Blend Optimization and Planning	REQUIRED	OPTIONAL
❑ Quality Giveaways	25-30 %	60-70 %
❑ Recipe Optimization	55-65 %	30-40 %
❑ Inventory Minimization	5-10 %	0 %
• Online Blend Control and Optimization	OPTIONAL	REQUIRED
❑ Quality Giveaways	70-80 %	70-80 %
❑ Recipe Optimization	10-20 %	20-30 %
❑ Inventory Minimization	0-5%	0%
• Regulatory Blend Control	REQUIRED	REQUIRED
❑ Increase in Production	10-15 %	

Figure 19.27—Relative economical benefit matrix for batch and run-down inline blenders. *Source:* Reproduced with permission from [1].

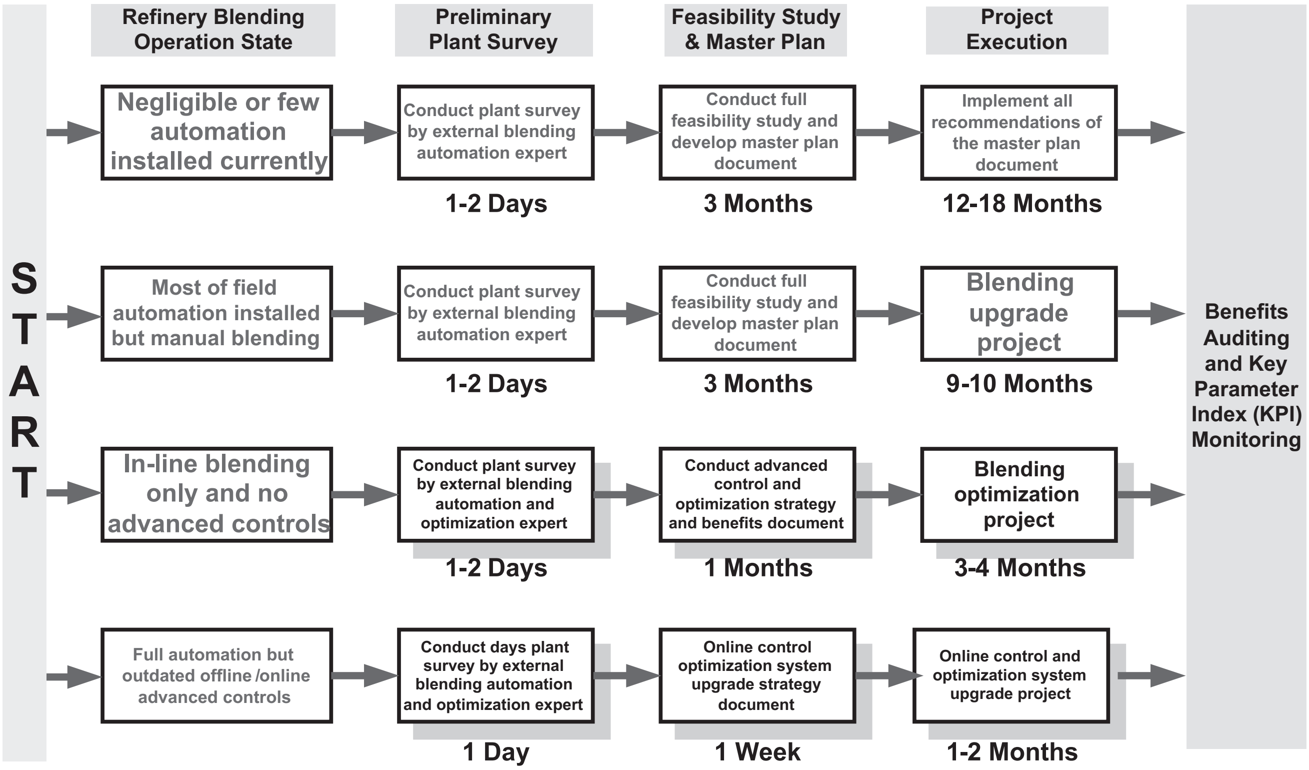


Figure 19.28—Recommended road map for an upgrade or revamp blending project. *Source:* Reproduced with permission from [1].

desirable benchmarks, or both. This index is usually generated by conducting a detailed plant survey of all automation components.

2. *Operational efficiency index:* This measures how well the blending is executed in terms of deployed blend models; extent of quality giveaways; and reblend control, optimization, and planning activities. This index is generated by a detailed analysis of 3–6 months of historical blend data to estimate various parameters to build this index.

Figure 19.29 shows a summary of these two indices for a typical refinery of 300 kbbl/day. The author of this chapter used data for an actual plant survey to analyze the data. Figure 19.29 shows that there is direct correlation within ±10% between the automation effectiveness index and the capital investment required for revamp or upgrades of the blending system. On the other hand, the operation efficiency relates the additional benefits that can be expected from the capital investment and improved operational efficiency. The ratio of required capital investment and expected benefits results in an ROI period of 18–24 months, which is average in the industry. The same methodology can be used to estimate the capital investments and tangible benefits for upgrading any state of automation of the blending system in a refinery.

19.7.4 Project Implementation Strategy

It is not very uncommon in a refinery that is considering the upgrade and revamp of the blending project to try to allocate $6–10 million for the capital investment before going ahead for the project. More often the blending project upgrade is put on hold and thus loses millions of dollars every year from the quality giveaway and reblends due to specification violations. Therefore, it is a better strategy to adapt "pay-as-you-go" implementation of blending automation components. In this respect, offline optimization is the fastest tool to implement at low cost to achieve maximal benefits in a short period.

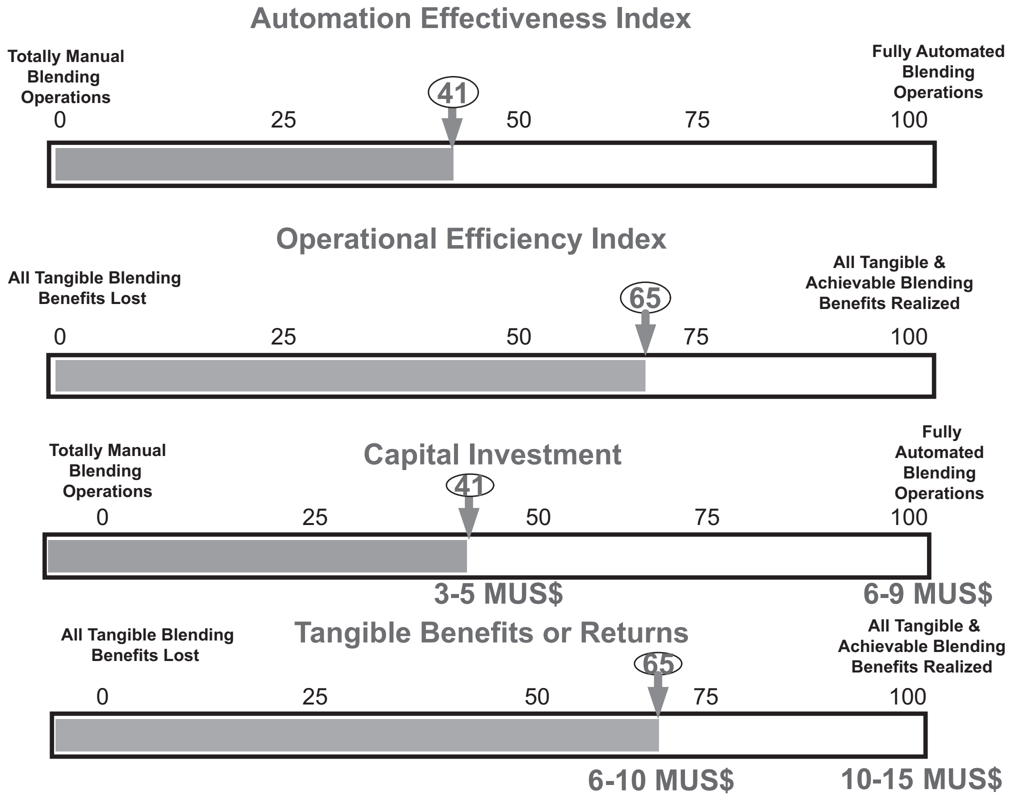
Figure 19.30 shows a typical blend project implementation schedule using the pay-as-you-go strategy and indicates ROI and cost along the project timeline.

19.8 SUMMARY

This chapter has discussed all technical and management aspects of a fuel blending system in a refinery. Because of space limitation, the focus has been mainly on the gasoline blending, but the concepts presented here can be extended and applied to other fuel blending such as diesel and fuel oils.

ACKNOWLEDGMENTS

The author thanks the management of Offsite Management Systems LLC, Sugarland, TX (www.globaloms.com), for permission to include most of the copyrighted figures and technology from their training manual—*Strategic Fuel Blending Technology and Management*.



Basis: 300 KB/Day Refinery, Figures shown are representative and not actual for a refinery

Figure 19.29—Correlations between effectiveness/efficiency indices. *Source:* Reproduced with permission from [1].

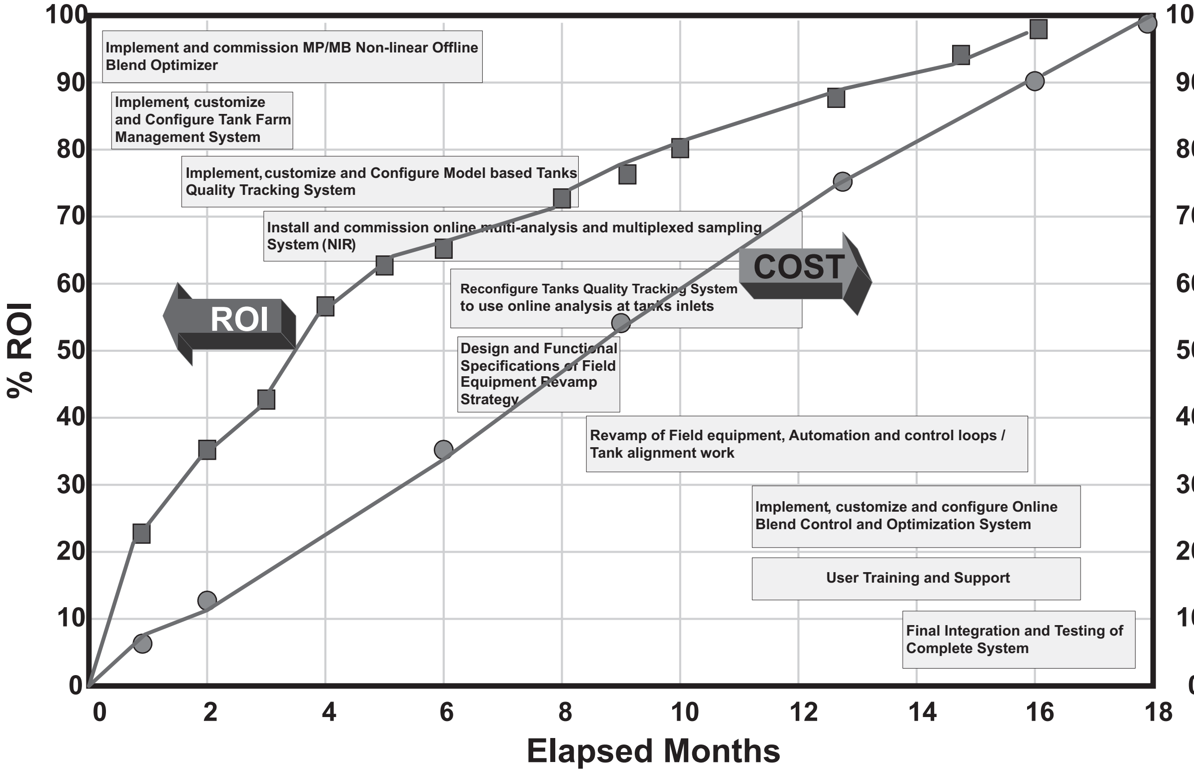


Figure 19.30—ROI versus implementation for a blending project. *Source:* Reproduced with permission from [1].

REFERENCES

[1] Offsite Management Systems, LLC (OMSLLC), "Strategic Fuels Blending Technology and Management-Training Manual," reproduced with permission from Offsite Management Systems, LLC, Sugar Land, Texas, USA, 2009.

[2] Ethyl Corporation, "The Ethyl Technique of Octane Prediction," report no. RTM-400b, 1981.

[3] Lambert, D., "Computation of Blending Indices," PTQ, Q4, 2007, p. 135.

[4] Naughton, M.J., and Agrawal, S.S., "Advanced Gasoline Blending-II," *Oil & Gas J.,* 103(7), 2007, p. 50.

[5] Agrawal, S.S., and Naughton, M.J., "Advanced Gasoline Blending-I," *Oil & Gas J.,* 103(7), 2007, p. 52.

[6] Agrawal, S.S., Leong K.M., Wee L.H., and ECT James CTJ, "Implementation and Benefits of Online Tanks Quality Tracking System in a Singapore Refinery," *Hydrocarbon Asia,* 15(1), 2005, p. 36.

[7] Agrawal, S.S., "Advances in Tank Quality Measurements Can Help Cut Operational Costs," *Hydrocarbon Processing,* 86(6), 2007, p. 67.

[8] Agrawal, S.S., "Model Based Online Analysis and Monitoring of Tank Qualities," Paper presented at AICHE Spring National meeting, Houston, April 24, 2007.

20

Tank Farm Management

Suresh S. Agrawal[1]

20.1 INTRODUCTION

Any liquid-based manufacturing facility, such as a refinery, petrochemical complex, beverage plant, etc., uses various types and sizes of tanks to receive, store, and dispatch products. A cluster of such tanks is called a “tank farm” and consists of 50 to 300 or more tanks in a refinery with, for example, 100,000–600,000 bbl/day of crude oil processing capacity. The efficiency and timely available information about the quality and contents of tanks can affect the operations and profitability of the plant. This chapter will discuss various aspects of tank farm management from its initial design methodologies to information management technology and will limit the discussion to a crude oil refinery. Nevertheless, most of the discussion in this chapter can also be applied to other relevant liquid-based plants.

20.2 OVERVIEW

20.2.1 Purpose and Role

The purpose of a tank farm is to receive crude and other feed stocks from external sources; store the intermediate products from onsite unit operations; and store the final products before dispatch to customers by terminals, marine, truck, railcar, and pipelines. This section will discuss various types of tanks installed in a plant for storage of feed and products.

20.2.2 Types of Tanks

There are three types of tanks used in a liquid-based plant: cylindrical tanks, spherical tanks, and bullet tanks (vertical or horizontal).

20.2.2.1 CYLINDRICAL TANKS

These tanks are the most common types and are used to store crude and products at atmospheric pressure. Their roof shapes can be cone or dome shaped, and the roof type can be fixed to internal or external floating roofs.

20.2.2.1.1 Fixed Roof Cylindrical Tank

The top of the cylindrical tank is fixed and it may be flat, cone, or dome shaped. It is suitable for smaller size and low-pressure applications. They are expensive to build because they require a thick top plate to resist deformation and visible bending. Fugitive emission is the problem for this type of tank because of the vapor gap between the liquid and the top plate.

The fixed roof can be cone or dome shaped. The cone-shaped tank is easier to fabricate than the flat type of roof and is less susceptible to spot deformation and bending. It is used for large storage capacities.

Dome-shaped tanks are built to minimize the effects of strong winds and they equalize the wind pressure better than flat- or cone-shaped tanks. Figures 20.1 and 20.2 show typical cone-shaped and dome-shaped fixed roof cylindrical tanks, respectively.

20.2.2.1.2 Floating Roof Cylindrical Tank

In this tank type, the top plate is not fixed and floats 8–12 in. above liquid separated by rim seals. It minimizes the fugitive emission because of the low vapor gap between the liquid and the top plate. This type of tank is further classified as an external floating roof tank or an internal floating roof tank.

The internal floating roof is similar to an external floating roof, but the top is covered with a cone or dome shape and there is an internal floating roof. It is again suitable for liquids with higher vapor pressure. The internal floating roof minimizes the leaks and fugitive emissions. Figures 20.3 and 20.4 show examples of internal and external floating roof types of tanks, respectively.

20.2.2.2 SPHERICAL AND BULLET TANKS

These tanks are used to store higher-pressure liquids and equalize pressure on the structure. Spherical tanks are built onsite and hence are expensive to build. They are built for large capacities. On other hand, bullet tanks are low-pressure tanks and are built in shop; hence they are less expensive than spherical tanks. They are meant for small-capacity storage and may be vertical or horizontal design. Figure 20.5 shows spherical and bullet tanks.

20.2.3 Tank Types versus Product Types

Table 20.1 lists the types of tank used in a typical refinery to store its crude feed and products.

20.3 DESIGN OF TANK FARM

A typical refinery or liquid-based plant uses the tanks for feed receipts, intermediate products, and dispatch of final products. Although plants are designed and built with adequate storage capacity for design and future production, there are still the following situations in which there are serious economic effects on the refinery bottom–line:

- Crude oil is stocked up in excessive inventory;
- Shipment is delayed because of insufficient products, product storage capacity, or both; and
- Process units are operating at less than optimal capacity.

Figure 20.6 shows several stages of storage requirement for a typical refinery.

There are methods to estimate the storage requirement either at the front-end engineering design (FEED) level or

---

[1] Offsite Management Systems, LLC, Sugar Land, Texas, USA

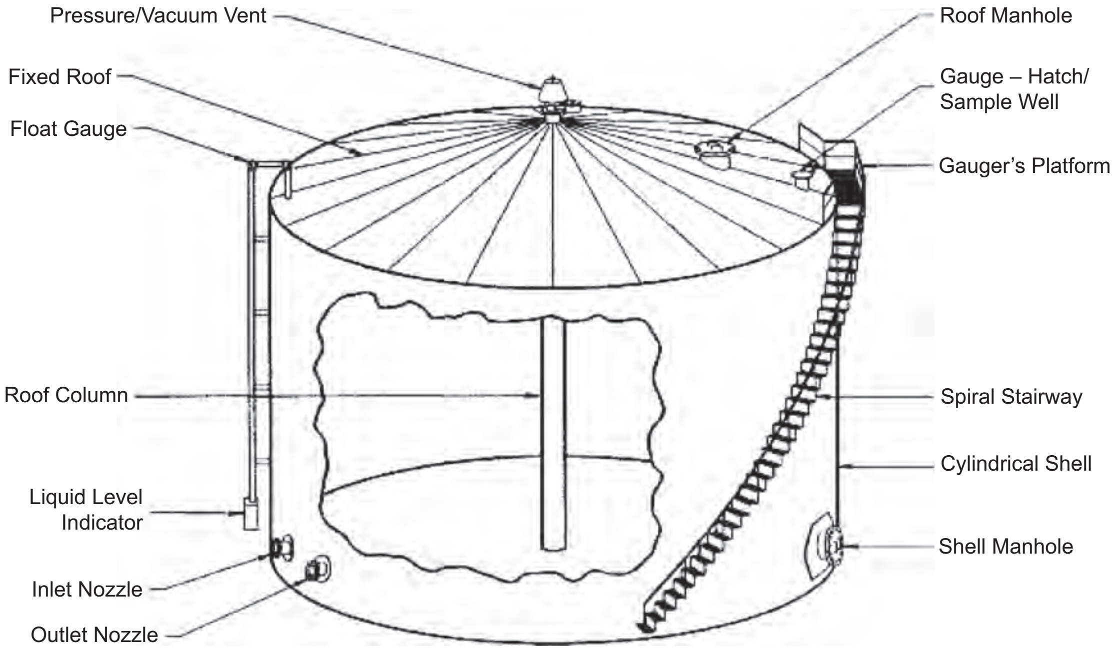


Figure 20.1—Cone-shaped fixed cylindrical tank.

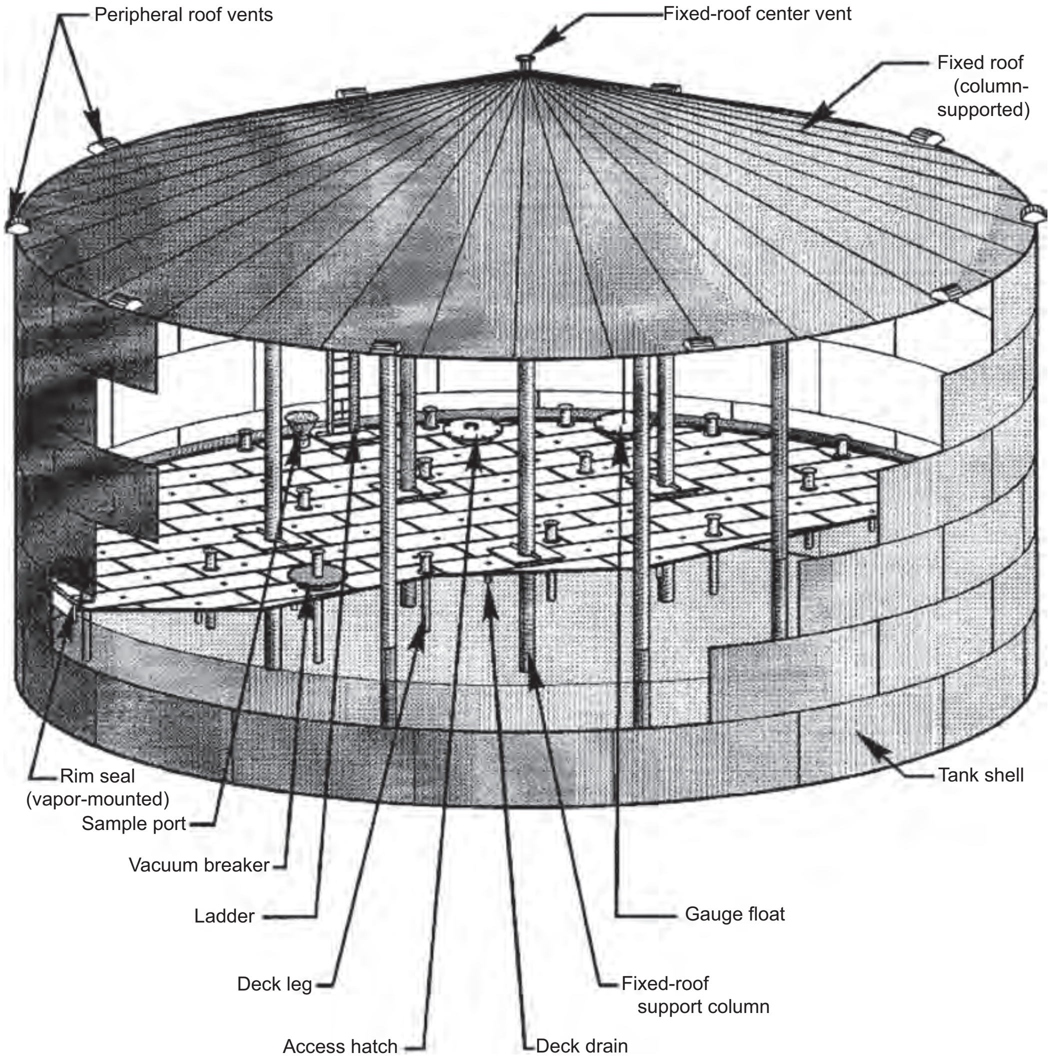


Figure 20.2—Dome-shaped fixed cylindrical tank.

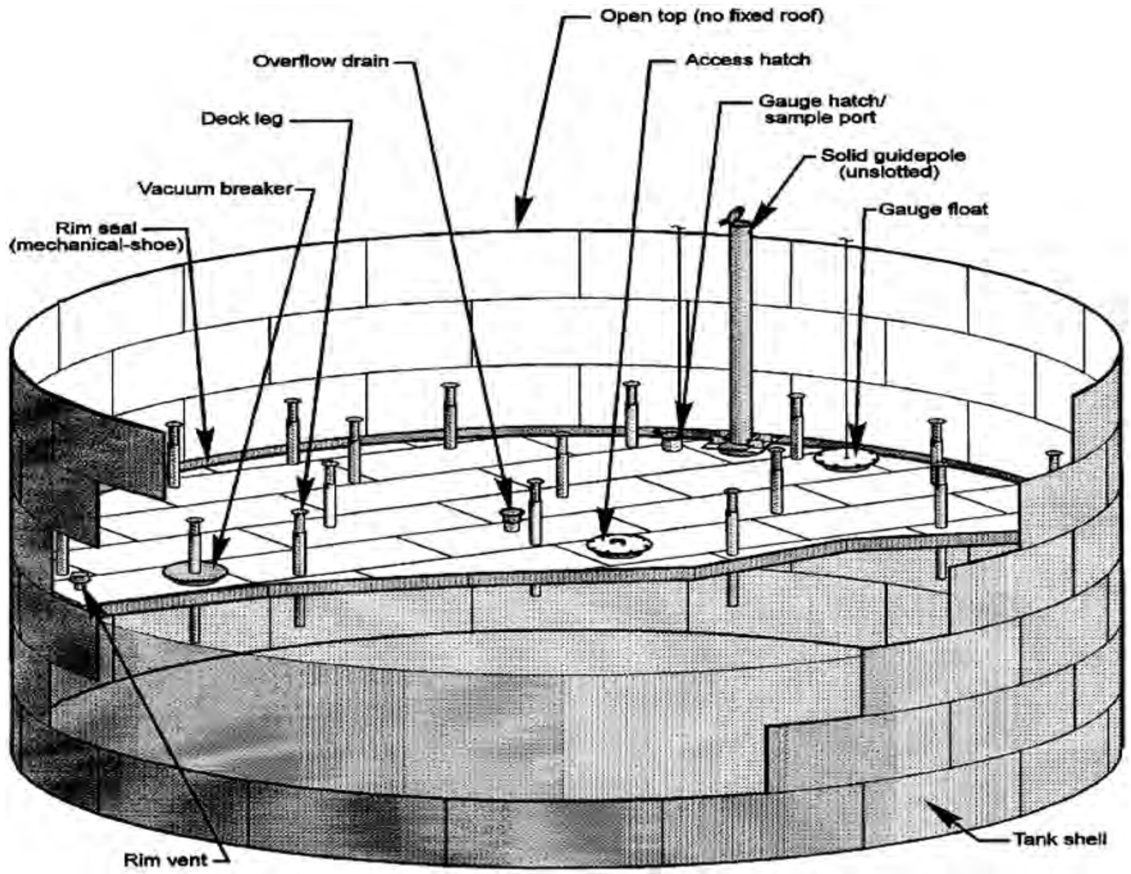


Figure 20.3—External floating roof tank.

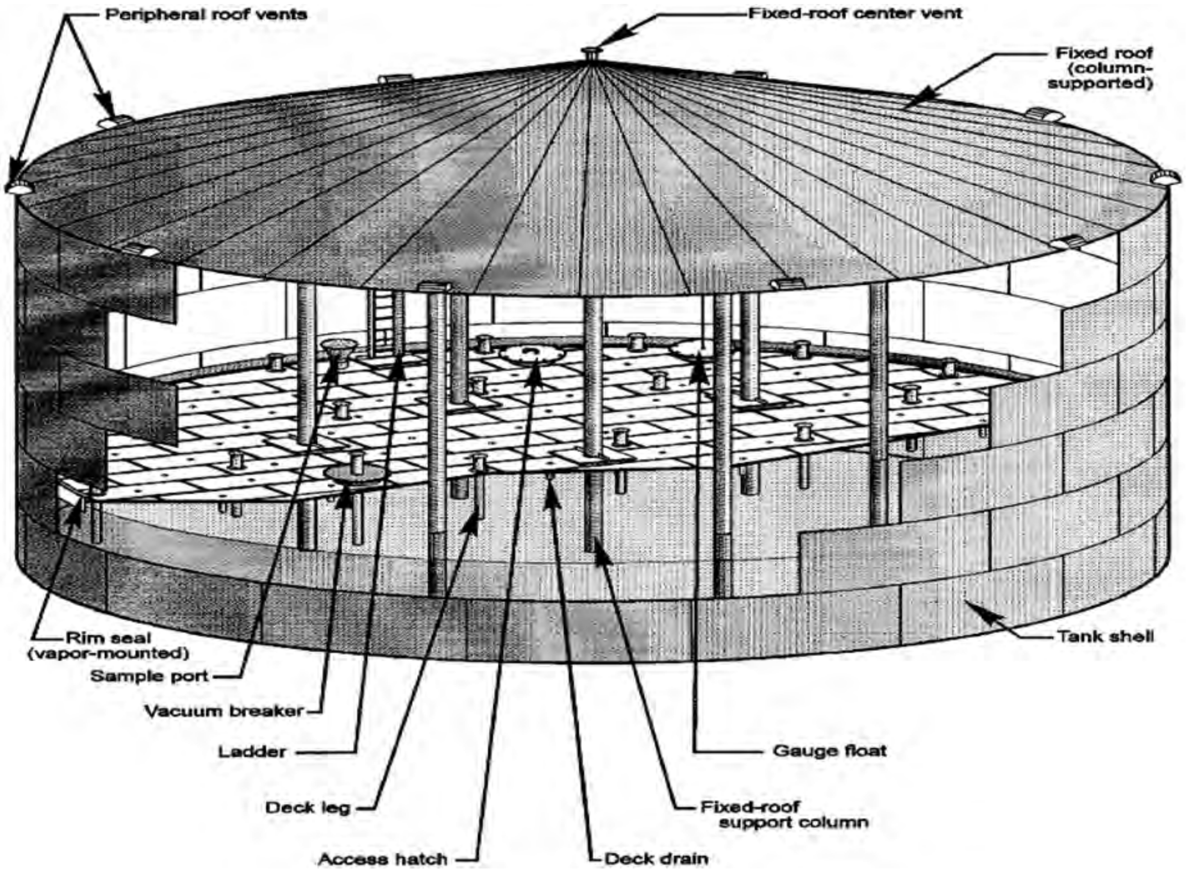


Figure 20.4—Internal floating roof tank.

Figure 20.5—Spherical and horizontal bullet tanks. *Source:* [1].

for expansion purposes after the plant is already operating. These methods are discussed in the following sections.

20.3.1 Empirical Correlations

Nelson proposed an empirical formula for the estimation of tank farm size on the basis of refinery complexity as follows [2]:

$$S = 1.75 \times P + 10 \tag{20.1}$$

TABLE 20.1—Types of Tank Used for Different Refinery Products	
Tank Type	**Product Type**
Floating roof cylindrical tanks	Crude oil, gasoline, naphtha
Fixed roof cylindrical tank	Diesel, kerosene, FCC feedstock, residual fuel oil
Spherical tank	Normal butane, propane, propylene
Bullet tank	Isobutene, normal butane

where:

S = barrel of product storage per daily barrel of crude oil processing capacity and

P = number of products produced by the plant (P = 8 for a simple plant and P = 36 for a complex plant).

Nelson later proposed an empirical formula for the estimation of tank farm size on the basis of historical data as follows [3]:

$$S = C + 4.5 \times P + 11 \tag{20.2}$$

where:

C = barrel of crude storage per day of crude oil processing capacity (C = 4 for refineries with crude supplied by pipeline and C = 55 for refineries receiving crude via tankers).

Gary and Handwerk presented a "rule of thumb" for the estimation of storage requirement [4]. They presented that 50 bbl of storage are required per barrels per day of crude oil processed. They estimated this for a typical refinery that receives and dispatches the crude and products by pipelines. However, this estimate may be off for refineries receiving the crude by tankers. They also presented that

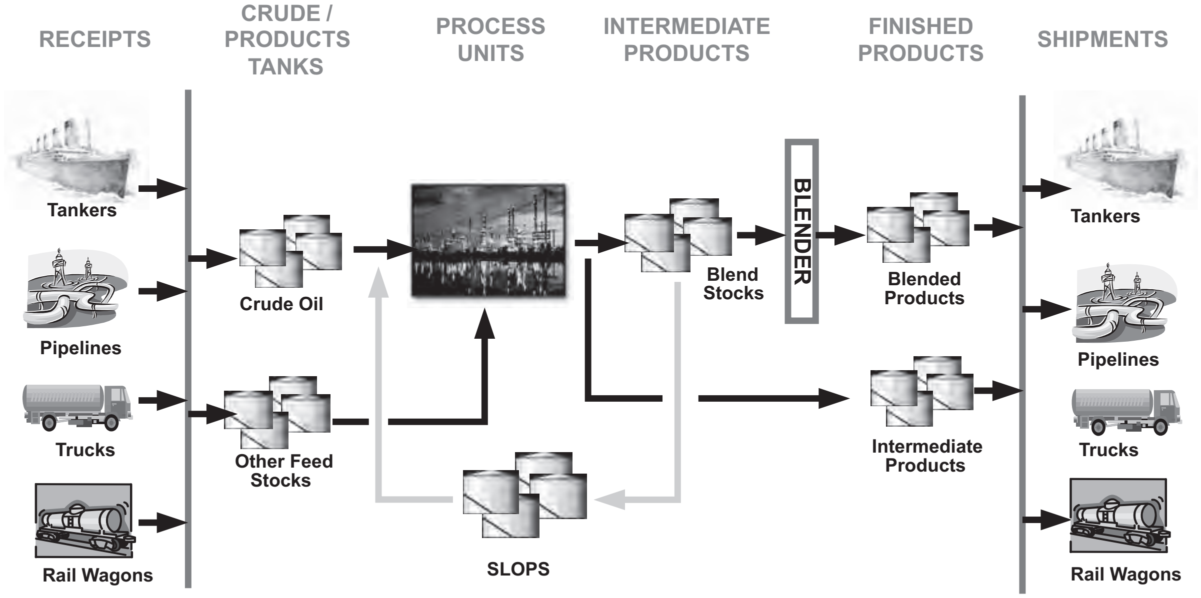


Figure 20.6—Several stages of storage for a typical refinery. *Source:* [1].

TABLE 20.2—Tank Farm Storage for a Typical Refinery

Number	Area Name	Total Number of Tanks	Total Tank Capacities (bbl)	Average Tank Capacity (kbbl)	Production Factor	Daily Production (kbbl/day)	Days of Storage
1	Aromatics	13	173,171	13	0.10	22	8
2	Ballasts and slop	7	235,547	34	0.01	2	105
3	Butane + propane	7	234,591	34	0.04	9	26
4	Crude oil	9	4,917,680	546	1.00	225	22
5	Fuel oils	16	3,164,851	198	0.04	9	352
6	Gasoil	19	1,380,404	73	0.42	95	15
7	Gasoline	30	2,330,849	78	0.21	47	49
8	Kerosine	5	460,313	92	0.10	23	20
9	Naphtha	2	81,598	41	0.02	5	18
10	Process units	6	4,831	1	0.03	7	1
11	Propylene	3	35,217	12	0.03	7	5
12	Truck terminal	24	133,180	6	0.77	173	1
	Total	**141**	**13,152,230**	**93**	**1.00**		

storage capacities should be approximately 13 days for crude storage and approximately 25 days for product storage.

Table 20.2 shows the data for a typical refinery with 225,000 bbl/day of crude processing capacity. This refinery receives most of the crude by tankers ($C = 55$) and is fairly complex ($P = 36$).

Table 20.3 compares the estimates of daily storage requirements by the above three methods and compares them with a typical refinery as shown in Table 20.2.

20.3.2 Statistical/Simulation Methods

Barsamian and Whitehead used historical data and a statistical model to estimate the refinery tankage for a Taiwan grassroots refinery [5]. Their model considered the following factors:

- Crude delivery and product shipment methods;
- Degree of refining complexity;
- Seasonal demands to create buffer storage;
- Plant turnarounds, shutdowns, and scheduled maintenance;
- Blocked operations using multiple feedstocks;
- Availability of inline blending;
- Optimal levels of tank inventory to respond to market demands; and
- Rental of tank storage if available off premises.

The model also inputs uncertainties such as ship delays, lifting schedules, natural disasters, power failures, and unit-stream factor, etc. Their model used Excel and its built-in random number generator to perform Monte Carlo simulation and optimized the tankage estimates using Excel's built-in linear programming solver. Barsamian and Whitehead reported a 20 % savings with 95 % confidence, resulting in a total savings of $58 million in capital investment for the Taiwan refinery [5].

Al-Otaib and Stewart used more elaborate simulation and linear programming techniques to determine the adequacy of existing tank farms at all three Kuwait refineries through 2010 and developed a solution to the refineries' tank farm needs for the refinery networks [6]. Because this work involved three refineries together in simulation as opposed to the single refinery simulation by Barsamian and Whitehead, it involved a non-Excel-based system and linear-programming-based multiperiod and multirefinery planning tools. This model also used Monte Carlo statistical methods to simulate the uncertainties similar to those used by Barsamian and Whitehead [5]. This study just focused on optimization tank farm usage by reallocating tankage and changes in operations to minimize the usage of tank capacities. The simulation predicted an overall savings of approximately $2.5 million by the following changes in the operations:

- Reallocate existing tankage,
- Inline finished product blending,
- Inter-refinery transfers (IRT) of finished products, and
- Eliminate dual-port product loading.

TABLE 20.3—Comparison of Tank Farm Storage Capacity

Method	Basis	Estimated Daily Storage/Crude Processing, No. of Days
Nelson (1959)	Based on only refinery complexity	73
Nelson (1973)	Based on refinery complexity and mode of crude receipts	69
Gary et al. (1994)	Rule of thumb	50
Actual refinery storage	Existing refinery storage Table 20.2	58

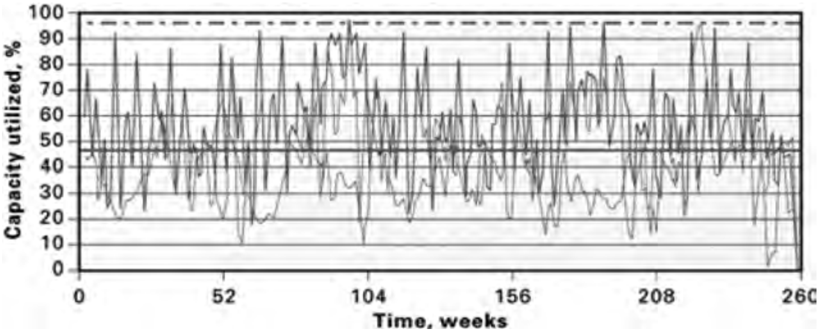


Figure 20.7—Tank capacity utilization before optimization.

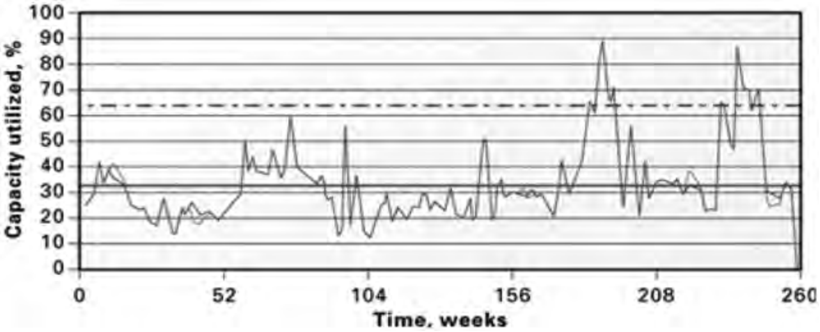


Figure 20.8—Tank capacity utilization after optimization.

Figures 20.7 and 20.8 show the tank capacity utilization before and after model optimization and clearly demonstrate that the simulation techniques used by Al-Otaib and Stewart for three Kuwait refineries were a success. They reported a payback period of 2 years [6].

20.4 REQUIRED TANK INFORMATION AND METHODS

The management of a tank farm requires that the following information be available to various departments/personnel in an online/offline manner to manage the plant efficiently, safely, and economically:

- Tank inventory,
- Tank qualities, and
- Estimate of fugitive emission.

The following sections will discuss the methodologies and technology for each these methods.

20.4.1 Tank Inventory

It is extremely important that the inventory of a tank in the tank farm be available in near real time for inventory control/management, to avoid spills during loading, and to safely operate the plant. This requires the measurement of the following five tank process parameters:

1. Level (mandatory),
2. Pressure (mandatory for high-pressured tanks),
3. Temperature (mandatory for custody transfer and for heated tanks),
4. Density (mandatory for mass-based custody transfer), and
5. Water level (optional but recommended for crude and fuel tanks).

These parameters are measured manually or by an automatic tank gauging (ATG) system as shown in Table 20.4.

These methods are discussed in the following subsections.

TABLE 20.4—Methods and Purpose of Tank Process Variables

Process Variable	Method(s) of Measurement	Purpose of Measurement
Level	Manual, ATG	• Issue alarms to avoid spills • Inventory calculations
Temperature	Manual, ATG	• Fugitive emission control and calculations • Temperature compensation in inventory calculations
Density	Laboratory, ATG, mass flow meters	• Mass-based inventory calculations
Pressure	ATG or none	• Fugitive emission control and calculations • Safety for pressurized tanks
Water level	ATG or none	• Limit water content and purge excessive water because it is detrimental to process units

20.4.1.1 MANUAL MEASUREMENTS OF TANK PARAMETERS

Although manual measurements of tank parameters are almost nonexistent for more than 50-kbbl/day-capacity refineries, they are still in practice for smaller refineries. In this method, two people climb up a tank at least 2 times a day and measure the level by using a calibrated gage tape and visual observation. They would then enter this information in the tank information system (TIS). This method of level measurement not only poses safety concerns but also illustrates that an inaccurate level measurement of ±6 mm multiplied by all tanks will considerably deviate the actual inventory estimate from such measurement.

20.4.1.2 AUTOMATIC MEASUREMENTS OF TANK PARAMETERS

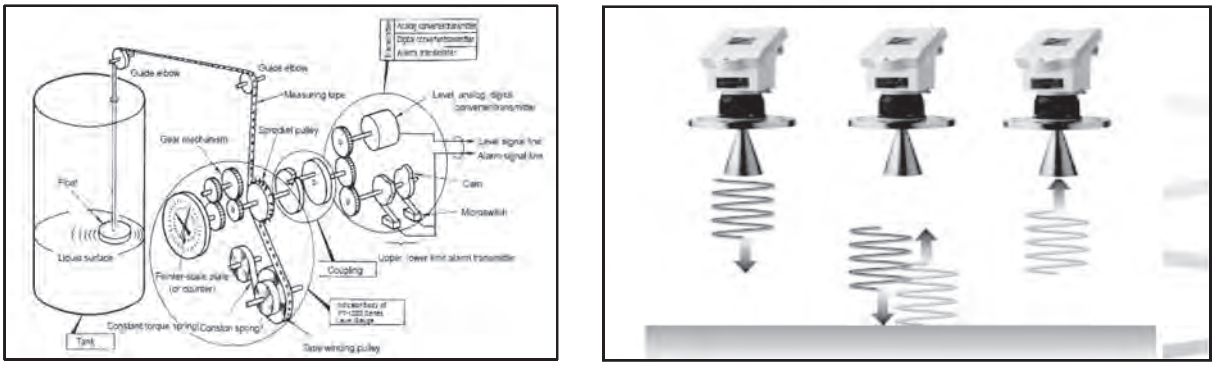
20.4.1.2.1 Hybrid Gauging System

A hybrid tank gauging system uses different instrument and technology for the measurement of tank parameters, namely level, temperature, density, pressure, and water level. We will briefly discuss only a few of the methods for the measurement of each of the process parameters because there are too many to enumerate in this chapter.

20.4.1.2.1.1 Tank Level Measurement There are two categories of methods for the measurement of tank level: the direct method and the inferential method. The direct method directly measures the liquid height compared with a datum reference line. On the other hand, the indirect method measures effects caused by the changing liquid position. We have listed some of the most common techniques used in the industry for direct and inferential (indirect) methods.

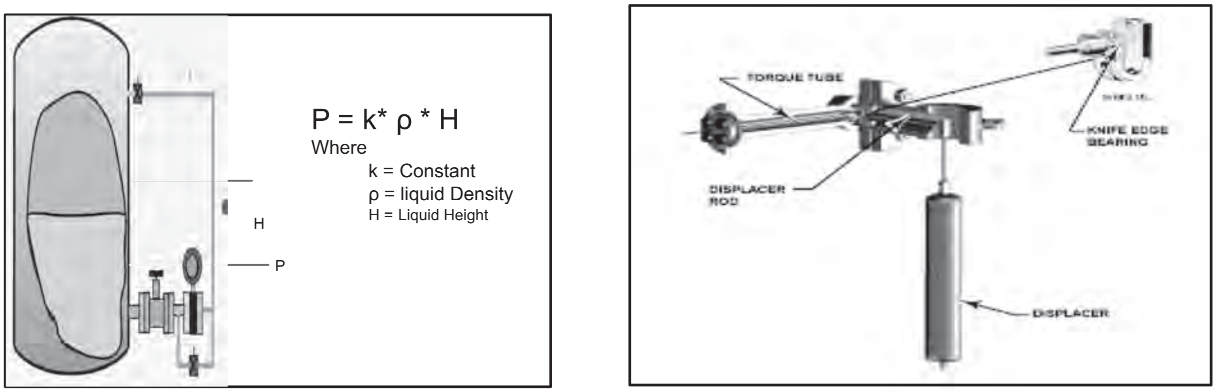
- Direct method techniques:
  - Direct visual observation on a calibrated scale (e.g., gage stick, hook gage, or gage glass);
  - Direct position of a float on the liquid surface;
  - Contact of electrode probe with liquid surface;
  - Interruption of light beam to photoelectric cell; and
  - Reflection of radio, radar frequency, or sonic waves from a liquid surface.
- Indirect or inferential method techniques:
  - Measurement of hydrostatic pressure,
  - Measurement of buoyant forces exerted by partially immersed object,
  - Thermal determination between liquid and vapor phases,
  - Based on physical or electrical properties of liquid to infer surface position, and
  - Attenuation of radiation through liquid and vapor phases.

Next, we will discuss the pros and cons for two of the most common techniques for each of the methods: the float type gage and the reflection of waves from the liquid surface for the direct method and measurements of hydrostatic pressure and buoyancy forces by a partially immersed object for the indirect method. Figure 20.9 shows the schematic diagrams of these two methods by direct and indirect methods, and Table 20.5 compares the pros and cons of the same.



Direct Method-Float Type gauge

Direct Method – Wave Refection from liquid Surface



Indirect Method – Measurement of hydrostatic pressure

Indirect Method – Measurement of Buoyancy force

Figure 20.9—Direct and indirect methods of level measurements. *Source:* [1].

TABLE 20.5—Summary of Pros and Cons of Direct and Indirect Methods of Level Measurement

		Advantages	Disadvantages
Direct method	**Float type gage**	• Can be used for unlimited tank height • Excellent accuracy of 4–5 mm • Comparatively low cost • Can be used for low- to medium-pressured tanks	• Intrusive sensors • Mechanical devices are subject to wear, corrosion, failure, and "getting stuck" • Subject to material buildup causing loss of accuracy
	Wave reflection from liquid surface	• High accuracy of 0.5–1 mm • No moving parts, nonintrusive components • Low maintenance, operational, and ownership cost; high mean time between failures (MTBF) of >60 years • Modular design to install in operation	• Can be applied for still liquid and not turbulent liquids • Higher cost compared with other technologies • Cannot measure interface • Effective for liquid and slurries but requires caution for granular material
Indirect or inferential method	**Measurement of hydrostatic pressure**	• Simple and familiar technology • Reliable method to measure level, density, mass, and volume • Can be calibrated from pressure standard • Reasonable cost • Typical accuracy is ±0.03 %	• Must be corrected for density • Susceptible to fugitive emission • Requires additional valves and pipes • Useful only for clear liquid applications • Not practical for slurries
	Measurement of buoyant forces by partially immersed object	• Limited motion and few moving parts • Proven for difficult hydrocarbon applications • Can be used for high temperature and pressure • Can measure interfaces	• Calibration is density-dependent • High cost with long spans • Awkward to install and requires careful and constant maintenance • Buildup on displacer can affect accuracy

20.4.1.2.1.2 Temperature Measurement The temperature in a tank can be measured either at one point for a well-mixed tank or at multiple points for a stratified tank. In the case of the latter, tank temperature is typically measured at 16 or so points using multiresistor thermometers and then averaged over all of those points to calculate an average tank temperature.

20.4.1.2.1.3 Density Measurement The measurement of density is measured by the hydrostatic (HTG) method to measure pressures at two points and then infers the average liquid density from their values using equation 20.3:

$$P_2 - P_1 = k \times \rho \times H \tag{20.3}$$

where:
P = pressure at point 1 and 2,
k = constant,
ρ = density, and
H = distance between points 1 and 2.

It is assumed that the liquid density is the same between points 1 and 2 and it may not be valid for a stratified tank.

20.4.1.2.1.4 Pressure Measurement The tank pressure is also measured traditionally by a hydrostatic method using pressure transmitters at a lower point above the water and sediment level.

20.4.1.2.2 Multifunction Gauging System

A multifunction gage uses a single instrument to measure all required parameters such as level, multiprofile temperatures and density, pressures, water levels, and tank empty space vapor pressure without the use of multiple instruments for each measurement. It consists of 4–12 measurement modules installed on a single steel pipe installed through only one tank opening.

A multifunction gage is a single instrument to provide all necessary data to calculate volume by either the hybrid method (level, temperature, density, and water) or the hydrostatic method (mass, density, and water) in real time directly from the gage. Its transmitter can support over 1,000 strapping points and can provide diagnostic measurements, raw measured data, or calculated data. It is the perfect gage for use with distributed control system (DCS), supervisory control and data acquisition (SCADA), and HMI software [1]. A multifunction tank gage has the following features:

- It provides the most accurate volume measurement for custody transfer, inventory, or loss control on the market by a tank gage.
- It provides real-time volume by hybrid or hydrostatic methods (all product variables are measured from one instrument, one tank opening, one electrical connection, etc.).
- It provides real-time profiling of product within a liquid storage tank (water, density, and temperature stratification). It does not require additional instruments, tank entries, electrical connections, etc.

- It determines the product quality (i.e., specific gravity, free water, and entrained water content in product).
- It provides vapor pressure and vapor temperature for hydrocarbon emissions reporting, gas blanketing regulation, or alarm indication of a stuck pressure relief vent.
- It is certified for leak detection (mass sensitivity).
- It provides volume calculations using measured variables for multistrata density (not reference/average density), free and entrained water (not just free water), actual vapor pressure and temperature, actual atmospheric pressure and temperature, actual mass, etc.
- It has no moving parts.
- It is self-diagnostic and self-calibrating.
- It is bottom referenced (standard). No reference point error as with roof-mounted level technologies.
- It installs in service with or without a gage well.
- When installed within the gage well, it provides a direct comparison of the ATG with the metrology reference point (i.e., the manual hand line and samples at the same physical location on the tank for level, temperature, density, and water. Thus, reducing measurement errors caused by multiple data locations from other hybrid-level gages.
- It has the lowest cost of ownership among inventory tank gauging technologies and the most benefits.

20.4.1.3 INVENTORY CALCULATIONS

20.4.1.3.1 Methodology

In this section, we will discuss and enumerate the steps to calculate tank inventory, our ultimate goal, in a step-by-step procedure. However, to understand the various terms that will be used in this section, let us examine a tank and its physical characteristics as shown in Figure 20.10.

The tank inventory calculations require tank parameters (height, diameter, and unusable volume), characteristics data (strapping table), and dynamic process parameters (level, temperature, density, pressure, water level). This process is shown in Figure 20.11.

The following steps are required, either manually or via software, to calculate tank inventory and other information needed for the real-time management of tank farm.

- *Step 1—Calculation of raw volume from liquid level measurement:* There are three methods available to convert liquid level to tank raw volume (i.e., without any temperature adjustment):
  - *Strapping table:* This is a table of tank volume versus tank level at very small intervals provided by the tank manufacturer in the form of a printed tabular format. It is useful for a deformed and aged tank and is also necessary for noncylindrical tanks because tank geometry is not uniform with respect to height. Because this table is very long, it is very resource-consuming for programming in a tank information automation system. This is especially true if the plant has old tanks and the tank tables were only provided on papers and not in electronic format.
  - *Strapping factor:* This can be calculated very easily to use as rough estimate of volume at a certain level using a simple calculator. It is accurate for cylindrical tanks and is easier to program. It is useful for calculating flow rates in and out of the tank on the basis of level changes and to estimate time for emptying and filling.
  - *Mathematical formulas:* This method uses the mathematical equations to calculate for a given tank geometry, but it cannot be used very easily

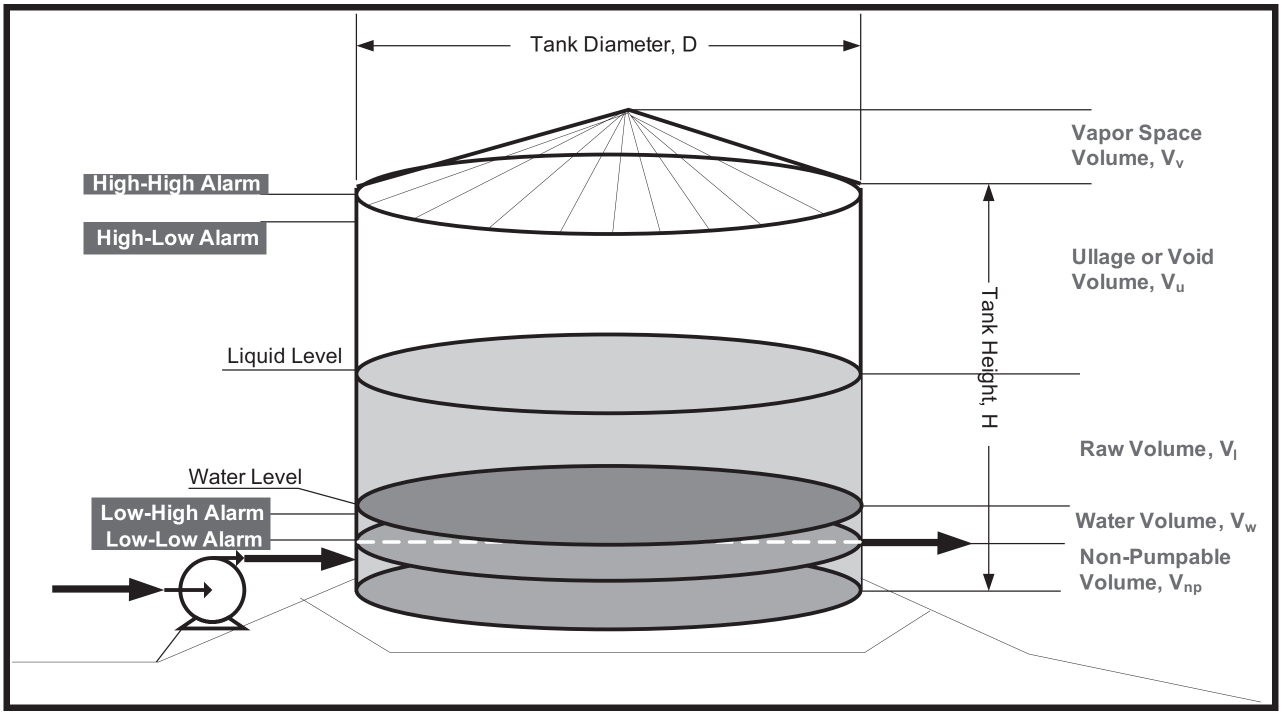


Figure 20.10—Tank's anatomical parameters. *Source:* [1].

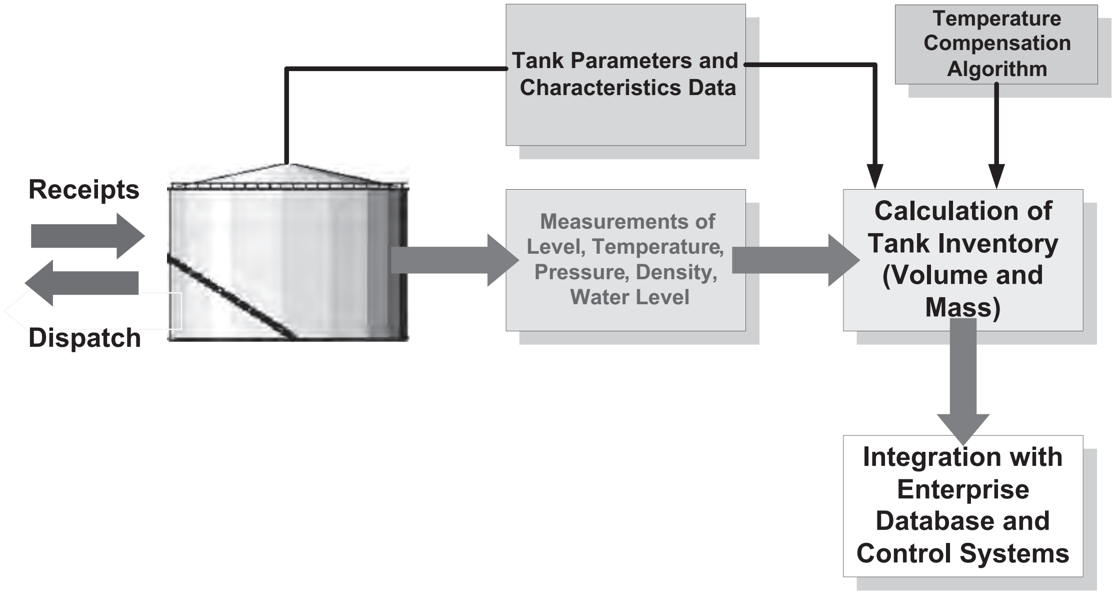


Figure 20.11—Flow diagram for the measurement and calculation of tank inventory calculation. *Source:* [1].

using a simple calculator. However, it is accurate for all tank geometries and may have errors for deformed and aged tanks. It is not difficult to program and is more accurate than the strapping factor. Figure 20.12 illustrates the mathematical formulas used for common tank shapes in a plant.

- *Step 2—Temperature compensation of raw volume:* Because the tank volume is dependent on the temperature, the raw volume cannot be used for custody transfer purposes and hence must be standardized to either 15 or 20°C using ASTM Table 54 and ASTM D125-80, respectively. This procedure can be used by using the

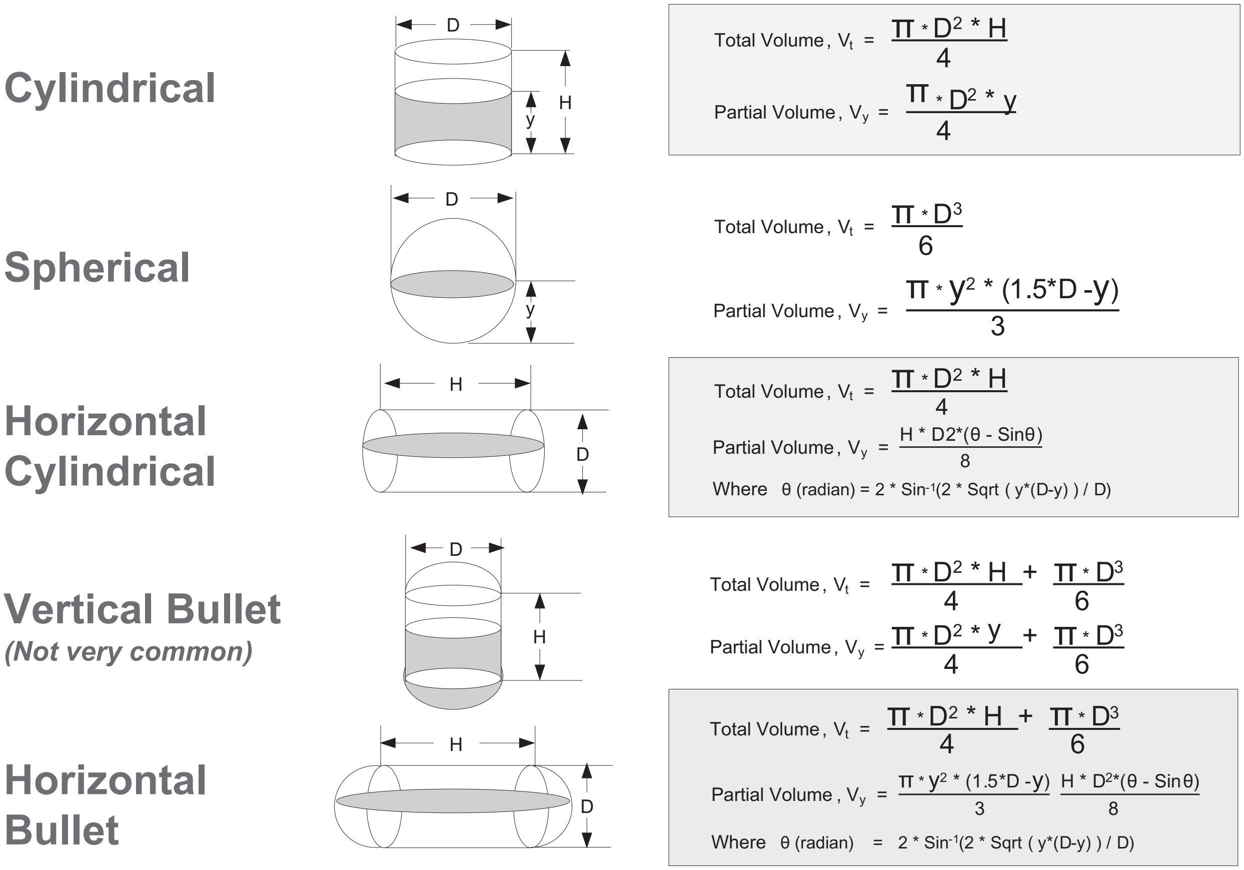


Figure 20.12—Calculation of tank volumes by mathematical formulas. *Source:* [1].

FORTRAN program available from ASTM and is not a manual calculation. The temperature used for the calculation of compensated volume must be the average temperature to account for the temperature stratification in the tank.

- *Step 3—Calculations of tank mass:* This step calculated the tank mass using the temperature-compensated volume from step 2 and density measurement at 15 or 20°C either in the laboratory or using the automatic measurement from the tank gauging system or mass flow meter.
- *Step 4—Calculation of net volume, mass, and other information:* This step uses the tank geometry using the nonpumpable volume to calculate the net mass and net volume of the tank for custody transfer, loading, and unloading purposes. Historical information is also at this step to calculate the status of tank movement at any instant.

Figure 20.13 shows the above steps for the calculations of tank inventory from measured tank process parameters and tank characteristics.

20.4.1.3.2 Equations

This section enumerates all equations used in a typical tank inventory calculation and management system.

- Gross or raw volume,

$$V_{\text{gross}} = \textit{level} \times \textit{strapping factor}, \tag{20.4}$$

or look up from strapping table or calculate using tank geometry and calculation equation.

- Compensated volume,

$$V_{\text{comp}} = V_{\text{gross}} \times \textit{VCFACT}, \tag{20.5}$$

where *VCFACT* is the temperature compensation factor calculated using ASTM methods at the reference temperature of 15 or 20°C.

- Void volume,

$$V_{\text{void}} = V_{\text{max capacity}} - V_{\text{gross}}. \tag{20.6}$$

- Percent void volume, which measures the void space at the top of the tank,

$$\%\, V_{\text{void}} = V_{\text{void}} \times 100/V_{\text{max capacity}}. \tag{20.7}$$

- Nonpumpable volume (V_{npv}) is the fixed and known characteristics of the tank and it represents the volume at the bottom of the tank that cannot be pumped out because it is below the suction line of the pump.
- Maximum available volume,

$$V_{\text{max}} = V_{\text{max capacity}} - V_{\text{npv}}. \tag{20.8}$$

- Gross weight,

$$W_{\text{gross}} = V_{\text{gross}} \times \textit{density at reference temperature} \tag{20.9}$$

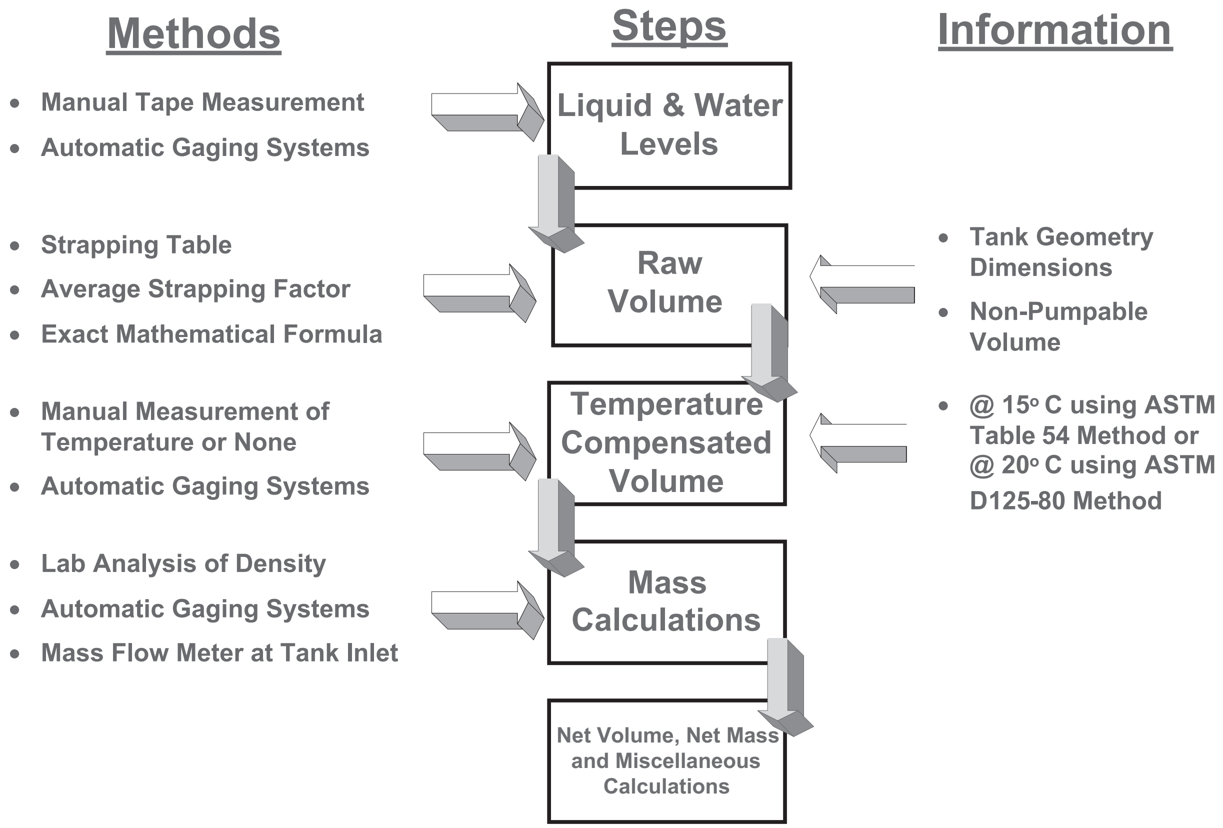


Figure 20.13—Steps to calculate tank inventory parameters. *Source:* [1].

- Net available volume,

$$V_{net} = V_{gross} - V_{npv}. \tag{20.10}$$

- Net weight,

$$W_{net} = V_{net} \times \textit{density at reference temperature} \tag{20.11}$$

- Tank status is estimated by comparing the old level versus the current level within a measurement error tolerance.
- Rate of change of level and estimation of tank fill-up or emptying can be estimated as shown in Figure 20.14.

20.4.1.3.3 Advanced Inventory Management

- *Tank leak detection:* If there are flow meters installed at tank inlet and outlets, then any leak can be detected by making a balance of total input/output flow and volume changes from the tank gauging system. However, variation in tank levels due to surface wave ripples should be considered before calculating actual volume changes.
- *Flow meter calibration offsets:* Just like leak detection, calibration of flow meters installed at upstream and downstream points of the tank can also be checked if the flow balance around the tank does not close within 2 % for a steady tank.
- *Mass reconciliation and oil loss estimation:* By balancing input and output flow and changes in tank inventories around a boundary of the tank farm, an estimate of oil loss can be arrived at in real time using a well-featured tank inventory management software system.

20.4.2 Tank Qualities

In addition to tank inventory, it is extremely important to know the qualities of tank for the following purposes:

- Tank certification before final sale to customer,
- Qualities of feed material purchased from external sources,
- Input feed qualities to process units, and
- Qualities of the blending component tanks to control the blend recipe.

These tank qualities are obtained in two modes: offline mode by laboratory samples and analysis and online mode by using the online analyzers. We will discuss these methods in the following sections.

20.4.2.1 LABORATORY ANALYSIS

First, we will discuss the method of laboratory sample and analysis for the tank qualities. In this method, the laboratory technician collects the tank samples 2–3 times either weekly or daily on the basis of the criticality of the qualities and analyzes them in the laboratory. Once, the results are available, they are entered manually in the LIMS (laboratory information system) and are available to other applications such as blending, planning, and process unit control and optimization systems. Laboratory analyses are available online only after a delay of 2–8 h, and the quality of the source may change in the meantime. Despite its delayed availability, it is the most common method of tank quality analysis.

Agrawal suggested a method to easily estimate the laboratory analysis load in a plant and be able to determine the benefits of other methods to compensate for the cost and availability of the laboratory analysis results to users [7]. Agrawal defined a laboratory analysis load measurement parameter, *SQS*, as follows [7]:

$$SQS = S * Q * S \tag{20.12}$$

where:

S = number of source (tanks or process streams) sampling points,

Q = number of qualities analyzed per sample, and

S = number of samples per tank.

The higher the SQS, the higher is the cost of laboratory analysis to the plant. Agrawal analyzed a laboratory sample schedule and analysis for a typical 300-kbbl/day refinery for analyses of onsite units and offsite tanks, and he summarized the frequency of SQS load, which is shown in Figure 20.15 [7].

The distribution of SQS load in Figure 20.15 shows that tank qualities are analyzed more often, but both samples are taken and qualities are analyzed less frequently. On the other hand, more process unit streams are sampled and analyzed but with a lesser frequency as evident from a flatter frequency plot for onsite (process units) operations.

The concept of the SQS parameter for laboratory analysis can also be used to estimate the cost of laboratory load in a plant within ±10 % and can be adjusted for a specific plant's laboratory operations. We have estimated the typical times taken by a laboratory technician to go and get a sample from a stream or tank and perform analyses

Time Left = Void Vol / Rate of Change of Volume

Rate of Change of Volume = Rate of Change of Level * Cross Sectional Area of Tank

Cross Sectional Area of Tank = $\pi * (\text{Diameter})^2/4$

Rate of Change of Level = $\dfrac{(\text{Level @ Time } T_2 - \text{Level @ Time } T_1)}{(T_2 - T_1)}$

Figure 20.14—Method to estimate time for cylindrical tank emptying and filling.

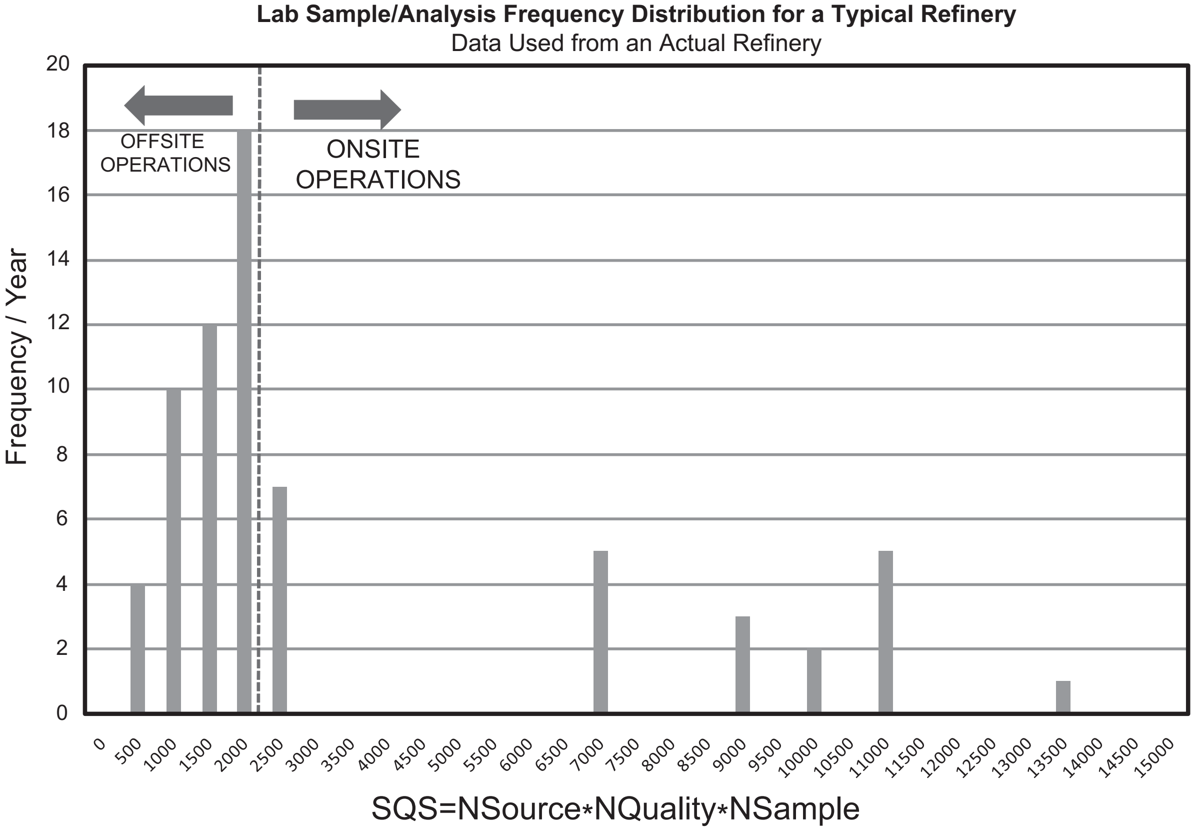


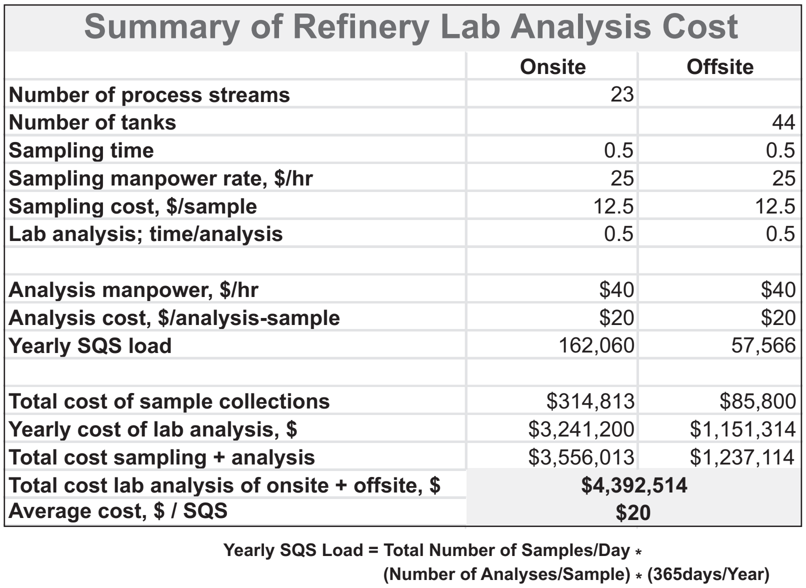
Figure 20.15—Typical laboratory analysis loads for onsite and offsite unit qualities. *Source:* [7].

of qualities in the laboratory. The analysis time could vary anywhere from 10 min to 2 h (octane) depending on the quality analyzed. We have assumed that on average it takes 30 min to analyze a quality. Also, the labor cost for sampling and analyzing may be different. We have taken all of these factors into consideration to estimate the cost of laboratory load for a refinery with 44 tanks and 23 process streams. This cost analysis for a 300-kbbl/day refinery is shown in Figure 20.16.

We will later discuss that the above cost analysis methodology for the laboratory analysis load in a plant can be used to evaluate other methods of quality analyses of tanks.

20.4.2.2 ONLINE ANALYSIS

Because some operations, such as unit control and optimization, and fuel and crude blending are critical to receive the qualities in near real time or within a short interval,



Summary of Refinery Lab Analysis Cost

	Onsite	Offsite
Number of process streams	23	
Number of tanks		44
Sampling time	0.5	0.5
Sampling manpower rate, $/hr	25	25
Sampling cost, $/sample	12.5	12.5
Lab analysis; time/analysis	0.5	0.5
Analysis manpower, $/hr	$40	$40
Analysis cost, $/analysis-sample	$20	$20
Yearly SQS load	162,060	57,566
Total cost of sample collections	$314,813	$85,800
Yearly cost of lab analysis, $	$3,241,200	$1,151,314
Total cost sampling + analysis	$3,556,013	$1,237,114
Total cost lab analysis of onsite + offsite, $	**$4,392,514**	
Average cost, $ / SQS	**$20**	

Yearly SQS Load = Total Number of Samples/Day * (Number of Analyses/Sample) * (365days/Year)

Figure 20.16—Typical cost of laboratory analysis for a 300-kbbl/day refinery. *Source:* [7].

plants started installing online analyzers. The installation of the online analyzers has following characteristics:

- Most online analyzers are installed at the exit points of process unit streams to control unit operations.
- Process unit outlet stream analyzers can also be at the inlet to a storage tank.
- Online analyzers are also installed at the location of tank exits such as for gasoline/diesel/fuel oil inline blending.
- A plant may also have analyzers installed at the blend header outlet that can thus indicate the qualities entering the final product tank.
- Online analyzers may be either discrete (one stream/one quality) or integrated (one stream/many qualities).
- Online analyzers may be multiplexed (shared) to give one or many qualities of more than one stream.

Online analyzers improved the availability of the quality results in real time for process streams and for blending tank qualities for blending control during blending execution. However, the online analyzers installed at the exit of the blending component tanks did not quite minimize or eliminate the need for laboratory analysis. Let us discuss the shortcomings of blending analyzers at the exit of the blend component tanks.

- The qualities of blend component tanks are analyzed only during the actual blend execution. At other times, they are turned off except for continuous blenders.
- During a nonblending period, the component tank qualities are again analyzed only by the laboratory and results are only available sometimes 2–8 h later.
- The blending planner or engineer cannot plan a new recipe until the blend component tank qualities are available to them.
- If the blend tanks are running (i.e., feeding as well) during the blending operations, these laboratory-analyzed qualities are already outdated and the blend recipe may be off, resulting in either violation requiring reblends or quality giveaways.
- Online analyzers such as near-infrared (NIR) analyzers are expensive and are utilized only during the blend runs. If only one blend batch of 8–10 h is executed per day, then the online analyzers are used only for 35–40 % of the day.

Figure 20.17 shows the online analyzers installed on the process stream at the exit of process units. This may also require laboratory analyses for the same analyzed quality for analyzer validation or of a different quality that has no online analyzers. Sometimes laboratory qualities may be manually input as constant values for unchanging qualities for streams (e.g., butane, methyl tertiary butyl ether, etc.).

Recent advances in quality-predictive methods have enhanced the usability of online analyzers, specifically those used in blending operations, and have made the blend component tank qualities available in real time for all control applications, planners, engineers, and operators. This method developed by Offsite Management System, LLC is discussed in the next section [8].

20.4.2.3 MODEL-BASED TANK QUALITY ESTIMATION

This method uses the same linear/nonlinear blending rules and models used in the advanced blend control optimization planning system that is commercially available and it has the following characteristics:

- The online analyzers, either discrete or integrated, are installed at the inlet of the blend tank components as opposed to installing them at the exit of the tank.
- An online software system tracks the qualities of the tank inlets and, integrated with the tank contents from historical data, applies blending models to calculate the blending quality of the component tank.

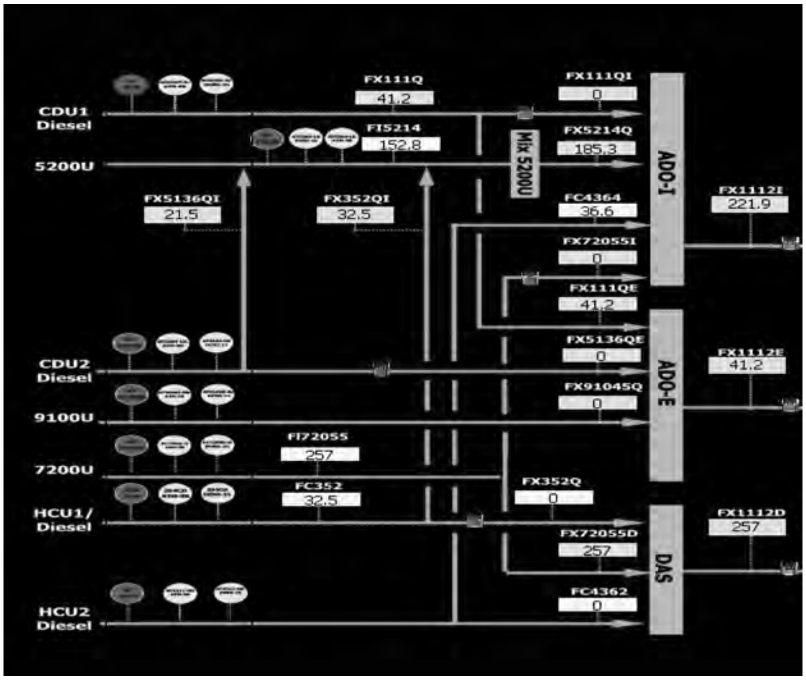


Figure 20.17—Example of online and laboratory analysis for a run-down diesel blending system. *Source:* [1].

- The software system tracks not only the qualities but also the composition of tanks for mixing model and density/quality segregation to predict the quality at the tank outlet during blending.

Figure 20.18 shows a schematic diagram of the model-based tank quality tracking system (gomsTQTS™) developed by Offsite Management Systems, LLC [8].

An optional online analysis as shown in Figure 20.18 is to install online analysis points at the inlet of the component tank, in which case the installation of a sampling point at the outlet of the tank becomes redundant. This is because the tank qualities will be calculated by the quality tracking module from the tank inlet qualities.

Details and a case study of the above system installed in an actual refinery can be found elsewhere to minimize the discussion in this chapter [8]. One of the drawbacks of this method is the long distance involved between the sampling and analysis points, but manufacturers of the NIR/nuclear magnetic resonance (NMR) system claim that sampling points can be as far as 2-3 km apart through the use of fiber optics.

20.4.3 Fugitive Emission

Fugitive emissions are the unintentional release of material from equipment and they can occur from any leaking equipment such as pumps and compressors, storage and processing vessels, flow control and pressure relief valves, pipelines, tanks, etc. Although the fugitive emissions are small in quantity, their origin exposes workers and they cumulatively cause concern for environmental pollution. It would be impossible to cover all technical and environmental aspects of fugitive emissions in this chapter. Hence, we will focus briefly here only on fugitive emissions from the following types of aboveground tanks to give readers an introduction to the material.

20.4.3.1 STORAGE TANKS

20.4.3.1.1 Fixed Roof Tanks

Although they are the least expensive, fixed roof tanks are mainly used for storing low-pressure liquids. The emissions from this tank are caused by the changes in temperature, pressure, and liquid levels while filling and emptying tanks. When the tank is filling, the displaced vapor vents directly to the atmosphere and fresh air fills in when the tank is emptying. This tank has minimal control over the fugitive emissions, and refineries are burdened with estimating the total vapor discharged per year on the basis of tank movements. This type of tank is also fitted with a pressure vacuum vent to bring in the fresh air on cooler evenings to balance the pressure below the vent pressure, thus minimizing the vapor discharge to the atmosphere.

20.4.3.1.2 Floating Roof

There are three types of floating roof tanks used to overcome the shortcomings of the fixed roof tanks.

- *External floating roof tanks:* They have an open-ended cylindrical steel shell that floats on the liquid surface

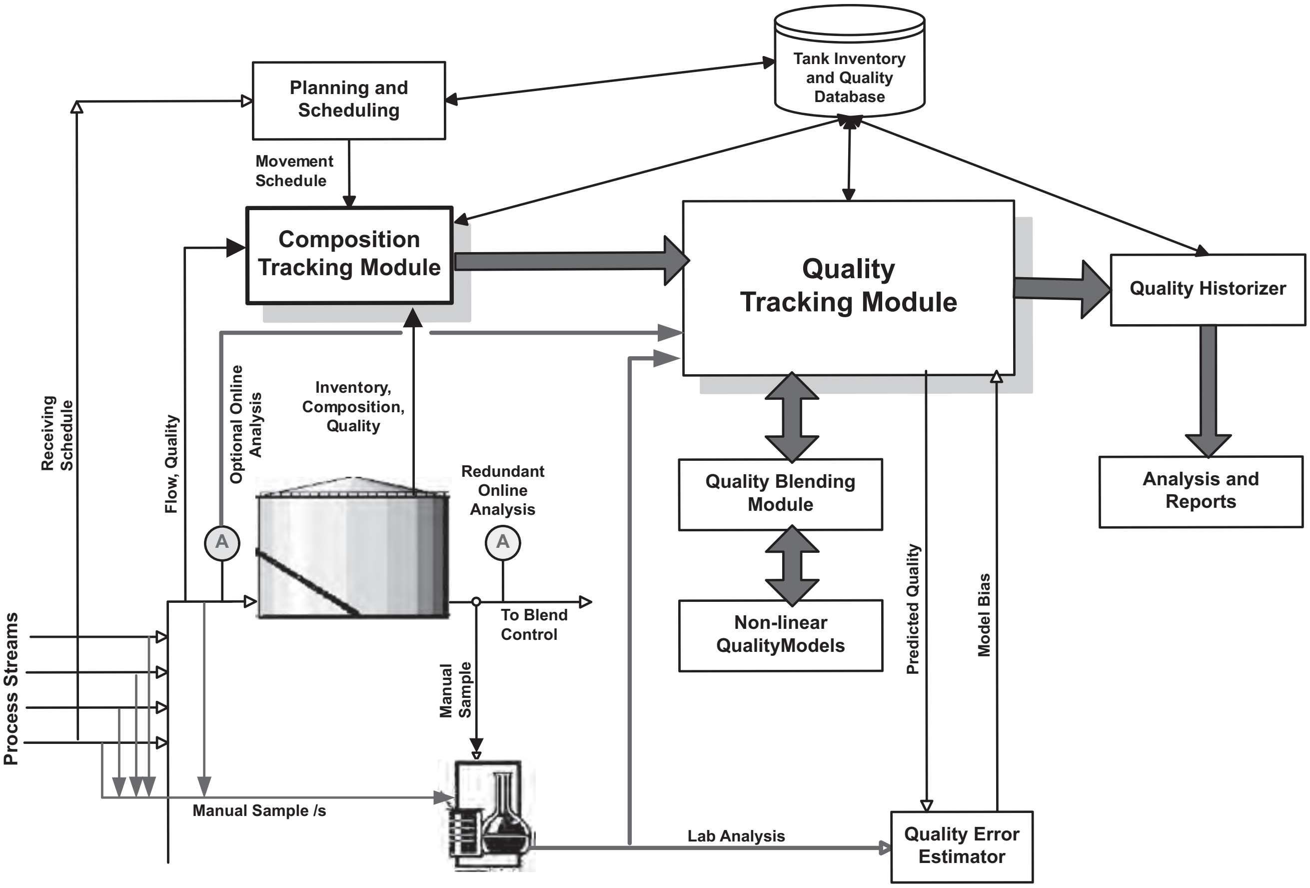


Figure 20.18—Advanced model-based tank quality tracking system. *Source:* [8].

to minimize the vapor space above the liquid level. The emissions from this tank are less than the fixed roof tanks and limit losses from the rim seal system, fittings, exposed liquid on the tank walls after the liquid is withdrawn (emptying tank), and the roof lowers.

- *Internal floating roof tanks:* These have an improvement over the external floating tank by installing a fixed roof to protect from sun and rain. They have limited emissions from docks fittings, docks seams, and the annular space between the floating internal roof deck and the tank wall. Top and side vents on the fixed roof allow for the discharge of vapor. The fixed roof may be dome shaped to block winds and minimize evaporative losses.
- *Closed floating roof tank:* This type of tank has closed vents on the fixed roof and a pressure-vacuum vent uses injection of an inert gas (e.g., nitrogen) to balance the pressure variation and provide essentially a zero-emission tank.

20.4.3.1.3 Pressure Tanks

Pressure tanks are spherical or bullets used for storing gases with high pressure such as butane and pentane. These tanks are equipped with pressure-vacuum vents to minimize losses from boiling and breathing loss from temperature and pressure changes.

20.4.3.2 ESTIMATION OF EMISSIONS LOSSES

- *Standing losses (L_s):* These happen when the tank is steady and are due to breathing of vapor above the liquid surface. They are estimated as follows:

$$L_S = 365\, V_V W_V K_E K_S \tag{20.13}$$

where:

$$W = \frac{M_V P_{VA}}{RT_{LA}}$$

$$K_E = \frac{\Delta T_V}{T_{LA}} + \frac{\Delta P_V - \Delta P_B}{P_A - P_{VA}}$$

$$K_S = \frac{1}{1 + 0.053 P_{VA} H_{VO}}$$

V_V = vapor space volume, m^3;
W_V = vapor density, kg/m^3;
K_E = vapor space expansion factor, dimensionless;
K_S = vapor space saturation factor, dimensionless;
365 = days/year;
M_V = vapor molecular weight;
R = universal gas constant, mmHg·L/K·mol;
P_{VA} = vapor pressure at daily average liquid surface temperature;
T_{LA} = daily average liquid surface temperature, K;
T_V = daily temperature range, K;
P_V = daily pressure range, mmHg;
P_B = breather vent pressure setting range, mmHg;
P_A = atmospheric pressure, mmHg;
HVO = height of a cylinder of tank diameter, D, whose volume is equivalent to the vapor space volume of a fixed roof tank, including the volume under the cone or dome roof, ft.

- *Working losses (L_w):* When the tank is either emptying or filling, the losses occur because of liquids adhered to tank walls or change in vapor space due to the rising liquid level in the tank. They are estimated as follows:

$$L_W = 0.0010 M_V P_{VA} Q K_N K_P \tag{20.14}$$

where:

M_V = vapor molecular weight;
P_{VA} = vapor pressure at daily average liquid surface temperature;
Q = annual net throughput, bbl/year (tank capacity, bbl times annual turnover rate);
K_N = turnover factor, dimensionless, for turnover > 36/year, $K_N = (180 + N)/6N$ for turnover ≤ 36 $K_N = 1$;
N = number of tank volume turnovers per year; and
K_P = working loss product factor, dimensionless, for crude oil = 0.75, for all other liquids = 1.0.

The U.S. Environmental Protection Agency (EPA) provides Tank 4.0 (http://www.epa.gov/ttnchie1/software/tanks/index.html) software for the calculations of fugitive emissions from tanks, and it generates detailed reports. This software is available free of cost and may be downloaded by anyone [9]. Further information can be obtained from the EPA document found at http://www.epa.gov/ttn/chief/ap42/ch07/index.html [10]

20.4.3.3 METHODS TO DETECT FUGITIVE EMISSIONS

Some common methods to detect the fugitive emissions from field equipment such as valves, relief valves, compressors, pumps, drains, etc., are

- Portable gas detectors,
- Catalytic beads,
- Nondispersive infrared detectors,
- Photoionization detectors,
- Combustion analyzers, and
- Standard gas chromatography with flame ionization detectors.

20.5 OIL MOVEMENT

20.5.1 Overview

One of the most manpower-intensive activities in a typical refinery is the movement of liquid material in and out of tanks in and across the plant boundaries. This is compounded by the problem of handling various equipment such as tanks, pumps, motor-operated valves, mixers, manual valves, and flow and temperature measurements. Agrawal (1996) summarized and compared the number of equipment/instruments used in oil movement activities in nine refineries as shown in Table 20.6 [11].

The number of limit switches is not shown in Table 20.6 because they are generally not available. However, a good guess would be that approximately 25–30 % of strategic manual valves have limit switches.

The management of the equipment and efficient operation of material movement activities in Table 20.6 is termed oil movement and storage (OM&S), and we will discuss the following technical, management, and economical aspects of such OM&S in this section:

- Problems and challenges,
- Operational data analysis,
- Estimation of automation incentives,
- Automation technology and strategy, and
- OM&S automation project implementation.

TABLE 20.6—Comparison of Oil Movement Equipment in Nine Refineries

	Other Refineries								
	1	2	3	4	5	6	7	8	9
Storage Tanks									
Remote level & temp	218	460	190	125	180	83	265	120	124
Local level & temp				180	120	40	304		
Valves									
Remote operations	1400	2000	490	160	400	300	320	200	31
Motorized (local)	250							200	67
Limit switches									
Manual	4000	3600	1950	465	300	700		2000	2532
Pumps									
Remote operations	60	330	106	95	100	130	28	100	20
Remote status	9								
Remote mixers		220	72	70	50	45	2	20	
Line segments		2300	1200	430		1200			

20.5.2 Problems and Challenges

It is quite natural that the management of such a large and complex network of equipment and transfer activities in a refinery has some problems associated with it. Problems typically associated with OM&S activities can be classified into the following four areas:

1. Decrease in plant profitability,
2. Operating losses,
3. Product losses, and
4. Operating costs.

The following sections will discuss each of these problem areas in detail.

20.5.2.1 DECREASE IN PLANT PROFITABILITY

The plant profitability may be decreased because of the following factors:

- *Product quality, quantity giveaway, or both:* This is encountered in activities such as blending and custody transfer because of a lack of inline blending and accurate measurements.
- *Product degradation due to displacement of previous line material:* Transfer of products of different qualities in activities such as tank-to-tank transfer, tank-to-ship transfer, etc., in the same pipeline segment degrades the products. The product degradation usually requires selling the product at a lower price or quality correction by reblending or addition of corrective components.

20.5.2.2 OPERATING PROBLEMS

Operating problems vary from areas related to man/machine interfaces to errors by field operators and they may result in economic losses. Some of most common operating problems are

- *Multiple operator interfaces:* It is one of the major concerns of the OM&S operations in a refinery as the operator has to work with as many as 7-8 different types of displays and systems such as tank gauging system, DCS workstations, blend control, MIS computer, laboratory information system and at times reduces his or her effectiveness and results in operational errors which may be at times very expensive for the refinery's profitability.
- *Line-up errors:* The refinery has a very complex network of pipelines and field equipment. To line up various valves, pumps, etc., for a transfer activity requires careful execution and may result in product contamination if any errors are made in the line-up. Line-up activity by itself is also time-consuming and requires the availability of field operators in a timely fashion.
- *Product contamination:* This may be the result of line-up errors or unplanned or unauthorized movements.
- *Pump cavitations:* This situation could occur if the valve before the pump is stuck or does not open fully. Failure of the valve downstream of the pump could also damage the pump.
- *Floating roof sinking:* This problem may occur if the liquid in the tank falls below a certain level because of a lack of timely action by the operator due to failure of a low-level alarm.

20.5.2.3 PRODUCT LOSSES

The direct effect of product losses is the decrease in plant profitability, and the following factors contribute to this problem area:

- *Inadequate or erroneous measurements or both:* OM&S activities involving movement of products across the refinery boundaries such as custody transfer and marine loading/unloading may incur product losses just because of inadequate or erroneous measurements.
- *Unplanned and unauthorized movements:* These are related to human error by the operator, field operators, or both. The product loss may occur in terms of the need to reprocess the contaminated products or sell at a lower price because of its downgraded quality.
- *Leaks:* Product leaks from valves and tanks result not only in products losses but also present environmental hazards. An unattended tank during its filling or failure of a high-level alarm may cause spills and thereby the product losses, environmental hazards, and clean-up cost associated with it.

20.5.2.4 OPERATING COSTS

In addition to economic loss to a plant from the problem areas discussed in earlier sections, a plant may also incur an increase in operating cost due to the following factors:

- *Large plant inventory:* In the absence of any on-line and timely information of availability of raw material and finished products, plant resorts to having a large plant inventory. Storage cost, unnecessary movement of products, not being able to respond to all market demands and fluctuation are some of the factors attributing to increased operating cost.
- *Underutilized tank capacities:* OM&S operators at times tend to fill tanks at levels lower their maximum due to fear of tank spills and failure of alarm. This results in under utilization of tank capacities and increase in operating cost as enough raw material and/or product may not be available for manufacturing or shipment.
- *Wasted energy:* This is from the electric utility cost increase as the transfers are repeated because of human error or from execution of avoidable transfer activities.
- *Demurrage charges:* This is quite a substantial loss to the refinery in terms of demurrage charges payable to shipping companies because of delays in marine loading and unloading and because ships must wait at port longer than necessary.
- *Large manpower:* Manual operations of opening and closing of valves and pump start/stop sequences require many field operators for the transfer activities. In addition, more maintenance personnel are needed to maintain the field equipment to repair them in time.
- *Improper and untimely reports:* Lack of any automation and implementation of information system or both may not provide inventory reports in a timely and accurate fashion for the day-to-day planning cycle of the refinery operation.

Most of the problems in the areas discussed in previous sections can be eliminated or reduced by implementing computer automation of OM&S. However, before implementing an OM&S automation project, a first step would be actually analyzing the OM&S operational data.

20.5.3 Operational Data Analysis

A refinery typically performs approximately 80–120 movement tasks on a daily basis. These tasks have various combinations of sources and destinations and vary in execution frequency and duration. Agrawal (1996) pointed out that a benefit study must establish the basis to recognize the estimated benefits from automation of OM&S and this is done by analyzing the operational data for a specific process unit or an entire area's operations [11]. The period for such operational data must be between 4 and 12 months. In the case of offsite operations in a refinery, it is necessary to collect the following information for each OM&S task for a period of a minimum of 4 months:

- Identification number;
- Start date, end date, and time;
- Source/destination identification;
- Source/product name;
- Initial/final levels of source;
- Initial/final levels of destination;
- Initial/final and total quantity transferred; and
- Planned volume or weight for transfer.

Table 20.7 shows a typical distribution of movement tasks in a 300-kbbl/day refinery and indicates that most prominent movement tasks are tank to tank, unit to tank, and tank to truck (terminal operations), composing approximately 56 % of the total tasks.

Agrawal (1996) reported that 40–45 % of the tasks in Table 20.7 take place in the fuel blending areas mostly for tank-to-tank transfers [11]. Also, it is interesting to note that only 3–5 % of the tasks occur on a daily basis and rest on slower frequencies, as shown in Figure 20.19.

Agrawal (1996) concluded that for a typical refinery, the following facts can be drawn from data analysis of OM&S operations [11]:

- *Major OM&S activities:* Typically, 75 % of OM&S activities in a refinery are tank to tank, unit to tank, tank to truck, and tank to ship.
- *Major refinery areas with most OM&S tasks:* Typically, aromatic, crude oil, gas oil, and gasoline and truck terminals have the most OM&S activities.
- *Task occurrence frequency:* Typically, 45–50 % of OM&S tasks occur less than once every 2 months and the remaining occur more than once every two months.

20.5.3.1 ESTIMATION OF AUTOMATION INCENTIVES

Agrawal (1996) categorized the estimation of benefits into two categories: tangible and intangible benefits [11]. Tangible benefits are actually estimated using the OM&S operation data. Intangible benefits are only good estimates of indirect incentives from the modernization of OM&S operations. Typically, potential OM&S benefits areas are

- Product contamination,
- Quality/quantity giveaway,
- Demurrage (marine operations),
- Batch product blending (other than inline product blending),

TABLE 20.7—Typical Distribution of OM&S Tasks in a 300-kbbl/day Refinery

No.	Transfer Task	Daily Number	Percent of Total
1	Pipeline to tank	4	4.6
2	Pipeline to unit	1	1.1
3	Recirculation	4	4.0
4	Ship to tank	3	3.4
5	Tank to pipeline	4	4.3
6	Tank to ship	8	9.4
7	Tank to tank	24	26.8
8	Tank to truck	12	13.1
9	Tank to unit	2	2.7
10	Truck to tank	1	1.3
11	Unit to pipeline	2	2.2
12	Unit to ship	1	1.1
13	Unit to tank	20	22.4
14	Unit to unit	3	3.7
		91	**100**

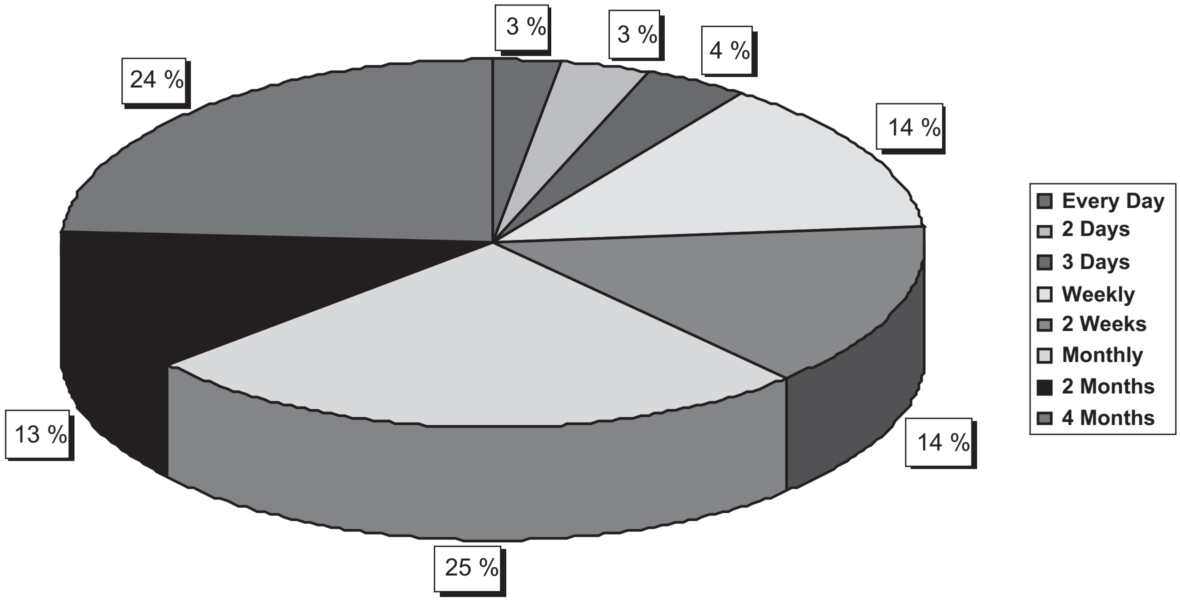


Figure 20.19—Percentage distribution of task occurrence frequencies.

- Crude blending, and
- Manpower reduction.

The following typical OM&S tasks are responsible for the possible cause of errors and their direct/indirect effects on the lost benefits.

- Line-up of movements,
- Drainage of water,
- Planning of movement schedules, and
- Loading/unloading of products/feeds.

Potential benefits areas and their sources must be cross-linked with respect to the following contributing parameters as shown in Table 20.8 for line-up of movement.

- Manpower,
- Demurrage,
- Quality giveaway,
- Quantity giveaway,
- Increased energy consumption, and
- Loss of opportunity.

20.5.3.2 BENEFITS MODEL EQUATION

Agrawal (1996) outlined a calculation model for the calculation of benefits contributed from various parameters discussed in Section 20.5.3.1 [11]. Each of the following equations can be applied to each and every cause of the lost benefits. For example, loss in tangible benefits from each incident of product degradation caused by line-up error can be attributed to losses from manpower, loss of opportunity, increased energy consumption (due to reprocessing), demurrage, etc. Therefore, "incident" would be "product degradation due to line-up error" in the following model equations. Also, all parameters do not necessarily contribute to all tangible OM&S benefits.

$$\textit{Total benefits}\ (\$/\text{year}) = MPL\$ + DEM\$ + QLG\$ + QNG\$ + ENG\$ + LOP\$ \qquad (20.15)$$

where:

$MPL\$$ = yearly benefits due to loss of manpower,
$DEM\$$ = yearly benefits due to demurrage,
$QLG\$$ = yearly benefits due to quality giveaway,
$QNG\$$ = yearly benefits due to quantity giveaway,
$ENG\$$ = yearly benefits due to increase in energy consumption, and
$LOP\$$ = yearly benefits due to loss in opportunity.

The above terms are defined as follows:

$$MPL\$ = (\textit{number of incidents/year}) \times (\textit{lost man-hours/incident}) \times (\textit{cost}, \$/\textit{man-hour}), \qquad (20.16)$$

TABLE 20.8—Matrix of Source of Benefits with Contributing Parameters of Line-Up of Movements

Sources of Benefits	Contributing Parameters					
	1	2	3	4	5	6
1. Line-up errors						
- Product degradation						
- Product to slop (or crude tanks)						
- Spills						
- Custody transfer inaccuracies						
2. Displacement of line material						
- Quality giveaway due to product upgrading						
- Product contamination						
3. Reduction in line-up time due to automation						
- Inline blending						
- Batch blending						
- Other products/crudes						

$$DEM\$ = (\textit{number of delayed ships/year}) \times (\textit{average hours of delays/ship}) \times (\textit{cost of demurrage, \$/hour}), \quad (20.17)$$

$$QLG\$ = (\textit{number of incidents/year}) \times (\textit{quantity of material}, \text{m}^3\textit{/incident}) \times (\textit{difference in quality giveaway}) \times (\textit{cost of quality giveaway, \$/quality giveaway } \text{m}^3), \quad (20.18)$$

$$QNG\$ = (\textit{number of incidents/year}) \times (\Delta\, \textit{quantity giveaway}, \text{m}^3\textit{/incident}) \times (\textit{cost of material, \$/}\text{m}^3), \quad (20.19)$$

$$ENG\$ = (\textit{number of incidents/year}) \times (\Delta\, \textit{increase in energy}, \text{kWh}\textit{/incident}) \times (\textit{cost of energy}, \text{\$/kWh}), \text{ and} \quad (20.20)$$

$$LOP\$ = (\textit{number of incidents/year}) \times (\Delta\, \textit{profit from sale of cargo/incident}) \quad (20.21)$$

Table 20.9 summarizes the typical range of tangible and intangible benefits from OM&S operations in a typical refinery of 300 kbbl/day [11].

It may seem that quality giveaway and product contamination is low in Table 20.9 for the specific refinery considered. Product contamination only occurs in oil movement line-up errors, whereas quality giveaway largely occurs in blending operations. Table 20.9 only considers all benefits for oil movement operations and not blending to keep the benefits of the two separate to justify an OM&S project.

The payback period for the automation of an OM&S project alone is 3–4 years. However, it is more beneficial to consider an OM&S automation project along with blending automation, and this has a quicker payback period. In the author's experience, it is very difficult to economically justify a project for the automation of OM&S after a blending automation has already been implemented.

TABLE 20.9—Summary of Typical Benefits from OM&S Automation

Benefit Area	Typical Benefits, Thousand Dollars/Year
Quality giveaway	40–50
Product contamination	4–6
Demurrage cost reduction	400–600
Quantity giveaway by measurement errors	500-700
Reducing or eliminating OM&S tasks	400–600
Increasing tank utilization	500–600
Integration of OM&S with computer applications	300–500
Increasing crude throughput by crude blending	2400–3000
Planning and scheduling of ship unloading	200–300
Crude feed quality control and monitoring	200–300
Minimization of spill and leakage	95–140
Line-up errors and illegal movements	50–315
Minimization of product loss in water drainage	25–40
Better utilization of OM&S equipment	60–155
Better planning and scheduling	60–100
Manpower reduction	40–1250
Total typical OM&S benefits	**5000–8500**

20.5.4 *Automation Strategy*

The automation of an OM&S operation requires that the computer system respond to the needs of the operator to perform the major functions discussed in Section 20.5.4.1.

20.5.4.1 FUNCTIONALITY

- Use remote readings from tank gages to
    - Calculate inventories, conditional events, and total volumes shipped.
    - Monitor tanks for improper movements and alarm on high or low levels.
- Respond to field element status:
    - Monitor remotely operated valves (ROVs), pumps, and mixers for alarm conditions and proper response operator requests.
    - Keep a list of out-of-service equipment.
    - Provide status information to operator.
- Monitor and control movements for receipts, rundowns, transfers, and shipments.
- Select equipment (tanks, valves, pumps, etc.) for movements required in the schedule.
- Automatically sequence equipment to implement and terminate movements.
- Terminate movements, swing tanks, start other movements, etc., when specified conditions are met.
- Provide interfaces between DCS and supervisory-level controls of inline blenders and equipment sequencing, movement monitoring, and customer's blend control strategy programs.
- Provide summary reports and movement logs and profiles that are defined by the customer.
- Use networked computers to receive operating data and to transmit historical data.

The above characteristics of a well designed and developed OM&S computer system provide interfaces and interaction among all activities of the OM&S operations in a refinery. Figure 20.20 shows the flow of information among OM&S activities and an OM&S computer system.

20.5.4.2 LEVELS OF OM&S CONTROL FUNCTIONS

The functionality of an automated OM&S system can be translated into various control levels, as shown in Figure 20.20:

- *Level 0:* This is the lowest level at which all field equipment such as pumps, ROVs, mixers, and control valves are controlled by the electronic system. Tank levels and temperature are also monitored at this level.
- *Level 1:* This level is called the supervisor control in which computer systems monitor the status of process variables or field equipment or send the command for remote control operation. For example, instead of starting or stopping a pump from the field or remote panel,

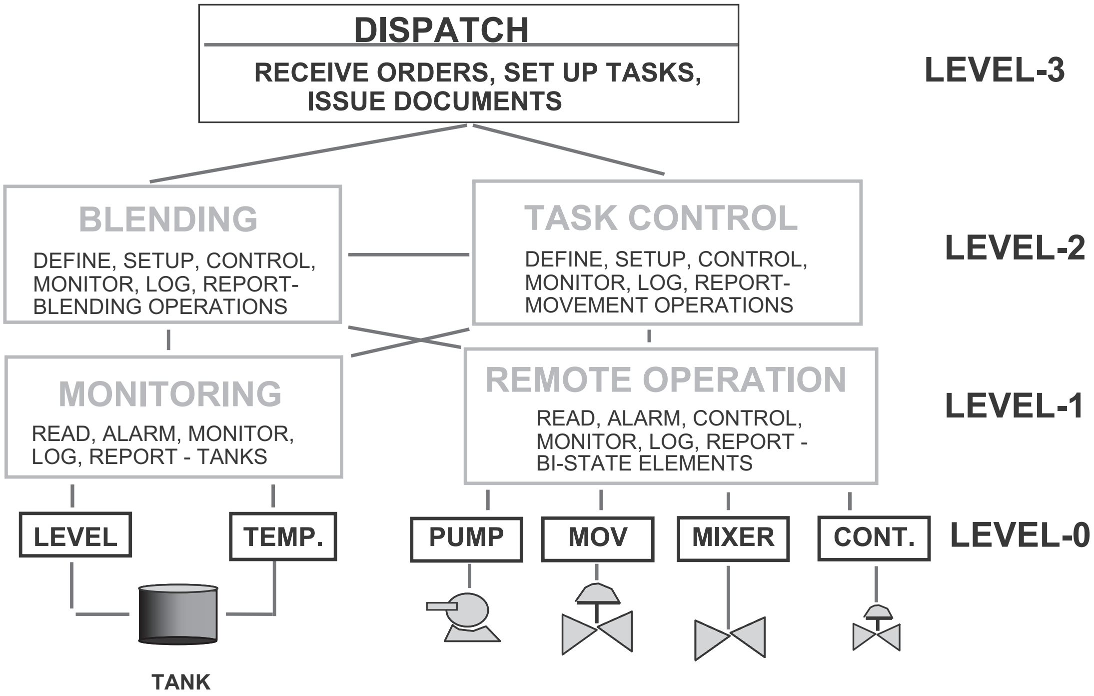


Figure 20.20—Control levels of oil movement system. *Source:* [10].

the operator could issue a command from the computer to operate a valve or pump. Tank gaging systems such as Wesson, Varec, Enraf, and Saab provide computer interfaces to monitor the tank levels and temperatures.

- *Level 2:* This level involves extensive application programming and offers the maximal benefits of automation. Various steps of executing an OM&S activity are automated at these levels and are categorized into separate modules such as task definition, sequence generator and control, task monitor, etc. Blending is also implemented at this level.
- *Level 3:* This is the topmost level and is usually termed as the information system level. Information about various refinery activities such as planning, scheduling, shipping, and dispatching is collected at this level and is interfaced with OM&S control modules for overall integration of the system.

20.5.4.3 CATEGORIES OF OM&S CONTROL FUNCTIONS

From a simplistic view of OM&S control functions, they can be divided into three basic categories:

1. What must be done?
2. What is going on now?
3. What has happened?

In the next sections, we will discuss that almost all functionality of an OM&S computer belongs to a category answering one of these three questions.

20.5.4.3.1 Steps to Execute an OM&S Activity

The following steps to execute an OM&S activity are valid regardless of their automation; that is, the operator goes through these steps even in manual operations.

- Selection of activity type,
- Task definition,
- Path selection,
- Sequence generation, and
- Sequence control.

We shall walk through an example of an OM&S task with all of these steps, along with representative displays, to illustrate how an OM&S operator would use an OM&S computer system to perform his daily transfer activities. Figure 20.21 shows the functional modules of a typical OM&S system.

20.5.4.3.2 Selection of Activity Type

This is the first step for the operator to select the type of transfer activity he wants to execute by choosing a task type from the menu. The operator can select the task type or enter the task identification number (ID) if he knows it already.

20.5.4.3.3 Task Definition

After selecting the activity type, tank-to-tank transfer in Figure 20.21, the next step is the task definition step. This step requires three inputs: source, destination, and stop condition or size of transfer. Because the task database has other information such as material, pump ID, and task ID, this information is shown only upon entry of source and destination. The operator can also enter the task ID if he already knows this information. The operator can always override the inferred data shown by the system with valid entries.

20.5.4.3.4 Path Selection

The next step of task implementation is the selection of a path through the refinery network. The path selected is governed by two specifications: the data defined for the task and the path/network database. A path for a specified task can be defined in one of two ways: the predefined or "canned" path or the dynamic and optimal path. The

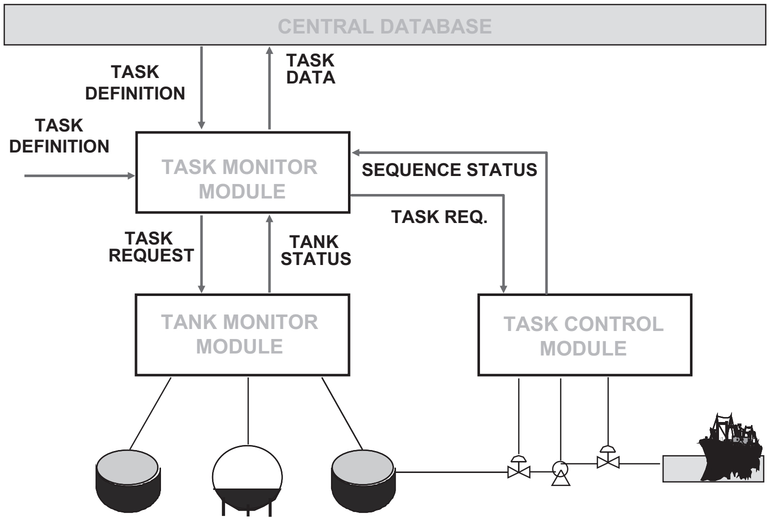


Figure 20.21—Functional modules of an oil movement control system. *Source* [12].

approach followed for a given refinery depends on the complexity of the network and the number of task types. The canned path algorithm is not very flexible compared with the dynamic path algorithm, but it takes less resources and is more efficient. In short, the dynamic path algorithm is recommended for a very complex and interactive network of field equipment.

The path selected for the specified task is displayed in two ways—tabular and graphical formats—as shown in Figure 20.22.

20.5.4.3.5 Sequence Generation

After the path is selected and approved by the operator, a sequence of operating the field equipment needs to be generated. This sequence consists of field equipment for the isolation of path and for flow path and startup (i.e., pump) of the task. Each piece of field equipment in this sequence of operations has a relevant action (of valve close or open) and its own individual modes of operation (i.e., manual, automatic or required operator initiation). This is shown in Figure 20.23.

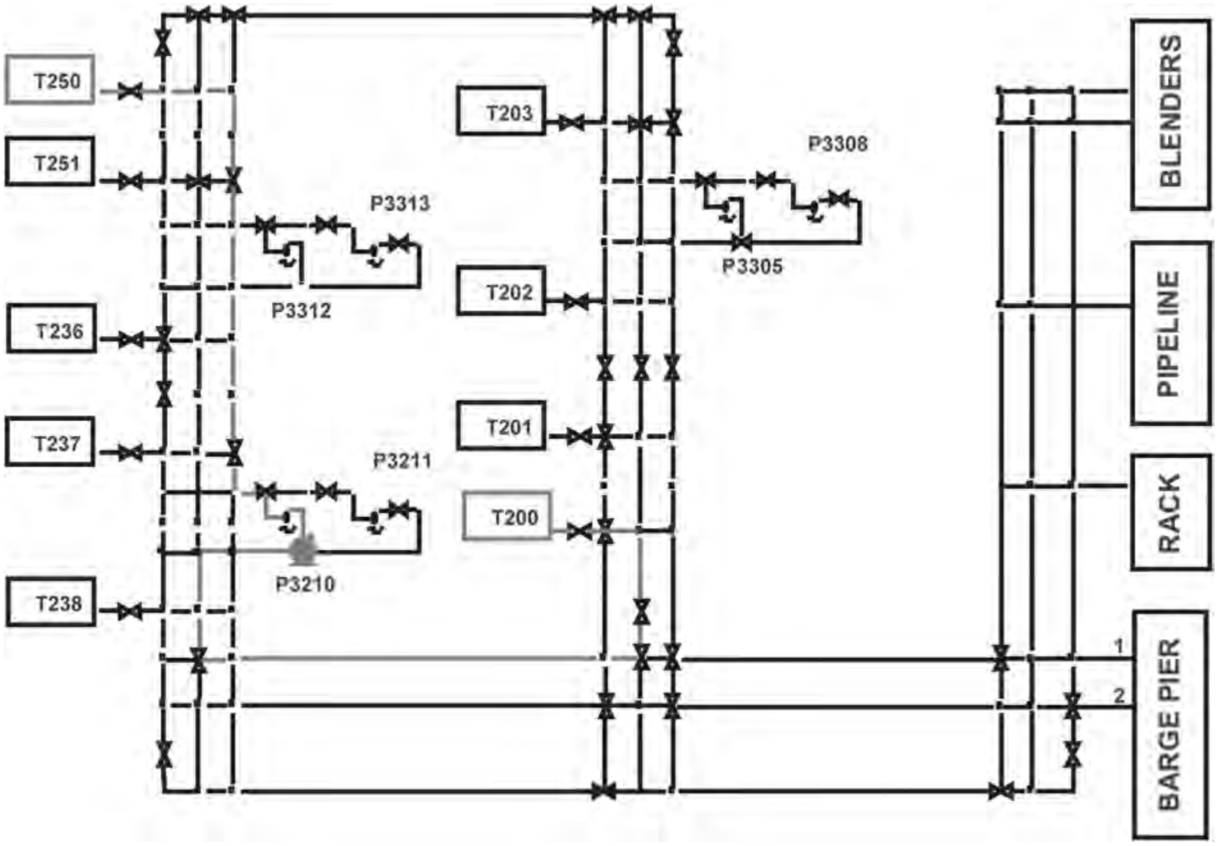


Figure 20.22—Path selection of an oil movement control system. *Source:* [13].

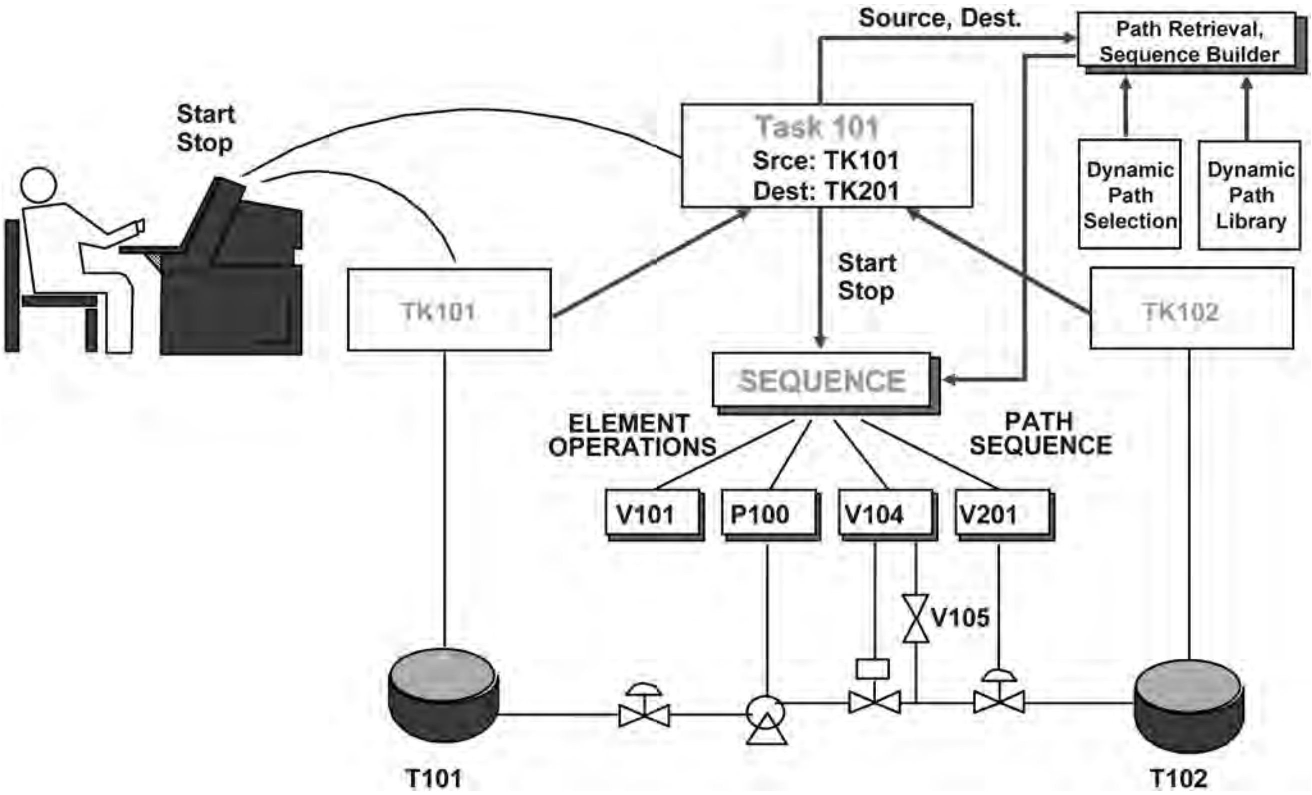


Figure 20.23—Sequence generation of an oil movement control system. *Source:* [12].

20.5.4.3.6 Task Status Monitoring

After the OM&S task is implemented, the operator can monitor the status of tasks in several ways, each displaying information from different perspectives. The task monitor status can be displayed as follows:

- Status of single task;
- Status of all tasks (active, defined, scheduled, committed, unassigned, etc.);
- Status of a group of tasks such as all those related to gasoline activities; and
- Screen report of tank inventory, which can again be grouped by products or area or tanks.

20.5.5 Integrated OM&S System

The components of an integrated OM&S computer system depend on the status of automation, the refinery information system in a particular refinery, and the computing platforms of the OM&S system. For example, some commercially available OM&S systems include blending as one of the modules. The OM&S algorithm as such does not include any linear programming (LP) algorithm, whereas the inline blending uses either LP or the nonlinear equation solver and optimization using nonlinear blend models depending on the type of product blend. In addition to this, a truly integrated OM&S system must interface with the refinery's information management system for history, databases, reports, reconciliation, etc. This results in the customized integration of an OM&S system for each refinery and may involve developing many interfaces for various modules and computers. Figure 20.24 shows a diagram for the integration of an OM&S system with refinery-wide planning and other applications.

20.5.6 Project Implementation

A typical OM&S automation project takes 18-24 months from start to finish. Table 20.10 shows a typical list of project activities and a project timeline to give readers an idea of what is involved in an OM&S automation project. Actual details, duration, and activities may vary from refinery to refinery depending on the project size and the allocated funds for the project.

20.6 TERMINAL OPERATIONS

Terminal operations handle crude/product receipts and product dispatch at marine, truck, railcar or wagon, and pipeline terminals, with each one having their own characteristics from an operational point of view as well as their own problems and challenges. Nevertheless, they all have the inherent problems and challenges of following custody transfer issues.

- Custody transfer is the reconciliation of accounting of the amount of refinery feed or product exchanged between the refinery and an external party (buyer or seller).
- The custody transfer error for crude oil receipts alone can cost a 300-kbbl/day refinery approximately $15–30 million (U.S.)/year on the basis of the assumption of a crude price of $50 (U.S.)/bbl and a best measurement accuracy of ±0.25-0.50 %.
- This can affect the bottom line by as much as 5–10 % on the basis of the assumption of a refinery profit margin of $2/bbl or less.
- Accurate measurement and accounting for water content in crude oil receipts can save further to avoid paying for water at crude oil prices.

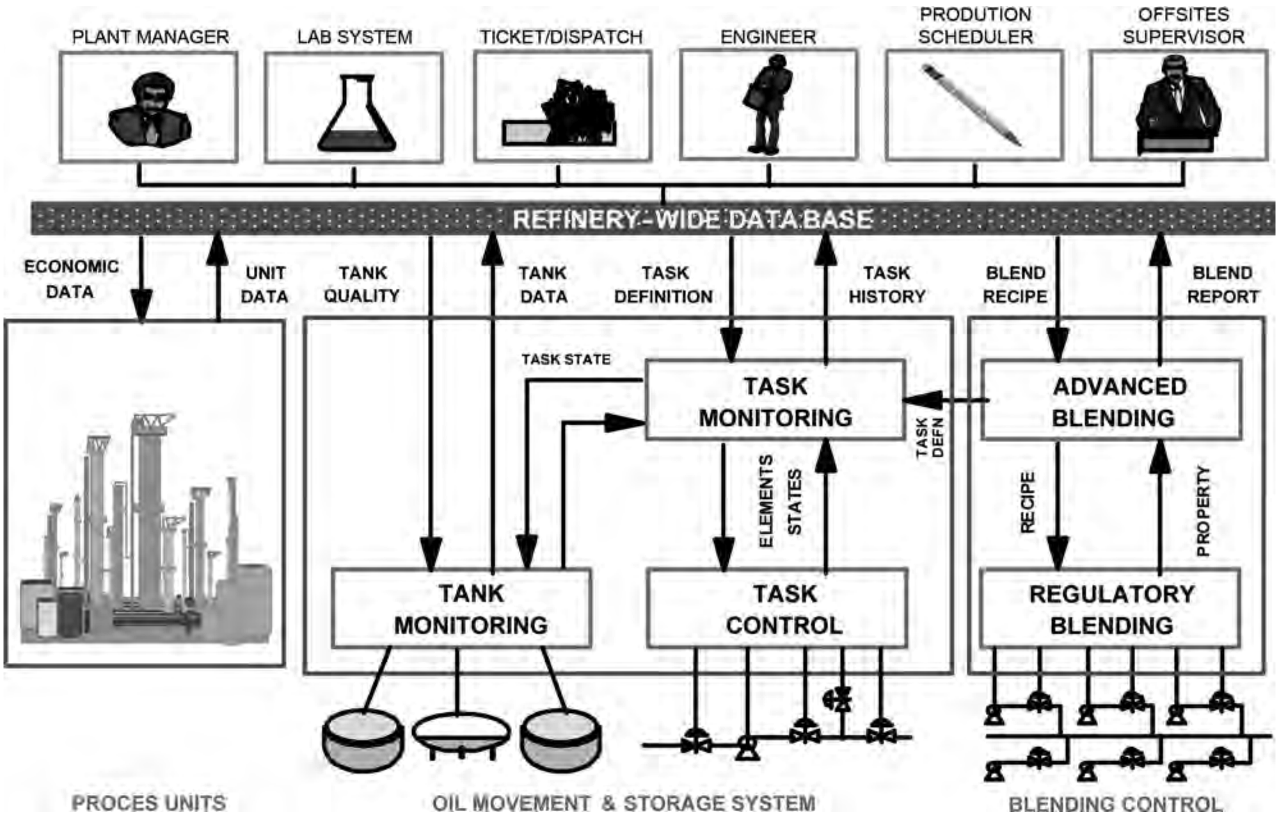


Figure 20.24—Integration of OM&S system with refinery-wide planning and scheduling system.

TABLE 20.10—Tentative Project Execution Plan

	Elapsed Months																	
Activity	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Project start	•																	
Site survey and project design basis	▨	▨																
Definition of tasks and path line-up			▨	▨	▨													
Application design basis	▨	▨	▨															
Interface development/testing		▨	▨	▨	▨													
Application design and development				▨	▨	▨	▨	▨	▨	▨								
Customization of application											▨	▨						
Order of computer systems											▨	▨						
Application commissioning													▨	▨	▨	▨		
Interface commissioning														▨	▨	▨		
Training and startup														▨	▨	▨	▨	
Project completion																		•

- Delayed reconciliation and documentation results in transfer disputes between supplier and refinery and a loss of revenues.

Figure 20.25 enumerates the challenge severity matrix of all terminal operations and indicates that marine and pipeline terminals pose the most challenges compared with trucks and railcar terminal operations.

20.6.1 Truck Terminals

Truck terminal operations face the following challenges:

- They require efficient planning and scheduling of 100–300 trucks/day.
- Tank compartments are manually gaged, leaving room for custody transfer discrepancies.
- Human errors can cause product contamination in truck compartments.
- Requires a minimum of 1 week of planning of product inventory to schedule incoming trucks.
- The trucks queues must be coordinated efficiently.

Figure 20.26 shows an example of truck terminal operation.

20.6.2 Marine Terminals

The challenges of marine terminal operations are

- Planning and scheduling,
- Demurrage charges,
- Accurate flow measurement,
- Flow meter proving,
- Water content analysis,
- Crude oil sampling point location,
- Representative sampling of crude oil, and
- Sampling system proving.

20.6.3 Railcar Terminals

Railcar terminal operations are similar in operations to the truck terminals. However, their activities are for longer periods of time and the scheduled wagons are less frequent than truck terminals on a daily basis.

20.6.4 Pipeline Terminals

Pipeline terminal challenges are as follows:

- They are the most difficult to manage because of distance.
- They need elaborate equipment (pumping stations) to send material over varying heights.
- Leaks may disrupt the service and cause safety hazards.
- Product contamination.
- They involve multiple enterprises and vendors.
- They require robust control systems and sophisticated remote monitoring instruments.

20.7 BLENDING

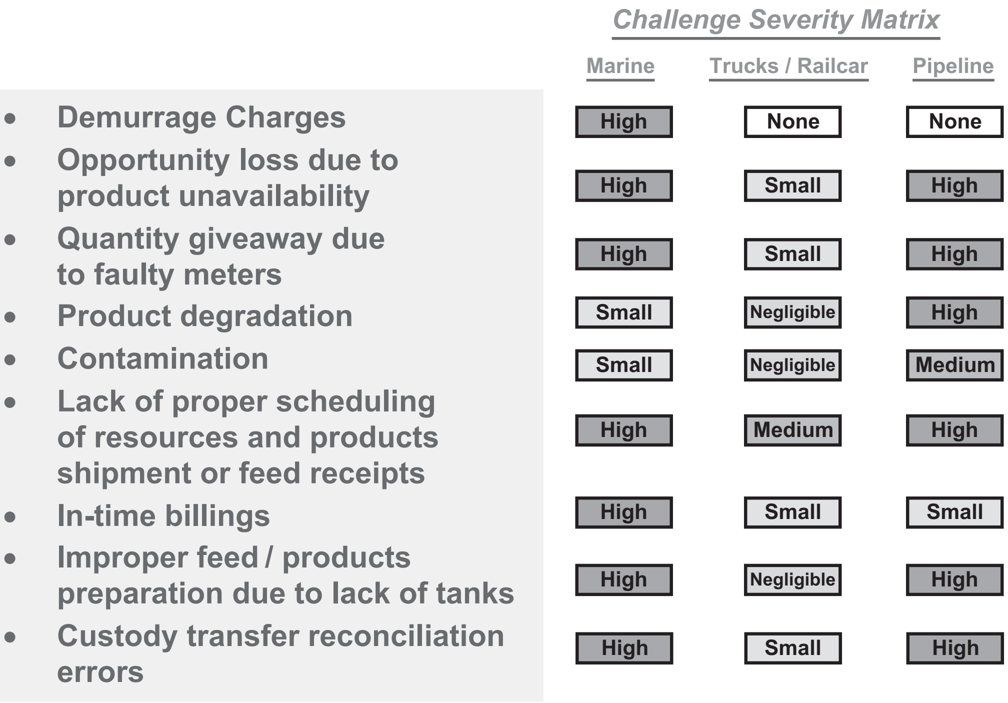
Blending can be defined as a process of homogenous mixing of two or more ingredients to produce a product with certain desirable qualities or attributes. The objectives of blending are

- The final product qualities must never violate the specified qualities or attributes.
- The final product must be produced with minimal cost or maximal profit.

The examples of blending in any liquid- or solid-based plant are shown in Table 20.11.

The blending operations in any industry are considered important because

- Sources for the product ingredients are becoming scarce and varying in qualities. For example, in the upstream refining industry, exploration of crude oil from offshore and onshore sources leads to varying crude quality and quantity.
- End-users are demanding more stringent product qualities. Technological advances in the end-user industry (e.g., automobile industry) are demanding efficient and low-emission fuels.



Challenge Severity Matrix

	Marine	Trucks / Railcar	Pipeline
• Demurrage Charges	High	None	None
• Opportunity loss due to product unavailability	High	Small	High
• Quantity giveaway due to faulty meters	High	Small	High
• Product degradation	Small	Negligible	High
• Contamination	Small	Negligible	Medium
• Lack of proper scheduling of resources and products shipment or feed receipts	High	Medium	High
• In-time billings	High	Small	Small
• Improper feed / products preparation due to lack of tanks	High	Negligible	High
• Custody transfer reconciliation errors	High	Small	High

Figure 20.25—Challenge severity matrix of terminal operations. *Source:* [1].

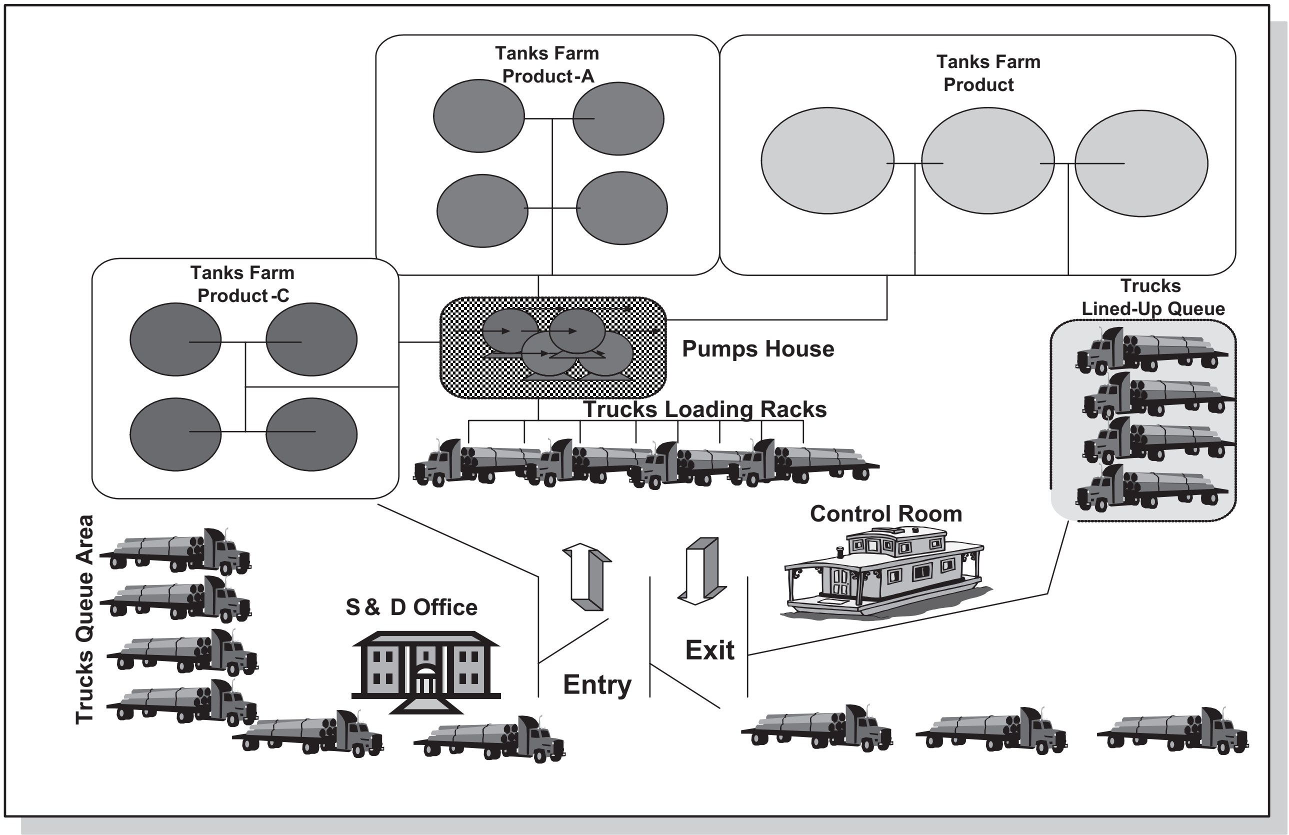


Figure 20.26—Example of truck terminal operation in a typical refinery. *Source:* [1].

- Strict government regulations on product qualities.
- Competitive business environment to minimize the cost of production. Crude oil refiners are getting complex in their conversion processes to maximize products from a barrel of oil yet be able to process crude of varying qualities.
- Environmental concerns and regulations restrict the method of production.

In this section, we will discuss some of the blending applications in refining and petrochemical complexes to give the reader an idea of the complexity involved in blending operations.

20.7.1 Crude Blending

The main objectives of a crude unit in a refinery are to optimize the quality and yields of cuts and operate the unit in a stable and safe manner. It is important that crude feed to a unit has uniform quality and availability. This is becoming difficult on a day-by-day basis for the refiners to obtain enough crude with consistent quality economically from one source of supply. It is therefore important to blend crudes from different sources with varying qualities to feed to the crude unit with crude of consistent quality. Therefore, the objectives of crude blending are

- Minimization of dependency on crude feed quality for stable and optimal operation,
- Maximization of product yields and quality,
- Improve crude oil inventory for "just-in-time" manufacturing, and
- Reduction in demurrage by better planning.

These objectives can be achieved by the following feed and product quality-control systems:

- Feed quality control
  - Marine planning and scheduling
  - Movement task monitor and control
  - Crude tank composition, monitoring, and optimization
- Product quality control
  - Crude unit model
  - Crude unit LP optimizer
  - Product blending optimizer

Figure 20.27 shows a schematic diagram to integrate all systems required to control the quality of crude feed to

TABLE 20.11—Example of Blending in the Manufacturing Industry

Industry	Blending Operation
Refining	Crude, gasoline, diesel, fuel, lube oils
Petrochemical	Naphtha
Power generation	Coal blending
Cement	Kiln feed blending
Paper and pulp	Pulp and fiber blending
Steel manufacturing	Blast furnace feed
Food and Beverage	Various food items

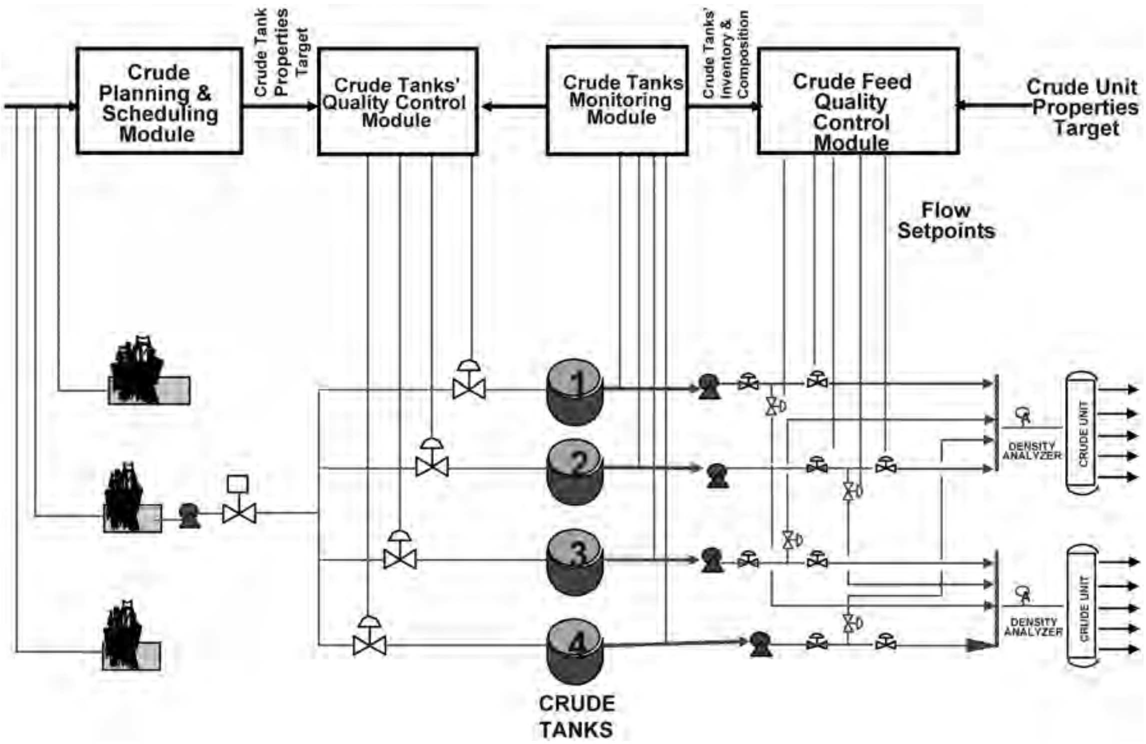


Figure 20.27—Integrated crude feed quality-control systems.

the crude unit. The main qualities controlled are density, sulfur, and water content in the crude feed [14].

Crude can be blended in any of the following modes:

- “Pipelines-to-tanks” blending,
- “Ships-to-tanks” blending,
- “Tanks-to-tanks” blending, and
- “Tanks-to-units” blending.

Crude blending can be very complex if the crude supply is via pipelines, and their source, types, and qualities vary extensively. Crudes from pipelines can be stored in tanks keeping their individuality, or they can be blended partly in the tanks to achieve uniform qualities for a particular type of crude (e.g., light crude, heavy crude, low- or high-sulfur crude, paraffinic or naphthenic crude, etc.). Figure 20.28 shows an example of a crude blending configuration receiving crude via pipelines and two-stage blending to prepare specific crude unit mixes.

The crude mixes are thus prepared and then again blended to a specific crude unit’s requirements using multitank and multiheader blending configurations as shown in Figure 20.29. In this design configuration, crude mixes are blended into six crude feed tanks for six crude units. Each of the crude units is designed to process only one type of crude.

Agrawal (1994) presented a design view to integrate crude blending feed-forward strategy with product blending feedback strategy to optimize crude and product qualities [14]. To the author’s knowledge there is no commercial system available as an integrated system for the overall optimization, but the idea and its feasibility still exists. This is shown in Figure 20.29.

20.7.2 Fuel Blending

The blending of gasoline, diesel, and fuel oils is termed “fuel blending.” Fuel blending is covered extensively by the author in Chapter 19 and hence will not be discussed here to avoid duplication of topics.

20.7.3 Lube Oil Blending

Lube blending is very different than crude blending or fuel blending. Lube blending is characterized by 300–400 types of finished products with smaller batches of 15–25 bbl. On the other hand, fuel blending produces 10–15 types of grades with 50,000- to 100,000-bbl batch size. Crude blending batch size could be approximately 100–300 bbl. Lube blending also has a risk of contamination leading to sending the batch to burners and loss of revenue. Inline blending for the lube plant is economical for plants producing more than 150,000 bbl/year. There are two methods of inline lube blending:

1. *Stationery batch tanks:* In this mode, the batch holding tanks remain stationery and can meet product demands rather quickly. On the down side, the mode requires a great deal of pipe and instrumentation to control the batch quality (see Figures 20.30 and 20.31).
2. *Moving batch tanks:* This mode keeps the batch tanks moving and as they pass the filling stations, recipe components are blended. The mode requires less manpower, piping, and valves and it has better quality controls (see Figure 20.32).

20.7.4 Naphtha Blending

Naphtha is a byproduct of crude distillation, and its boiling point is between 30 and 200°C. It consists of a complex mixture of hydrocarbon molecules generally having between 5 and 12 carbon atoms. It typically constitutes 15–30 % of crude oil, by weight. Light naphtha is the fraction boiling between 30 and 90°C and consists of molecules with five to six carbon atoms. Heavy naphtha boils

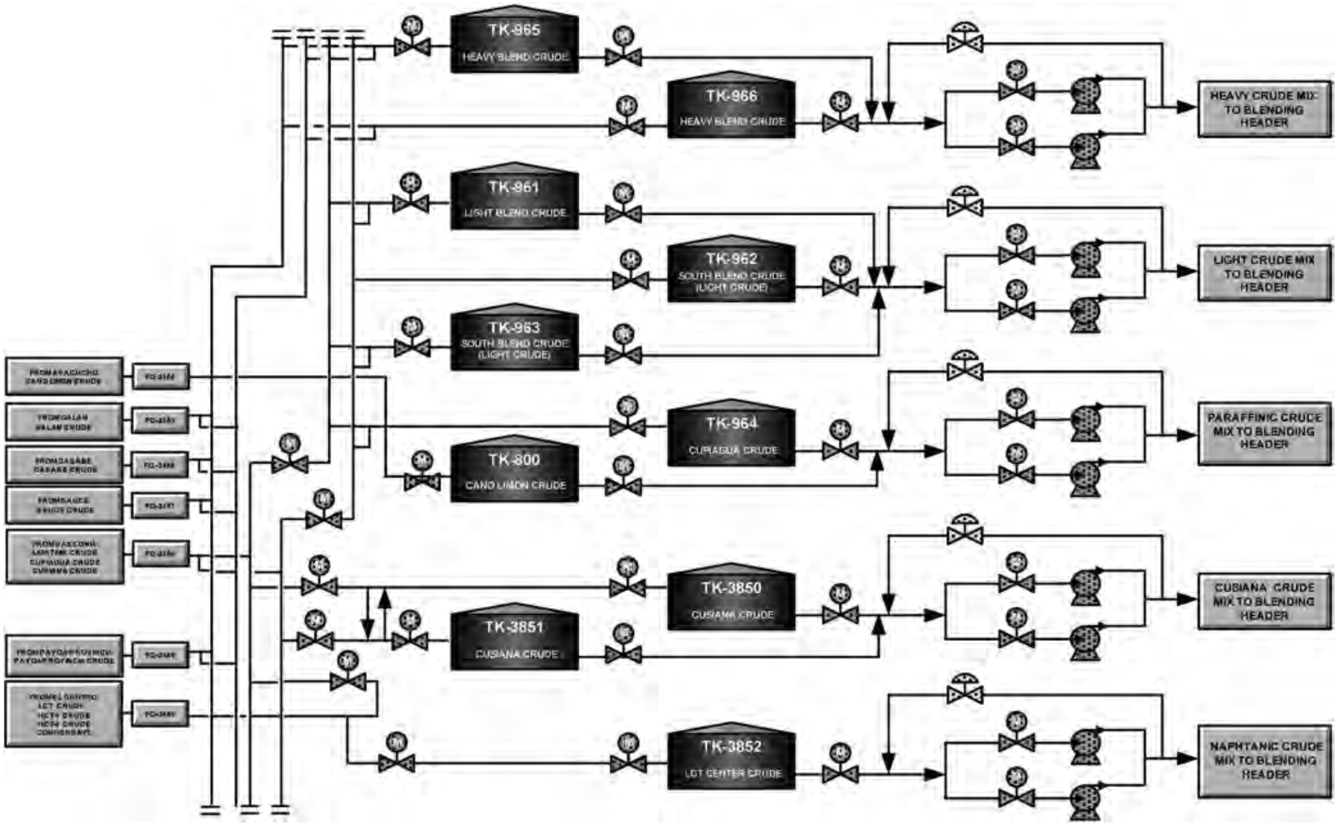


Figure 20.28—Typical example of pipelines-to-tanks crude blending.

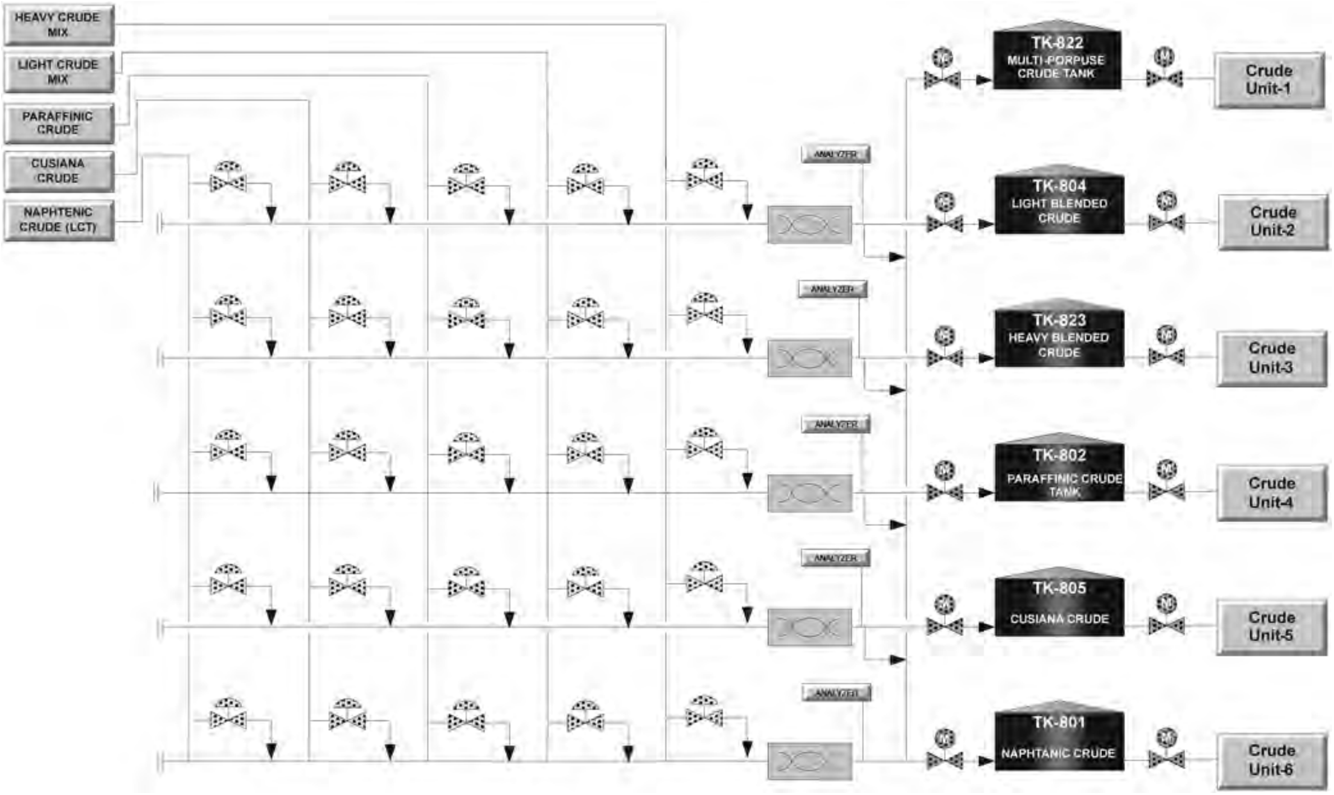


Figure 20.29—Multiheader crude blending.

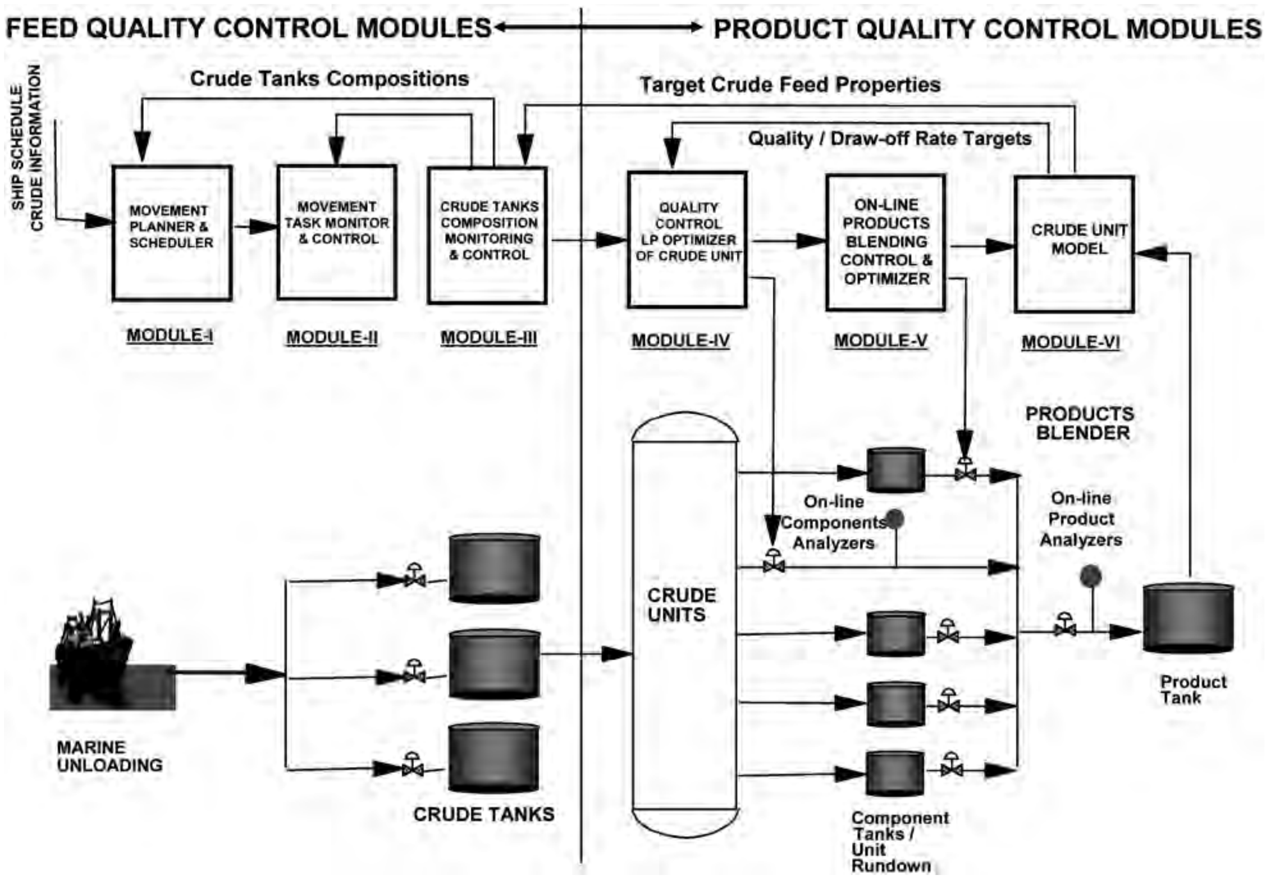


Figure 20.30—Integrated crude and product blending and optimization strategy.

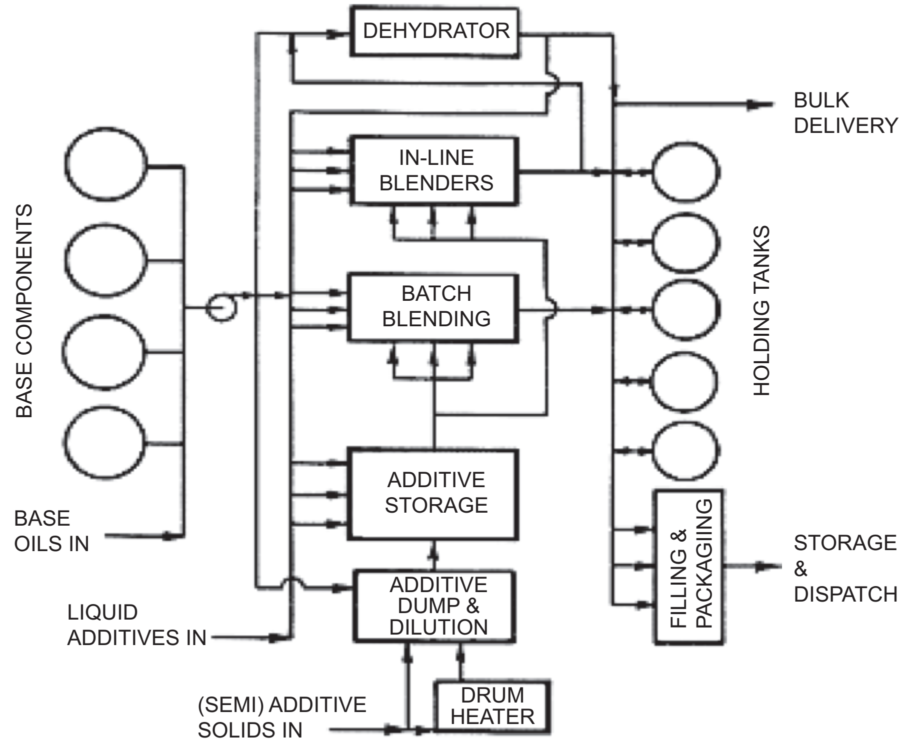


Figure 20.31—Stationary tank lube inline blending. *Source:* [15].

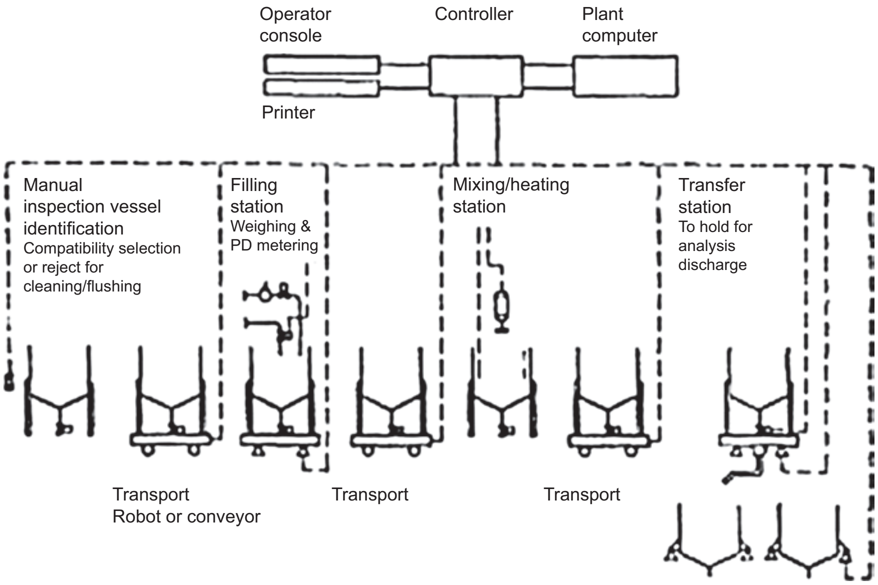


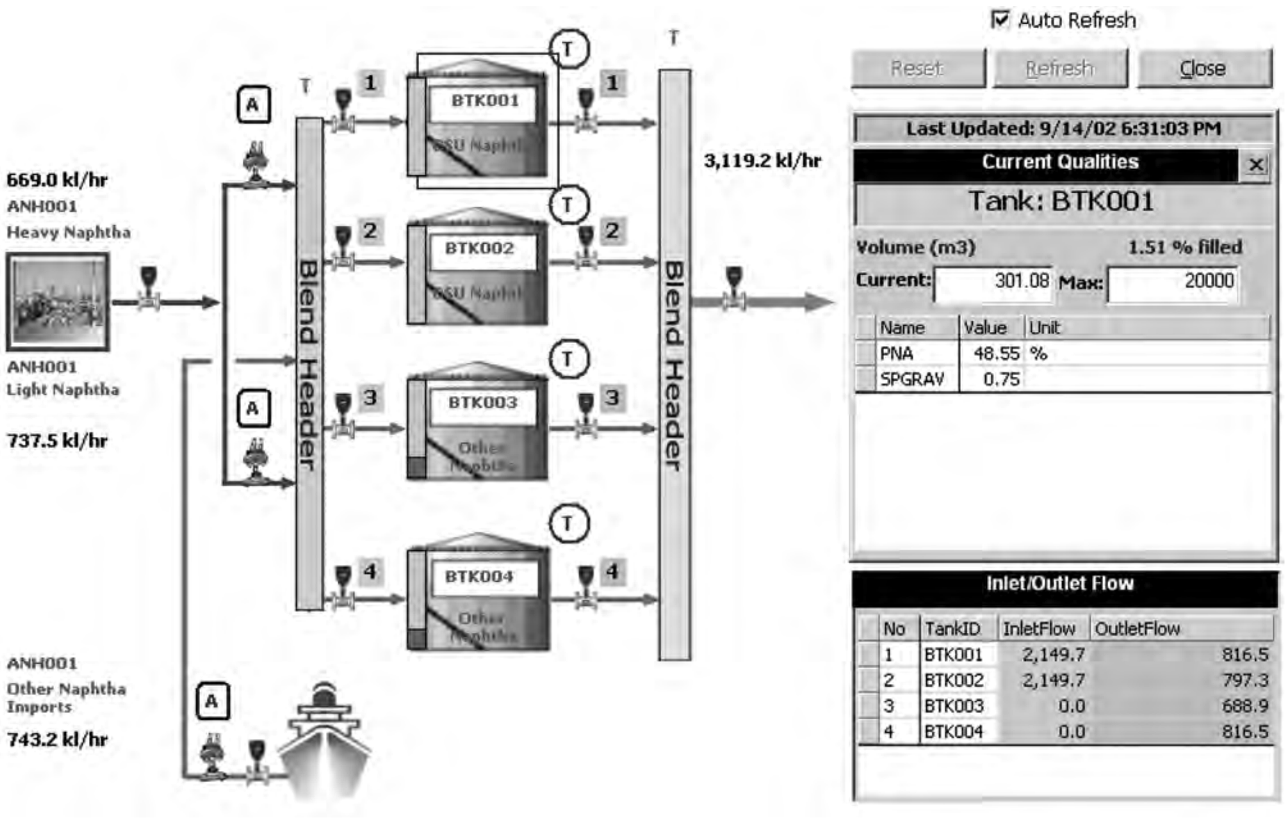
Figure 20.32—Moving tank lube blending. *Source:* [15].

between 90 and 200°C and consists of molecules with 6–12 carbons [15].

Naphtha is used primarily as feedstock for producing high-octane gasoline (via the catalytic reforming process). It is also used in the petrochemical industry for producing ethylene. Natural cut naphtha can have 100 or more components and requires characterization based on boiling range; density; and content of paraffins (n-alkanes), isoalkanes, olefins, naphthenes, and aromatics (PIONA) by carbon number.

Naphtha blending is needed for ethylene manufacturing and it requires precise control of density and PIONA. In a typical naphtha blending strategy, naphtha from different sources are blended into tanks as shown in Figure 20.33.

The next stage of naphtha blending takes the naphtha tanks as blended in stage 1 and the blends into tanks feeding to olefin cracking units as shown in Figure 20.34.



Last Updated: 9/14/02 6:31:03 PM

Current Qualities

Tank: BTK001

Volume (m3) 1.51 % filled

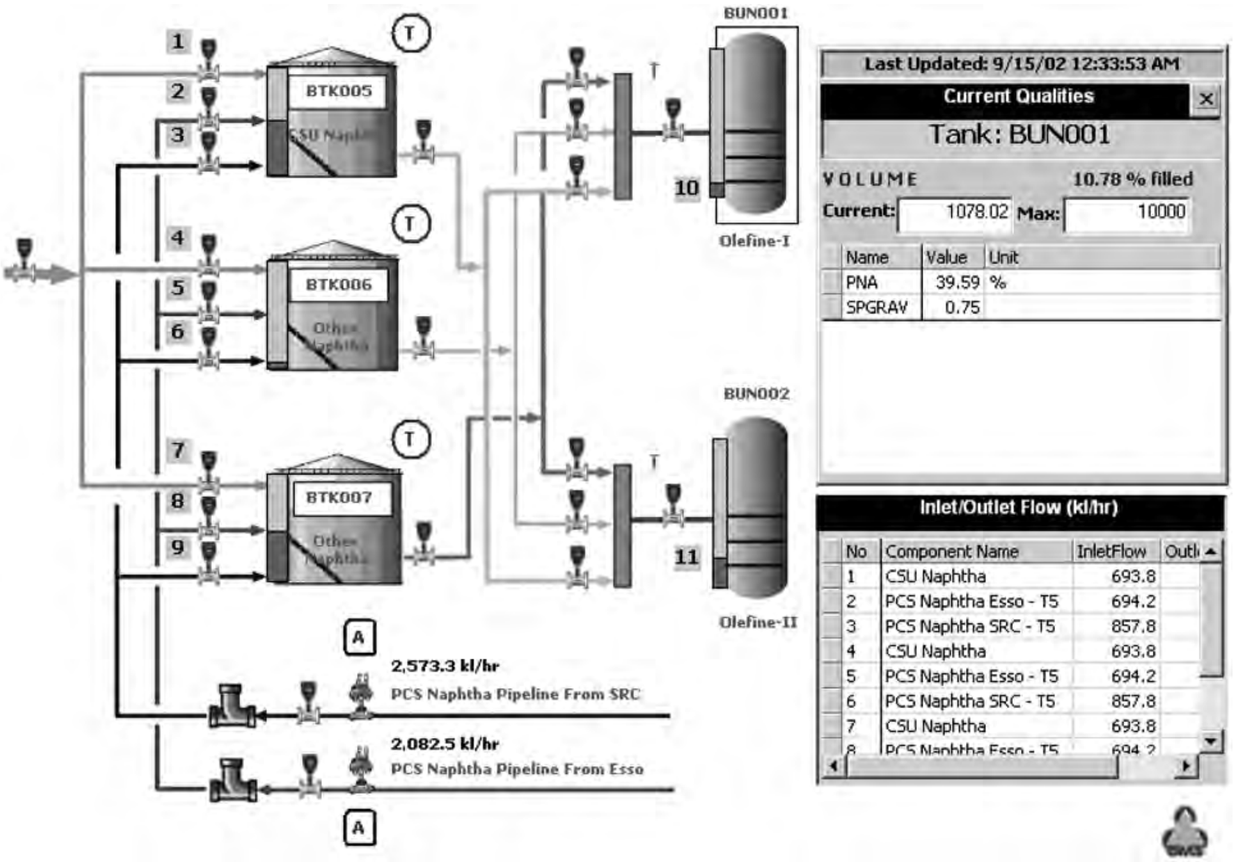
Current: 301.08 Max: 20000

Name	Value	Unit
PNA	48.55	%
SPGRAV	0.75	

Inlet/Outlet Flow

No	TankID	InletFlow	OutletFlow
1	BTK001	2,149.7	816.5
2	BTK002	2,149.7	797.3
3	BTK003	0.0	688.9
4	BTK004	0.0	816.5

Figure 20.33—Stage 1 naphtha blending from supply sources to tanks. *Source:* [1].



Last Updated: 9/15/02 12:33:53 AM

Current Qualities

Tank: BUN001

VOLUME 10.78 % filled

Current: 1078.02 Max: 10000

Name	Value	Unit
PNA	39.59	%
SPGRAV	0.75	

Inlet/Outlet Flow (kl/hr)

No	Component Name	InletFlow	Outl
1	CSU Naphtha	693.8	
2	PCS Naphtha Esso - T5	694.2	
3	PCS Naphtha SRC - T5	857.8	
4	CSU Naphtha	693.8	
5	PCS Naphtha Esso - T5	694.2	
6	PCS Naphtha SRC - T5	857.8	
7	CSU Naphtha	693.8	
8	PCS Naphtha Esso - T5	694.2	

Figure 20.34—Stage 2 naphtha blending from blended naphtha tanks to feed tanks. *Source:* [1].

20.8 SUMMARY

This chapter has briefly but adequately discussed all aspects of tank farm management. Some of the topics could not be discussed in detail because of space limitation, but the author has made an effort to present the reader with an overview of tank farm management. The reader should follow the literature and online resources for more specific details about any of the topics presented in this chapter.

REFERENCES

[1] Offsite Management Systems, LLC (OMSLLC), *Training Manual*, OMSLLC, Sugar Land, TX, 2009.

[2] Nelson, W.L., "What Is Adequate Storage Capacity?," *Oil & Gas J.*, September 7, 1959, p. 184.

[3] Nelson, W.L., "How Much Refinery Storage?," *Oil & Gas J.*, April 23, 1973, p. 88.

[4] Gary, J.H., and Handwerk, G.E., *Petroleum Refining-Technology and Economics*, Marcel Dekker, New York, 1994, pp. 354–355.

[5] Barsamian, J.A., and Whitehead R., "Statistical Method Used to Estimate Refining Tankage," *Oil & Gas J.*, February, 2000.

[6] Al-Otaib, G., and Stewart, M., "Simulation Model Determines Optimal Tank Farm Design," *Oil & Gas J.*, February, 2004.

[7] Agrawal, S.S., "Advances in Tank Quality Measurements Can Help Cut Operational Costs," *Hydrocarbon Process.*, Vol. 86, 2007, p. 67.

[8] Agrawal, S.S., Leong, K.M., Wee, L.H., and James, C.T.J., "Implementation and Benefits of Online Tanks Quality Tracking System in a Singapore Refinery," *Hydrocarbon Asia*, Vol. 15, 2005, p. 36.

[9] "TANKS Emissions Estimation Software, Version 4.09D," http://www.epa.gov/ttnchie1/software/tanks/index.html.

[10] "Emissions Factors & AP 42, *Compilation of Air Pollutant Emission Factors*," http://www.epa.gov/ttn/chief/ap42/index.html.

[11] Agrawal, S.S., "Economics Justifications of an Integrated Oil Movement & Storage Control System," presented at the ISA'96 Conference and Exhibit, Chicago, IL, October 9–12, 1996.

[12] "Oil Movement and Storage," (sales brochure), Honeywell, Inc., Morristown, NJ.

[13] Agrawal, S.S., "Scope of an Integrated Oil Movement and Storage (OM&S) Control System," Proceedings of ISA Conference, New Orleans, LA, October, 1995.

[14] Agrawal, S.S., "Scope and Feasibility of Integrated Crude Blending Control and Optimization System," presented at the ISA'94 Conference and Exhibit, Philadelphia, PA, May 9–12, 1994.

[15] Lube Oil Blending—An Overview for Lube Plants, http://www.jiskoot.com/downloads/TB008%20-%20Lube%20Oil%20Blending.pdf.

21

Refinery Planning and Scheduling

Nan Zhang[1] and Marc Valleur[2]

21.1 INTRODUCTION

To construct an optimization problem in mathematics, there are three main elements: variables, an objective function, and process model/constraints. Optimization variables are always involved in tradeoffs to seek the best objective value, with their changes bringing a certain impact on the objective value. Optimization variables can be either continuous or discrete in nature and therefore can be classified as continuous variables and integer variables. There is a special subclass of integer variables—binary variables. A binary variable can take either 0 or 1 and is very useful to model some discrete conditions such as on/off, yes/no, etc.

The objective function is expressed in terms of optimization variables. The goal of optimization is then to find the values of all of the variables that yield the optimal value of the objective function, which can either be minimization or maximization of a real function.

Depending on the nature and scope of the optimization problem, process model/constraints arise from kinetics; thermodynamics; mass and energy balance; and physical bounds on variables, physical laws, empirical correlations, etc. These constraints are in the form of either equalities or inequalities.

The whole set of equalities and inequalities plus the objective function constitutes an optimization model, which describes the interrelationships among all optimization variables. The general formulation of an optimization problem can be summarized as follows:

$$\begin{array}{ll} \text{Maximize (or minimize)} & f(x, y) \\ \text{subject to:} & h(x, y) = 0 \\ & g(x, y) \leq 0 \\ & x, y \geq 0 \end{array}$$

where:
x is a set of continuous variables and y is a set of integer variables.

21.2 THE PROBLEM OF REFINERY OPTIMIZATION AND DEBOTTLENECKING

Oil refining is one of the most complex chemical industries and involves many different and complicated processes with various possible connections. The task of refinery operation is to generate profit as much as possible by converting crude oils into valuable products such as gasoline, jet fuel, diesel, and so on. Refineries are currently facing stiff competition under more and tighter environmental regulations. The most successful refineries are those that closely monitor their performances, adjust their operations correspondingly, identify their key weaknesses, and correct them promptly. Although these principles are easy to understand, achieving them is very difficult. There are so many decisions involved to achieve the optimal operation for a refinery. From the managerial level, managers need to decide which crudes to process, which products to produce, which operating route to follow, which catalyst to use, which operating mode to choose for each process, etc. From the process level, operators have to determine detailed operating conditions for each piece of equipment, such as temperatures, pressures, detailed process flows, etc. All of the decisions interact with each other. For example, temperature change in a reactor will result in different product distribution and utility consumption, hence different process performance. It may further affect the decisions at the managerial level in terms of feed selection for this process and even overall plant operating route. A cycle of operations [1] has been formed in the refining industry to achieve profitable manufacturing by producing quality products under a safe operating environment (Figure 21.1).

The cycle starts with central planning to determine long- and mid-term operations. Scheduling then deals with short-term day-to-day operations. Advanced control and online optimization translate the goals set by planning and scheduling to real-time process targets, which are executed by regulatory control. Monitoring and analyzing the results provide feedbacks to the initial decision-making procedure. The cycle is completed with overall refinery optimization, the task of which is to find the best combination of those decisions to maximize the overall profit. Because overall refinery optimization almost covers all of the aspects relating to profit-making refinery operations, it is therefore considered one of the most difficult and challenging optimization tasks.

Refinery optimization is to push operation toward the maximal profit until it reaches the limit. Once the profit limit is reached, the only way to further increase profit is to make some changes to the existing plant. For an existing plant, especially when it has been in operation for a considerable period of time, more and more shortcomings emerge, largely because of the change of market situation and the evolution of science and technology. For example, an existing plant does not have enough throughputs to meet current and future market demand, it cannot satisfy new environmental regulations, it consumes too much energy, it does not have sufficient reliability, etc. Spending major capital to build new units can directly solve those

---

[1] The University of Manchester, Manchester, UK
[2] VAL Innovation Consulting, Le Chesnay, France

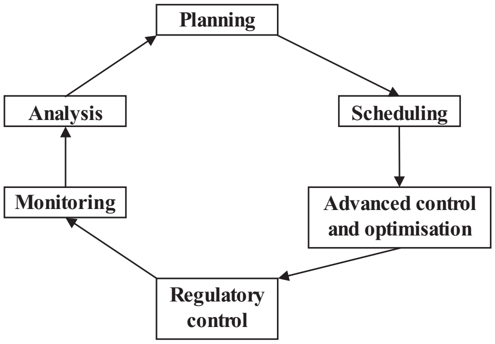


Figure 21.1—The cycle of refining operations.

problems. But more often, revamping (debottlenecking) the existing plant is a more attractive option because an existing plant can usually be modified more quickly with less capital and risks than installing a new unit. To remain competitive, oil refineries are constantly searching for potential debottlenecking opportunities to improve their operations.

21.3 MATHEMATICAL METHODS

In mathematical terms, an optimization problem in oil refineries can be expressed as objective function:

Maximize profit = product sale – material cost – operating cost

or

Minimize cost = operating cost + material cost

subject to:

- Process operations (e.g., kinetics, temperatures, pressures, flow rates);
- Process connections;
- Various limitations (e.g., throughput, product specifications, market demand, and environmental regulations);
- Resource utilization (e.g., power, steam, and hydrogen).

This mathematical formulation can be generally classified as linear programming (LP) and nonlinear programming (NLP). If all of the objective functions and constraints are in linear form, it is LP formulation. If any of them are nonlinear, it is NLP formulation. Because of the economic significance and strong competition, oil companies tend to develop and maintain LP models in-house and there are very few publications available to the general public.

21.3.1 Linear Programming-Based Methods

By assuming complete segregation between defined elements, LP is widely used in refinery optimization. In fact, the state of the art is to use LP or mixed integer linear programming (MILP) for planning purposes of overall refinery operations (e.g., optimizing selections of raw materials and products). LP techniques for overall refinery optimization are relatively mature. In the meantime, many petroleum companies have developed their own LP tools in-house. It is not only because of the speed and robustness of LP, but more important, a complete value structure in terms of marginal prices can be easily obtained, which provides meaningful information on solution explanation and sensitivity analysis [2]. However, LP and MILP models are built based on simplified correlations, which are just a rough approximation for many processes with nonlinear natures. As a result, this kind of model cannot accurately describe the nonlinear aspects.

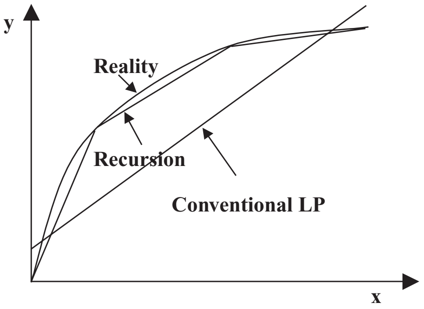


Figure 21.2—Comparison between conventional LPs and recursions.

To mimic nonlinear behavior while maintaining linear formulation, recursion techniques in LP are commonly used, which require sequential execution of several LPs. The solution from the current LP is used as a starting point for the next LP (Figure 21.2).

Although recursion gives more accurate solutions, it not only increases computing time, but it also reduces the transparency of LP's value structure and its economic driving forces and therefore reduces users' confidence [3].

In general, because of the simplistic nature of LP, LP approaches are restricted to long- and medium-term planning for plant-wide optimization and are not suitable for day-to-day and real-time operations.

21.3.2 NLP-Based Methods

The refinery optimization problem is nonlinear in nature, and people have been trying to solve such problems as they are, with some success, especially in local operations such as individual refining processes and blending operation. Furthermore, Aspen PIMS® Advanced Optimization (Aspen PIMS-AO) is a commercial package that allows certain nonlinear features to be solved as a part of the overall refinery model. However, Aspen PIMS-AO cannot be considered as a solution for rigorous overall refinery optimization. In theory, a rigorous NLP model for overall plant operation could be formulated by lumping all of the rigorous process models together. However, to date, there is no commercial NLP software available for rigorous overall refinery optimization. Even suppose that we had such an NLP model built, we would have great difficulties in mathematics and computation to solve such a complex overall plant model [4]. Therefore, layered approaches have been developed [5,6] to overcome such difficulties. Aspen PIMS-SC® also adopts similar ideas in their commercial applications. The essential idea is that a communication mechanism is created between different levels of refinery optimization, with a simplified overall model on top, supported by individual process models, so that a large problem is decomposed and then solved at a relatively small scale.

For individual process optimizations, detailed models are typically used to optimize operating conditions, such as temperatures, pressures, detailed process flows, etc. The results from this kind of optimization are much closer to the reality. However, there is no proper coordination between an overall plant LP optimization and different process NLP optimizations. Therefore, no guideline is provided from the overall plant optimization to process optimizations, which means that individual processes are optimized based on a standalone basis. Consequently, the synergy between plant-wide aspects and process operations cannot be exploited properly, which greatly limits the economic contribution of process optimizations.

21.3.2.1 CASE STUDY

An example of NLP (mixed integer nonlinear programming, MINLP) optimization problems in oil refineries is the design of a heat exchanger network (HEN) for the vacuum gas oil (VGO) hydrotreater unit of an oil refinery [7]. The VGO hydrotreating unit takes VGO and treats and upgrades it to more useful products. During this hydrotreating operation, the boiling range of the feedstock is not altered significantly. Normal hydrotreater reaction temperatures are approximately 300–400°C and the reactions are catalytic. Moreover, the process of hydrotreating consumes large amounts of hydrogen.

In the hydrotreating operation, the feed is first mixed with the hydrogen and heated to the reactor inlet temperature. This can be done by a single furnace but is more efficiently done by reusing waste process heat first and using the furnace to provide the high-temperature heat. Although many reactions take place inside of the hydrotreating units, the net reaction is of exothermic nature and the reactor outlet temperature tends to be somewhat higher than the inlet temperature. Then, the reactor effluent is cooled down and passed to a series of flash separators to separate and recycle hydrogen for reuse. The products are then passed through a hydrogen sulfide stripper to remove most of the hydrogen sulfide present. Finally, a series of distillation columns (simple or complex) separates light hydrocarbons, gasoline, diesel, and gas oil.

During the duration of the hydrotreating process, the catalyst used in the reactor gradually loses its activity. Therefore, to compensate for the loss of reaction rate due to loss of catalyst activity, the reactor inlet temperature is gradually increased. This causes not only disturbances to the HEN in terms of stream inlet and outlet temperatures, but also in terms of reactor outlet compositions, which are the result of changes in operating conditions. This change in composition then affects the flow rates of the diesel and gasoline formed as well as the amount of hydrogen used and recycled. These changes in operating conditions give rise to the need for designing multiple period HENs that are not only feasible for these different conditions but can also provide optimal solutions for all operating conditions.

HYSYS simulation software was used to model the steady-state performance of the VGO hydrotreater unit and subsequent separation units. The operating conditions and some unknown parameters were obtained from the specification of the distillate products in terms of boiling point curves. From the simplified flow sheet, the necessary hot streams (streams which need to be cooled down) and cold streams (streams which need to be heated up) were identified, and the necessary stream data were collected from the simulation. This simulation was repeated for three operating periods:

1. Start of run (SOR),
2. End of run (EOR), and
3. Middle of run (MOR), which uses the average values of SOR and EOR.

These three periods are assumed to have equal durations. In the model it is possible to specify the duration of each period by adjusting parameter DOP(p). The data extracted from the flowsheet are

- Stream inlet and outlet temperatures,
- Stream-specific heats at heat exchanger inlet and outlet, and
- Stream mass flow rates.

The identified streams are presented in Table 21.1.

TABLE 21.1—Stream Identification

Stream Name	Description of Stream in Flow Sheet
H1	Reactor outlet stream to be cooled down
H2	Diesel stream from distillation side stripper to be cooled down
H3	Gas oil stream from reboiler to be cooled down
C1	Reactor inlet stream to be heated to reaction temperature
C2	Stream from low-pressure separator heated to hydrogen sulfide stripper
C3	Stream from hydrogen sulfide stripper heated to distillation inlet temperature
C4	Side stripper reboiler

In this case, the distillation column uses steam stripping in the main column and therefore does not need a reboiler at this position. At higher distillation temperatures, steam stripping proves to be more beneficial than the use of a reboiler in many cases.

The necessary data obtained from the HYSYS simulation are combined in Tables 21.2, 21.3, and 21.4 representing periods SOR, MOR, and EOR, respectively.

The heat capacity flow rates shown in these tables are the average heat capacity flow rates of each stream. It is possible to obtain linear or higher level polynomial functions of C_p with respect to temperature. Constant C_p values were chosen as input to the MINLP model discussed below to allow a robust and reasonably fast solution.

This multiperiod MINLP model minimizes the total annualized cost (TAC). The costs included are capital costs for heat exchanger area and unit and operating costs for utility consumption. The match between two streams is denoted by a binary variable. This binary variable takes the

TABLE 21.2—Extracted Stream Data for SOR

Stream	Inlet Temperature (°C)	Outlet Temperature (°C)	Heat Capacity Flow Rate *F* (kW/K)
H1	393	60	201.6
H2	160	40	185.1
H3	354	60	137.4
C1	72	356	209.4
C2	62	210	141.6
C3	220	370	176.4
C4	253	284	294.4

TABLE 21.3—Extracted Stream Data for MOR

Stream	Inlet Temperature (°C)	Outlet Temperature (°C)	Heat Capacity Flow Rate *F* (kW/K)
H1	406	60	205.0
H2	160	40	198.8
H3	362	60	136.4
C1	72	365	210.3
C2	62	210	141.0
C3	220	370	175.4
C4	250	290	318.7

value of 1 if a heat exchanger exists in any of the operating periods and the value of 0 if no heat exchanger exists in any of the operating periods. The continuous variables to be optimized are stream temperatures for each stage and heat loads for each match in each period.

The constraints consist of a series of equality constraints representing the heat balances at different levels and several inequality constraints for assessing feasibility and defining logical operations.

The overall stream heat balances make sure that each stream receives the amount of heating or cooling that is required for each period.

$$\begin{aligned}&[Tiin(i,p) - Tiout(i,p)] \cdot Fi(i,p)\\&\quad = \sum_{k\in ST}\sum_{j\in CP} q(i,j,k,p) + qcu(i,p), \quad \mathrm{i\in HP, p\in PR}\end{aligned} \tag{21.1}$$

$$\begin{aligned}&[Tjin(j,p) - Tjout(j,p)] \cdot Fj(j,p)\\&\quad = \sum_{k\in ST}\sum_{i\in HP} q(i,j,k,p) + qhu(j,p), \quad \mathrm{j\in CP, p\in PR}\end{aligned} \tag{21.2}$$

To determine the temperatures at each stage, stage-wise heat balances are necessary, which define the total amount of heat rejected or received by a stream in any stage.

$$\begin{aligned}&[ti(i,k,p) - ti(i,k+1,p)] \cdot Fi(i,p)\\&\quad = \sum_{j\in CP} q(i,j,k,p), \quad \mathrm{k\in ST, i\in HP, p\in PR}\end{aligned} \tag{21.3}$$

TABLE 21.4—Extracted Stream Data for EOR

Stream	Inlet Temperature (°C)	Outlet Temperature (°C)	Heat Capacity Flow Rate *F* (kW/K)
H1	420	60	208.5
H2	160	40	175.2
H3	360	60	134.1
C1	72	373	211.1
C2	62	210	140.5
C3	220	370	174.5
C4	249	286	271.2

$$\begin{aligned}&[tj(j,k,p) - tj(j,k+1,p)] \cdot Fj(j,p)\\&\quad = \sum_{i\in HP} q(i,j,k,p), \quad \mathrm{k \in ST, j\in CP, p\in PR}\end{aligned} \tag{21.4}$$

At both sides of the superstructure, the variable temperatures need to be assigned by the inlet and outlet temperatures of all streams. The inlet temperatures of the hot streams will be at temperature location k = 1, and the inlet temperatures of the cold streams will be at temperature location k = NOK + 1.

$$Tiin(i,p) = ti(i,1,p), \quad \mathrm{i\in HP, p\in PR} \tag{21.5}$$

$$Tjin(j,p) = tj(j, NOK+1, p), \quad \mathrm{j\in CP, p\in PR} \tag{21.6}$$

To make sure that there is a monotonic decrease or increase in temperature from the inlet to the outlet temperature, the following constraints are used. Also, the temperatures at the outlet of the superstructure are limited by the stream outlet temperatures. If no utility exists from one given stream, then the outlet temperature of the superstructure equals the stream outlet temperature. If utilities exist for the given stream, then the superstructure outlet temperature can be either greater than the stream outlet temperature (cold utility) or less than the stream outlet temperature (hot utility).

$$ti(i,k,p) \ge ti(i,k+1,p), \quad \mathrm{k\in ST, i\in HP, p\in PR} \tag{21.7}$$

$$tj(j,k,p) \ge tj(j,k+1,p), \quad \mathrm{k\in ST, j\in CP, p\in PR} \tag{21.8}$$

$$Tiout(i,p) \le ti(i, NOK+1, p), \quad \mathrm{i\in HP, p\in PR} \tag{21.9}$$

$$Tjout(j,p) \ge tj(j,1,p), \quad \mathrm{j\in CP, p\in PR} \tag{21.10}$$

Similar to the energy balances for the main set of heat exchangers in the superstructure body, there are energy balances for the utility matches, forming the relationship between the outlet temperatures of the superstructure and the stream outlet temperatures.

$$[ti(i, NOK+1, p) - Tiout(i,p)] \cdot Fi(i,p) = qcu(i,p), \ \mathrm{i\in HP, p\in PR} \tag{21.11}$$

$$[Tjout(j,p) - tj(j,1,p)] \cdot Fj(j,p) = qhu(j,p), \ \mathrm{j\in CP, p\in PR} \tag{21.12}$$

The following logical constraints form the relationship between the existence of a match, its heat load, and the upper bound to this heat load. When a match exists, heat load *q* is bounded by its upper bound, and when no match exists, *q* is forced to zero.

$$q(i,j,k,p) - Qup \cdot z(i,j,k) \le 0, \ \mathrm{i\in HP, j\in CP, k\in ST, p\in PR} \tag{21.13}$$

$$qcu(i,p) - Qup \cdot zcu(i) \le 0, \ \mathrm{i\in HP, p\in PR} \tag{21.14}$$

$$qhu(j,p) - Qup \cdot zhu(j) \le 0, \ \mathrm{j\in CP, p\in PR} \tag{21.15}$$

$$z(i,j,k), zcu(i), zcu(j) \in \{0,1\} \tag{21.16}$$

To ensure feasible driving forces for the heat exchangers, temperature differences for each side of the heat exchanger are calculated and activated by binary variables if the match exists. When no match exists between a pair of streams at a given stage, there is an upper boundary for active temperature differences. For the hot and cold utilities, similar equations exist on the variable temperature side.

$$\begin{aligned} dt(i,j,k,p) &\le ti(i,k,p) - tj(j,k,p) \\ &+ DTup \cdot (1 - z(i,j,k)), \quad \mathrm{i \in HP, j \in CP, k \in ST, p \in PR} \end{aligned} \tag{21.17}$$

$$\begin{aligned} dt(i,j,k+1,p) &\le ti(i,k+1,p) - tj(j,k+1,p) \\ &+ DTup \cdot (1 - z(i,j,k)), \quad \mathrm{i \in HP, j \in CP, k \in ST, p \in PR} \end{aligned} \tag{21.18}$$

$$\begin{aligned} dtcu(i,p) &\le ti(i, NOK+1, p) - Tcu, out \\ &+ DTup \cdot (1 - zcu(i)), \quad \mathrm{i \in HP, p \in PR} \end{aligned} \tag{21.19}$$

$$\begin{aligned} dthu(j,p) &\le Thu, out - tj(j,1,p) \\ &+ DTup \cdot (1 - zhu(i)), \quad \mathrm{j \in CP, p \in PR} \end{aligned} \tag{21.20}$$

The temperature difference on each side of each heat exchanger is then limited by

$$dt(i,j,p) \ge DT\min \tag{21.21}$$

Next, the total hot utility available can be limited by the following constraint:

$$\sum_{j \in CP} qhu(j,p) \le HUup, \quad \mathrm{j \in CP, p \in PR} \tag{21.22}$$

The objective function in [7] contains the following elements:

- Unit costs for all heat exchangers including utility exchangers,
- Mean area costs for all matches (i,j,k),
- Mean area costs for cold utility matches,
- Mean area costs for hot utility matches,
- Weighed cold utility costs, and
- Weighed hot utility costs.

Finally, the objective function is defined as

min TAC =

$$\begin{aligned} & AF \cdot \left[\sum_{i \in HP} \sum_{j \in CP} \sum_{k \in ST} Cf \cdot z(i,j,k) + \sum_{i \in HP} \sum_{CU} Cf \cdot zcu(i) + \sum_{j \in CP} \sum_{HU} Cf \cdot zhu(j) \right] \\ & + AF \cdot \sum_{p \in PR} \frac{1}{NOP} \cdot \sum_{i \in HP} \sum_{j \in CP} \sum_{k \in ST} C \cdot \left[\frac{q(i,j,k,p)}{LMTD(i,j,k,p) \cdot U(i,j)} \right]^B \\ & + AF \cdot \sum_{p \in PR} \frac{1}{NOP} \cdot \sum_{i \in HP} C \cdot \left[\frac{qcu(i,p)}{LMTDcu(i,p) \cdot U(i,cu)} \right]^B \\ & + AF \cdot \sum_{p \in PR} \frac{1}{NOP} \cdot \sum_{j \in CP} C \cdot \left[\frac{qhu(j,p)}{LMTDhu(j,p) \cdot U(hu,j)} \right]^B \\ & + \sum_{p \in PR} \frac{DOP(p)}{NOP} \cdot \sum_{i \in HP} Ccu \cdot qcu(i,p) \\ & + \sum_{p \in PR} \frac{DOP(p)}{NOP} \cdot \sum_{j \in CP} Chu \cdot qhu(j,p) \end{aligned} \tag{21.23}$$

TABLE 21.5—Multiperiod Simultaneous Model

DTmin	HU up	Objective Function
20	50,000	6,439,285
	45,000	6,418,713
	40,000	6,435,752
	35,000	6,491,251
	30,000	6,435,752
	25,000	7,625,869
	20,000	7,295,796
	17,000	INFES
	10,000	INFES
25	50,000	6,416,403
	45,000	7,591,377
	40,000	6,431,203
	35,000	6,410,355
	30,000	6,431,203
	25,000	6,641,023
	20,000	INFES
	18,000	INFES
	10,000	INFES
30	50,000	6,436,234
	45,000	6,435,856
	40,000	6,436,234
	35,000	6,320,508
	30,000	6,437,870
	25,000	6,644,294
	20,000	INFES
	18,000	INFES
	10,000	INFES

To solve the MINLP problem, the model is implemented in the general algebraic modeling system (GAMS), in which CONOPT is used as the default NLP solver and CPLEX for the relaxed MIP problem. The solution to the problem was obtained in 45 s using an AMD Athlon™ 1.66-GHz processor. Table 21.5 shows the results of the combined MINLP-NLP model for minimal temperature differences ranging from 20 up to 30°C. In Table 21.5, the term "INFES" is used when it is impossible to achieve a feasible network featuring those upper limits to the hot utility for the given DTmin. These observations are confirmed by using the pinch analysis to show that the minimal hot utility target is violated.

DTmin has been chosen to vary from 20 up to 30°C for the following reasons:

- Some heat exchangers are able to handle minimal temperature differences that approximate zero.

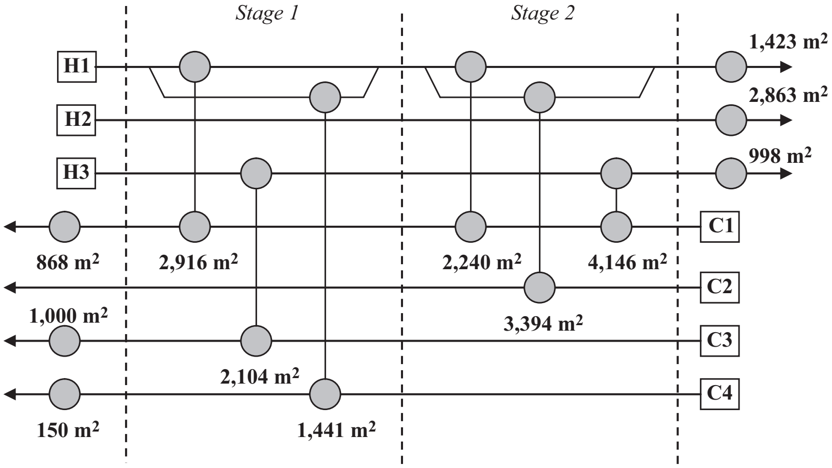


Figure 21.3—Final optimal HEN structure.

- The choice of minimal temperature difference depends mainly on the fluid used, on the application, and on the heat exchanger type.
- For general hydrocarbon oil heat exchangers, temperature differences below 10ºC on either side of the heat exchanger cause early fouling of the exchanger.
- Many hydrocarbon oil exchangers prefer a temperature difference of 20ºC or higher.
- The lowest minimum has been obtained in this range of temperatures.

The maximum value of 30ºC has been chosen because, at higher bounds on temperature difference, there is an increase in annualized cost because of the increase in hot and cold utilities used.

The optimal network for the new model is obtained at a temperature difference bound of 30ºC and a hot utility bound of 35 MW and has a total annual cost of approximately €6.32 million. The optimal design of the HEN is shown in Figure 21.3.

21.3.3 Stochastic Optimization

Deterministic approaches to solve HEN design problems always have their limitations. Sequential approaches decompose the problem into smaller-scale problems at the cost of losing accuracy and optimality. Simultaneous approaches take into account the tradeoff among area, units, and utility cost but need simplifying assumptions to reduce the model to a manageable size. From this limitation, the need for stochastic optimization approaches emerges. Stochastic optimization methods do not rely on any form of superstructure and are often not subject to any decomposition or simplification. Some of the most frequently used methods are simulated annealing (SA), genetic algorithm (GA), and the Tabu search method.

21.3.3.1 SIMULATED ANNEALING

Simulated annealing (SA) is a combinatorial optimization technique that is based on the Monte Carlo principle. The name originates from the analogy with the process of physical annealing, which is the cooling of atoms into a low-energy solid state. This analogy introduces a fictitious temperature, the ”annealing temperature,” into the optimization process. SA relies on a series of random ”moves” that can be either integer moves (match exists or not) or continuous moves (increase or decrease flow, heat transfer, and area). The detailed analogy on which SA is based may be found in Kirkpatrick et al. [8]. For any random move, the difference in cost function is then calculated, and the probability of accepting this move is defined by

$$P = \exp\left(\frac{-\Delta C}{T_{SA}}\right) \tag{21.24}$$

Many random changes in the design are attempted as the annealing temperature is gradually reduced. While one is far away from the global optimum and the annealing temperature is high, the probability of an accepted move is very high. The closer one gets to the global optimum, the lower the annealing temperature becomes and the smaller the probability of accepting a new move. The global optimum is reached when the annealing temperature equals absolute zero and no more moves are allowed. In practice, zero annealing temperature can only be obtained after an infinite amount of time, for which the global optimum is guaranteed to be found. As can be noticed, “It is the ability to accept ‘uphill’ moves in cost that guarantees that SA will generate the globally optimum system if the annealing temperature is reduced to an infinitesimal rate.” [9]

Some papers successfully combined SA with deterministic optimization methods such as NLP. Athier et al. [10] proposed an approach in which the HEN configuration is chosen by SA and an NLP formulation is used to optimize the operating conditions (temperatures and split rates) for a fixed HEN structure. The four moves in their SA algorithm are as follows:

1. Add a heat exchanger at a randomly chosen point in the network.
2. Delete a randomly chosen heat exchanger and remove a split if necessary.
3. Add a splitter on any randomly chosen point in the network and add one or two heat exchangers depending on the topology of the current configuration.
4. Modify a utility level at a randomly chosen hot or cold utility.

The algorithm also features a restore unit that makes it possible to save and restore the previous configuration before the next iteration when a move is rejected. SA has the advantage that it can reach the vicinity of the global optimum for nonconvex, nonlinear, or discrete functions given sufficient solving time. When the problem size is increased to, for example, a multiperiod HEN design, it has not been investigated yet what effect this will have on the CPU solving time.

21.3.3.2 GENETIC ALGORITHMS

Genetic algorithms (GA) are a relatively new method of stochastic optimization that draws the analogy between combinatorial optimization and natural evolution processes. The first papers on GA were published in the late 1970s.

In the process of optimization, a set of chromosomes, which represent possible candidate solutions, evolves toward better solutions. This evolution starts from a random population and evolves through different generations. In each generation, the fitness of the whole population is evaluated and chromosomes are stochastically selected from this population to form the next generation of population, introducing the next iteration in the algorithm. According to Ravagnani et al. [11], the most important genetic parameters are the size of the population (affecting the global performance and efficiency of the algorithm) and the mutation rate (avoiding random search and avoiding stationary points).

21.3.3.3 TABU SEARCH

Originally proposed as an optimization tool in 1977, this stochastic method received little attention until the 1990s. In general, Tabu search is an iterative improvement procedure, starting from an initial feasible point while trying the better solutions. The search for improvement in the objective function is based on the greatest-descent algorithm. Similar to other stochastic optimization approaches, Tabu search has the ability to escape local optima by using a short-term memory of previous solutions. Also, Tabu search allows for backtracking to previous solutions, which might lead to a better optimum in subsequent steps.

In 2004, Lin and Miller [12] introduced Tabu search as a method to design and optimize HENs. In their work, Tabu lists consist of the set of binary variables that represent the heat exchanger match. According to the authors, if the best neighbor is not better than the current solution, it will be classified as "Tabu" (forbidden) and added to a recency-based Tabu list. Old entries are released from the Tabu list at the bottom and new entries are added at the top of the list. This list forms the short-term memory of the program. The frequency-based Tabu list keeps track of the frequency at which a certain solution has been visited and provides the long-term memory of the program. The frequency index allows Tabu search to determine whether the solution is trapped in a certain optimum.

21.3.3.4 OTHER STOCHASTIC METHODS

A few other stochastic approaches have been studied, such as the randomization approach by Chakraborty and Ghosh [13], in which the network design problem is reduced to randomly chosen feasible points. The designer needs to predefine the maximal number of exchangers per stream, and, in this model, no stream splits are allowed, which is a major drawback when compared with other existing approaches.

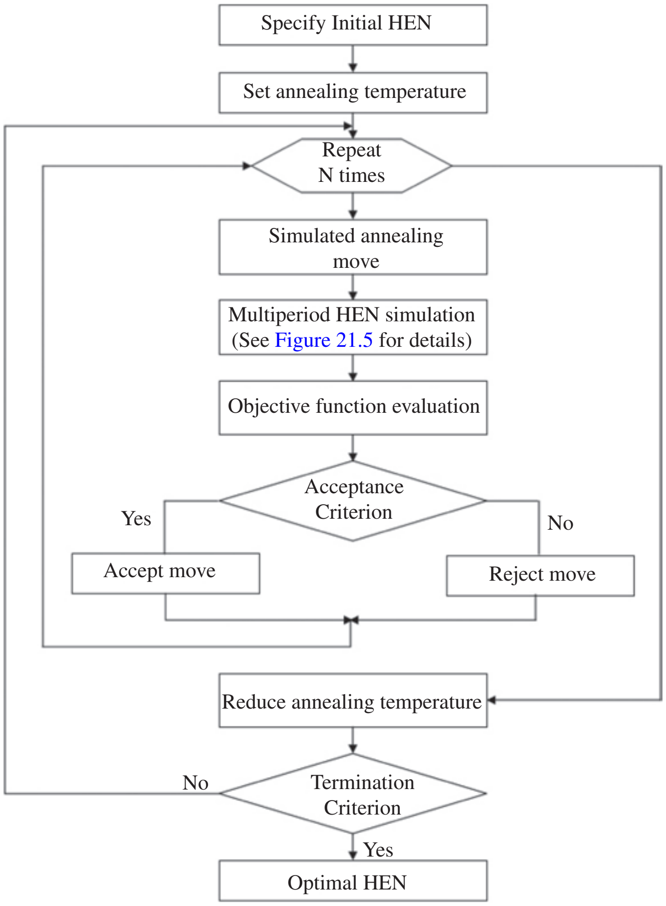


Figure 21.4—SA algorithm for multiperiod HEN design.

21.3.3.5 CASE STUDY

Here the same problem described in Section 21.3.2.1 is solved with SA, to design the HEN in a VGO hydrotreating process [14]. The same objective function for a multiperiod HEN is used to minimize the TAC (i.e., the sum of capital costs [heat exchanger unit costs and maximal area costs] and operating costs [hot and cold utility costs] for all of the periods of operation under consideration). The algorithm for SA is shown in Figure 21.4.

The modifications made by the SA algorithm to a current trial solution are known as random moves. The random moves made by the algorithm depend on the nature of the optimization problem and the variables involved. Table 21.6 presents a list of possible SA moves for modifications to a HEN.

TABLE 21.6—SA Moves for HEN Design

Continuous Moves	Structural Moves
Heat duty change Splitter flow fractions change	Repipe a heat exchanger Resequence a heat exchanger Add a new heat exchanger Remove a heat exchanger Add a splitter-mixer unit Remove a splitter-mixer unit

TABLE 21.7—SA Parameters Used for Optimization of HENs in This Work

Initial annealing "temperature"	0.10E+10
Final annealing "temperature"	0.10E-07
Cooling parameter	0.50E-02
Markov chain length	50
Acceptance criterion	Metropolis

The SA parameters used to obtain HEN for multiperiod operation with minimal TAC are presented in Table 21.7. The TAC for the multiperiod HEN obtained using the proposed methodology for the same minimal approach temperature is 6.34 million (MM) €/year and corresponds to a reduction of 1 % (65,000 €/year) to the minimum value of the objective function obtained using multiperiod MINLP model. The HEN configuration for multiperiod operation obtained by SA is presented in Figure 21.5, which shows the maximal heat duty of each match from all of the three operating periods under consideration.

In this case study, SA gives better results than the deterministic method (CONOPT + CPLEX) for the MINLP problem. However, this is not to say that SA is better for solving general optimization problems. Because of random search algorithms, stochastic methods such as SA, GA, and Tabu search tend to be more time-consuming in computation, less consistent in solution quality (different solutions for different runs), and less efficient in dealing with continuous variables. There is a growing trend nowadays to adopt hybrid optimization approaches that combine deterministic methods (methods for LP and NLP such as Simplex and SQP) and stochastic methods.

21.4 THE CHALLENGES OF REFINERY OPTIMIZATION

The refining industry deals with one of the world's longest and most complex supply chains, beginning at a natural resource in the ground and continuing all of the way through to the end-users. The current picture of the refining industry is characterized by stiff competition; stricter environmental regulations; and heavier, sourer, and costly crude oils, accompanied by possible disruptions caused by various factors that companies cannot control. Therefore, to maintain the profit margins in this ever-changing market environment, refiners need to have smarter strategies for flexible and adoptive operations.

Refinery optimization is to push toward the maximal profit under certain limitations. The potential benefits of optimization for process operations in oil refineries have long been observed, and refiners are increasingly concerned with maintaining their profit margins in changing situations by improving their optimization strategy. The most successful refineries are those that closely monitor their performances, adjust their operations correspondingly, identify their key weaknesses, and correct them promptly. Although these principles are easy to understand, achieving them is very difficult because of the complex nature of the refining business. There are so many decisions involved to achieve the optimal operation for a refinery. All decisions are highly interrelated and the interactions have a large effect on overall refinery profit. Optimization of an individual department or decision does not guarantee the optimal performance of the overall refinery.

21.5 EMERGING TECHNIQUES

Facing various challenges in the ever-changing refining landscape, it is essential that refiners raise their operations to new levels of performance. To gain the greatest potential benefit, some of the key areas related to refinery optimization are identified:

- Moving toward molecular management,
- Improved solution strategies for planning and scheduling,
- Multisupply chain management, and
- Refinery reliability and maintenance management.

Because crude oils and high-boiling crude oil fractions are composed of many members of a homologous series of relatively few hydrocarbons, the composition of the total mixture, in terms of elementary composition, does not vary a great deal. However, small differences in composition can greatly affect the physical properties and the processing required for producing saleable products. In the meantime, refinery products are increasingly specified according to

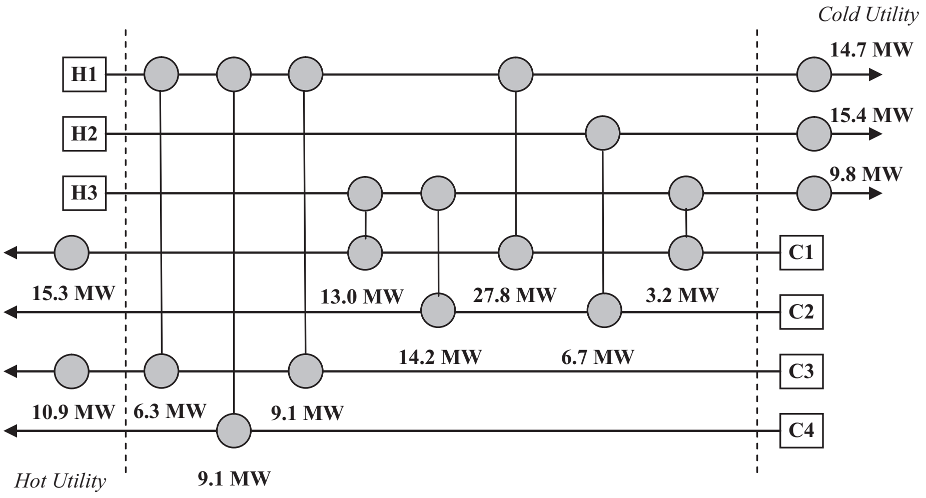


Figure 21.5—HEN for multiperiod operation by SA.

their molecular composition. Therefore, it is inevitable to include molecular information in petroleum mixture characterization [15]. The representation of petroleum mixture composition in a modeling and optimization framework is currently limited by a lack of availability of laboratory data (composition, thermodynamics, and kinetic properties estimation) and available numerical methods to solve large size problems with detailed representation. However, a promising development has been made to overcome this major obstacle [16].

In addition to molecular characterization of refinery streams, today's ever-increasing computing power combined with advances in optimization techniques makes it possible to robustly solve large and complex refinery optimization problems that were previously not feasible, such as integration of cargo scheduling, feedstock managing and monitoring, refinery scheduling, and pipeline scheduling throughout the whole oil supply chain. Deterministic and heuristic solvers have been developed to allow us to extend traditional LP optimization to include nonlinear and mixed integer optimization and therefore accurately reflect the actual operational capability and the constraints of a particular refinery. However, much research is required before the daily or hourly decision-making process in refineries can be practically optimized.

It is also important to recognize that more supply chains intersect the refinery in addition to oil. Among them are petrochemical, gas, hydrogen, and power supply chains. There is no doubt that it has great economic potential to simultaneously address the planning of these multiple supply chains, with major challenges in quality/composition management as well as process integration for tailor-made feedstocks and intermediates to suit consumers in different supply chains. Some companies and researchers are beginning to address this problem.

Unscheduled shutdowns are always moaned by refineries. However, most refineries do not plan for them because it is a common belief that it is something not predictable. Although the unscheduled shutdowns may not be entirely avoidable, they are certainly reducible by using real-time operating information to predict the health of the equipment and process and performing necessary preventive maintenance actions. Progress has been made in various technologies such as equipment monitoring, dynamic performance management, prediction of process degeneration, and preventive maintenance scheduling. The major challenge in this area is how to integrate the individual techniques to form a systematic procedure. Some promising progress has been made in the example of liquefied natural gas plants, but not to the overall refinery to date.

21.6 REFINERY PLANNING AND SCHEDULING

It is essential to recognize that scheduling is about finding feasible operating instructions under short-term constraints. In that respect, the initial goal of the scheduler is to operate the plant within the constraints of a mostly fixed feedstock receipt and product delivery schedule (with some flexibility) to satisfy the optimal plan objectives (operations and ending inventories) while not overflowing any tank or sucking any tank dry.

Although not the only constraint, scheduling inventory is a prerequisite to more elaborate or optimal schedules. Scheduling has the challenging task to translate planning economic objectives into time-stamped operating instructions such as lining up a tank to a jetty or setting a component flow to a gas oil blender. Somehow, scheduling is the bridge between traders and operators. In that respect a refinery scheduler is probably the staff member having the widest knowledge of practical operations.

Proper scheduling of operations is becoming more important because the economic environment is increasingly demanding.

- New commercial specifications, most particularly the low sulfur content of automotive fuels, have an effect on the proper scheduling of tank allocations, line-up selection, and blend sequences to minimize the risks of contamination.
- New crudes or condensates are processed with increasing requirements of segregation by yields, suitability for bitumen production, and sulfur and metal content.
- Shareholders generally limit the available storage for crudes, intermediate streams, and products to minimize the financial costs of excessive inventory.
- Market trends are becoming more dynamic, requesting frequent swings of operating conditions and tank allocations. This is in particular critical for processing refineries.
- Laaschuit [17] and Pinto et al. [18] provide good introductions to scheduling as part of a global supply chain and to planning and scheduling in oil refineries.

21.7 DEFINITION OF OIL REFINERY SCHEDULING

The oil refineries short-term scheduling problem can be formulated as follows:

- Given
    - LP plan averaged targets over the reference time horizon (typically a month);
    - Present status of inventory and process conditions;
    - Present and planned equipment availability and schedule of turnarounds; and
    - Future receipts/liftings qualities, volumes, and dates.
- Find the sequence of optimal dates for
    - Crudes and condensates atmospheric distillation unit (ADU) feed mix and swings;
    - Crude, rundown, and finished product tank allocation changes;
    - Process unit operating mode changes;
    - Oil movement operations, such as transfers from tanks;
    - Batch operations, such as blends and transfers via shared process lines; and
    - Commercial product blending recipe changes.
- Under the following constraints:
    - Thermal constraints, such as furnace duties and skin temperatures;
    - Hydraulic constraints;
    - Hydrogen balance;
    - Environmental constraints and sulfur balance;
    - Fuel gas and steam balance; and
    - Storage segregation requirements.
- Subject to unexpected events, such as
    - Changes from marketing (crudes and products);

- Modification of planning objectives due to a new economic environment;
- Unplanned shutdowns of process units;
- Unavailability of major equipment;
- Process units upsets;
- Estimated time of arrival (ETA) changes; and
- Weather conditions affecting operations, liftings, and receipts.

Unit prices and costs are generally not used by scheduling systems as the economical optimization is performed by the planning tools. In case of significant changes to the economic environment, the LP model can be adjusted to produce new targets for the scheduling. In some cases, notably blending, there can be opportunities for local economic optimization by the scheduling system but always constrained by the LP target.

21.8 BUSINESS INCENTIVES

Benefits from optimal scheduling are always site specific and therefore need to be computed on a case-by-case basis. They generally fall into the following main categories:

- Higher throughput
    - Crude distillation (swings, mix, and tanks)
    - Blenders (tanks, marketing)
- Improved balances
    - Hydrogen (process units operations)
    - Sulfur (environmental constraints)
- Lower operating costs
    - Tank inventory
    - Demurrage
- Enforcement of planning objectives
- Increased flexibility
    - Reaction to unexpected events
    - Capture of marketing opportunities.

In addition to quantitative benefits, an integrated scheduling system also brings qualitative rewards, including better teamwork across marketing, technical services, and operation departments.

21.9 PLANNING VERSUS SCHEDULING

Planning and scheduling systems, although tightly integrated, have different goals and require different techniques [19]. In scheduling tools that provide feasible operation short-term plans, the target provided by the LP model is taken as the economic objective with penalties in case of deviations.

The main question for schedulers is "when?" regarding events and constraints that are generally not represented in the planning model. Scheduling requires tools other than LP to cope with unexpected upsets, short-term fluctuations of demand and supply, transient situations, and limitations of inventory.

One of the major challenges in mathematical programming for oil refineries is the proper integration between the planning LP models and the scheduling tool. LP models are excellent tools for planning activities, such as equilibrium between supply and demand over a month. Planning models can be classified into

- Long-term strategic planning for such exercise as the 5-year capital investment plan, frequently making use of integer programming;
- Tactical planning for annual operating budgets and implementation of new refining schemes; and
- Operations planning, typically the monthly plan, the link with scheduling.

The limitations of LP are well known and have been in particular listed by Neiro and Pinto [20] and by Hartmann [3]:

- All processing options are preselected. In some situations, the scheduler shall have to use additional degrees of freedom and find alternate paths to provide a feasible execution plan.
- Not all constraints can be modeled, for instance, because they are highly nonlinear or heavily depend on real-time process conditions. Constraints are generally limited to mass balances and inventory limitations.
- The consideration of time is limited to the starting and end dates of the LP model period. LP does not answer the essential requirement of scheduling: when to perform actions. In particular, such control variables as blend recipes or conversion unit severities are only averages over the plan time horizons.
- All streams are assumed to be segregated. However, see reference 3 for the use of recursion techniques (successive linear programming).
- Nonlinear properties in the gasoline and middle distillate pools are simulated with blend indices that may have limited accuracy. However, there has been significant progress in the recent years.
    - NLP technology can include a blending library to rigorously model complex blending correlations.
    - Blend indices can be updated from near-infrared (NIR) spectra.
- Changes in a few input data can induce significant modifications to the optimal solution.
- Complex LP models are difficult to maintain so that they keep reflecting the reality of the refinery (crude slate, import feeds or blend components, yields, topology, limitations, and other databook elements).
- Users of LP solutions are engineers of the planning/scheduling department of the refinery, not the control room operators.
- Economics are of interest, with an optimal gross margin as objective function and marginal costs of constrained variables.
- Outputs of LP models are inventory levels at the end of the period and mean targets for selected operating parameters such as blend recipes or process units severities.

A monthly refinery LP model definitely remains the best possible tool to have an economical target, the optimal economic function, considering supply, demand, prices, and some constraints. For the above reasons, it is not the tool to produce feasible short-term operational schedules. Progress has been made in recent years to automatically update parts of the LP model, in particular using blend indices computed from NIR spectra [21].

21.10 SCHEDULING AND COMPLEXITY

21.10.1 Scheduling Time Horizon

The scheduling time horizon is generally defined by the availability of reasonably firm receipts and lifting dates. In some easy cases, the supply chain is very regular with significant advance notice of changes to the lifting plan.

Coastal refineries can face significant time variations because of weather conditions. For example, North Sea crude receipts can be delayed by several days. As a consequence, scheduling time horizon can vary between a week and a month. It is important to choose a representative period and whenever possible to be in line with the planning period. As an example, a 10-day scheduling time integrated with a 3 × 10 day rolling multiperiod LP plan is generally convenient.

21.10.2 Data Granularity and Precision

Short-term scheduling is interested in precise prediction of future operations; for instance, filling an expedition tank with the right quality determinations at the right time to meet a contractual lifting. This requires precise timing and high-fidelity quality predictions. Consequently, the real-time database must collect simultaneous variables with a time granularity compatible with the most dynamic operating conditions, generally a few minutes. To avoid any bias, all critical process variables should also be reconciled by proper real-time algorithms.

21.10.3 Offsite Scheduling

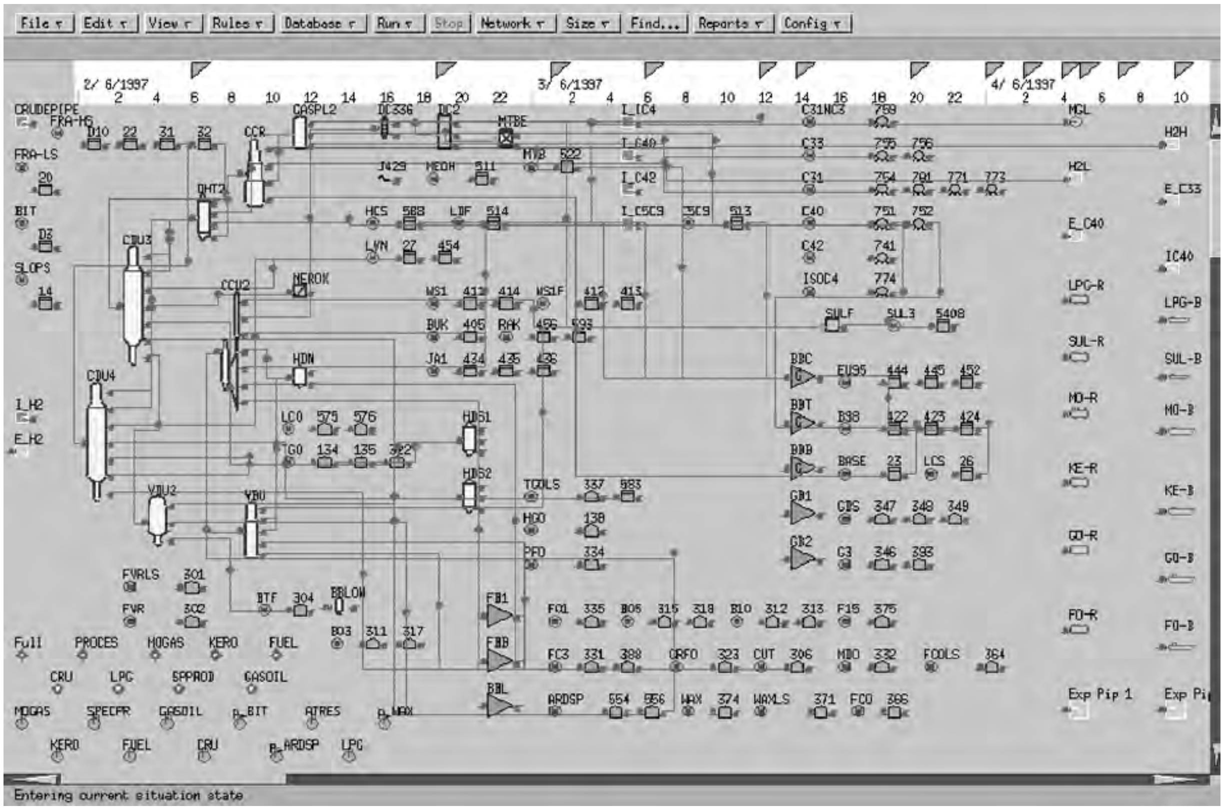
Refinery offsites are a challenge for a scheduling system because they offer many degrees of freedom [22]. As illustrated by Figure 21.6, a medium-size refinery can offer many possible routes.

It is very important to select which offsites decision variables shall be manipulated by the scheduling system such as assignment of one out of N unloading jetties to one out of M crude tanks. There is no practical possibility or even interest to explore all routing alternatives as part of a scheduling tool, and this task should be left to the distributed control system-based oil movement systems that have powerful algorithms to search complex graphs and rank alternative line-ups with such criteria as minimizing flushing or pumping costs. However, many of the scheduling decisions should relate to offsites, which is one of the reasons why scheduling is so complex, as illustrated by the typical dimensions for a refinery offsite system (Table 21.8).

With limited storage dictated by financial considerations, offsite scheduling is becoming increasingly critical.

TABLE 21.8—Western European Refinery Scheduling Complexity

Crude slate	20–40 different crudes per year
Tank farm	100–400 tanks
Product grades	20–50 Mogas, middle distillates
Imports	10–20 feeds, blend components
Process units	10–50
Mogas blend components	6-18
Middle distillates components	4–12
Ships and barges	50–250 ships per month
Trucks	300–900 trucks per day
Crude swings	3–10 per week
Oil movement operations	10–100 per day



Entering current situation state

Figure 21.6—Offsite scheduling.

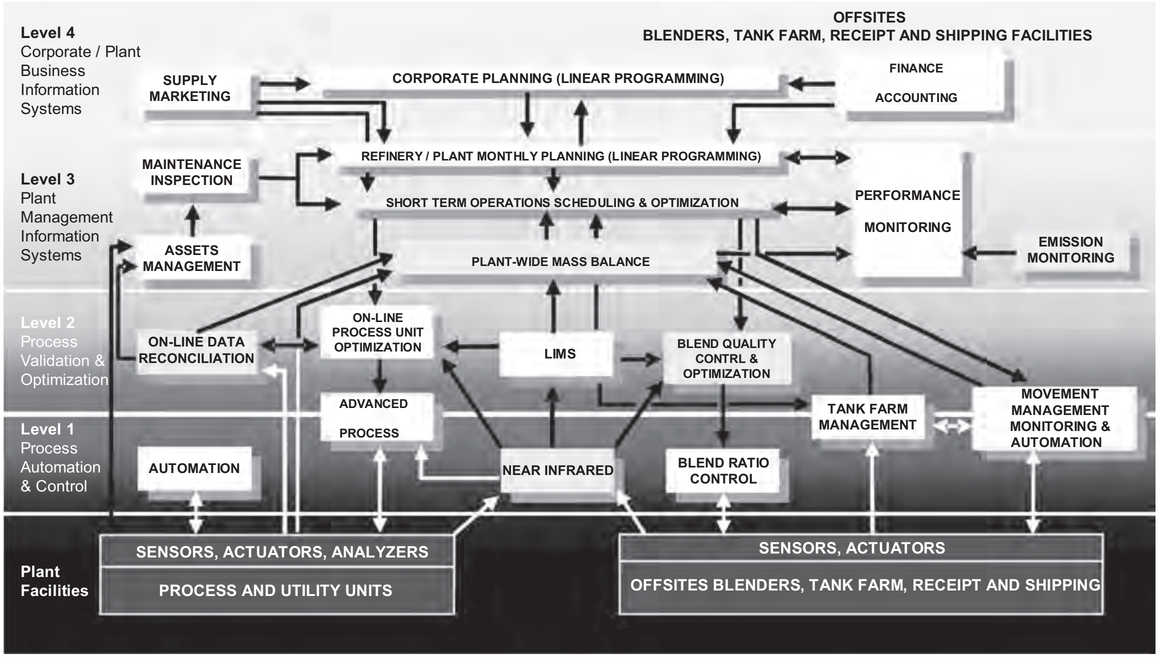


Figure 21.7— Information flows in refinery decision support systems.

21.10.4 Scheduling and System Integration

21.10.4.1 GENERAL

As illustrated by Figure 21.7, scheduling is a node for information flows.

21.10.4.2 SYSTEM ARCHITECTURE

To avoid large combinatorial problems that are difficult to solve in a reasonable time, three main subsystems that address different areas of the processing can be solved concurrently:

1. Crude optimization,
2. Process unit scheduling, and
3. Gasoline blend scheduling.

These subsystems are integrated so that decisions and results are automatically passed from one subsystem to the others. The scheduling application is also integrated within the refinery system environment to facilitate the access to input/output data.

To be practical, a scheduling system must apply the following main concepts:

- The scheduling application is a rolling application and the time horizon can be different for each subsystem.
- All decisions generated by the application can be overwritten by the user.
- The application must allow teamwork.
- The application must be robust and must provide results easy to understand and to check.
- The application must provide facilities to store case studies as reference files.

21.10.4.3 INTEGRATION WITH MANAGEMENT INFORMATION SYSTEMS

A successful implementation of scheduling in complex refineries is highly dependent on a robust and efficient management information system (MIS) that automates secure flow of information between scheduling and the following subsystems:

- Laboratory information management system (LIMS),
- Computerized maintenance management system (CMMS),
- Planning system,
- Performance monitoring system, and
- Offsites management system (tank management and line-up management).

Information requirements typically include

- Structural data
  - Refinery topology
  - Process unit capacities
  - Tank capacities and possible allocations
  - Description of loading/unloading facilities
- Crude data
  - Crude assays (sufficiently detailed)
- Real-time data
  - Tank inventory
  - Process stream flows and quality determinations
- Marketing data
  - Crude availability: quality, volume, and ETA
  - Forecasted liftings: grades, volumes, and ETA
- Planning data
  - Monthly LP plan: average targets

21.11 MATHEMATICAL TOOLS FOR SCHEDULING

21.11.1 General

With high process scheme complexity, large crude slate, and very dynamic markets, scheduling departments need more than a spreadsheet to find an optimum among a myriad of feasible alternatives. Optimal scheduling is a challenging problem from the mathematical viewpoint because it combines discrete and continuous time representation with hundreds of discrete decision variables. Scheduling deserves its reputation of complexity and remains the subject of university research [23–27].

21.11.2 Requirements for Scheduling Tools

Scheduling systems are used to provide an answer to the following questions: When and how do we modify operating conditions, and what do we do in case of an unexpected event? Users are the engineers of the planning/scheduling department of the refinery and control room operators. Outputs are warnings on constraints violations and instructions to the control room operators that can be translated into set points or instructions to field operators. Economics are considered as given by the LP model through the mean optimal operating conditions. Unlike LP models, scheduling systems are connected to the real world in real time and take into account unexpected events. Special care must be given to the integrity of automated data collection.

21.11.3 Mathematical Programming Technologies

Scheduling systems typically combine several software technologies to solve the scheduling problem [28,29].

21.11.3.1 SIMULATION

Whenever there is a need for accuracy, using LP yield and quality vectors to represent the output of a process unit is not sufficient. Consequently, scheduling systems can in some instances have a library of simplified process unit models that use shortcut methods or correlations that can be tuned to the actual plant operations. For example, this possibility has proved to be useful for such major units as the ADU or for fluid catalytic cracking (FCC), for instance, to have an accurate prediction of middle distillate pool qualities.

21.11.3.2 RULES

Rules can be used, sometimes as part of an expert system, whenever operational practices can be modeled. These rules include those of tank allocation for process units feeds or rundowns and rules for settling or draining tanks. In some cases, expert systems and mixed integer programming can be used as a hybrid system [30].

21.11.3.3 CONSTRAINT PROGRAMMING

Constraint programming is a logic-based optimization tool to take care of multiple constraints and reduce the combinatorial aspect of the scheduling problem. Constraint logic programming (CLP) is well suited to solving large combinatorial problems [31], known as NP-complete, that can be found in resource allocation (e.g., ships to births). Such large problems can easily exceed present and near-future computing capabilities if they are tackled by systematic search procedures that explore all tree branches and backtrack when reaching dead ends. CLP includes specific knowledge about variables and makes use of constraints to limit the search domain.

Constraint handling languages allow for controlling the search strategy and the definition of such global constraints as

- Cumulative constraints to express cumulative resource limits over a period;
- Disjunctive constraints to express nonoverlapping tasks, a frequent problem in discrete manufacturing; and
- Precedence constraints.

An example is given in reference [32] for the lubricant manufacturing industry.

21.11.3.4 DISCRETE OPTIMIZATION METHOD

A review of optimization techniques is given in references [33] and [34]. Enormous progress has been made in the last 25 years, and mathematical programming techniques are now being used in real time to optimize nonlinear processes. Microsoft Excel includes a gradient-based NLP solver.

Optimization techniques used for scheduling include essentially MILP and MINLP, today certainly the most appropriate technologies to solve large supply chain optimization problems, in some cases with over 100,000 variables. An introduction to MINLP is given in references [35–37].

Subject to constraints on the number of binary variables and the stability of the solution, MILP is well suited to solve combinatorial problems. However, MILP problems are NP-complete; that is, the computation time increases exponentially with the number of decision variables. This remains a limitation when solving large scheduling problems [38]. More recently [39], scheduling optimization under uncertainty is becoming feasible using concepts from fuzzy set theory and interval arithmetic.

21.11.3.5 OTHER NLP TECHNIQUES

One example is the use of zonotopes to maximize the flexibility of producing future blends. The technology is used to solve the problem of the paint dealer that has units of gray, white, and black paints and must satisfy successive client demands by mixing its stock. The problem is how to manage this stock and maximize the probability of answering future client orders.

This geometric management of the stock has been applied by TOTALFINAELF [40] on middle distillates. When the demand statistical distribution can be estimated, the method can incorporate this partial knowledge of the future to provide an optimal sequence of blends. Other potential techniques for optimization include

- Direct search methods and derivative-free optimization (DFO),
- SA,
- Ant colony algorithm,
- GA,
- Greedy algorithms (often used to find initial solutions),
- Tabu search,
- Variable neighborhood search, and
- Smoothing methods.

21.12 INDUSTRIAL APPLICATIONS OF SCHEDULING

The most famous industrial scheduling applications include

- The travelling salesman problem,
- Time table optimization, and
- Fleet routing.

In the oil refining industry, the most common scheduling applications relate to crude oil, blending, and logistics.

21.12.1 Crude Oil Scheduling

Regarding advanced process control (APC), the crude distillation units are primary targets for optimal scheduling [27,41–46]. In many process schemes, it is essential to operate the crude unit at its maximal capacity and with proper cut points to obtain the best possible feeds for downstream units.

The problem is not always trivial because it is unusual for a refinery to process only a couple of crude oils with

TABLE 21.9—Crude Scheduling Problem Size

Crude slate	20–40 different crudes per year
Crude tankers capacity	200–1,000 kbbl
Crude jetties	2–4
Remote crude tank farm	5–12 tanks
Refinery crude feed tanks	2–5 tanks
ADU units	1–4
Vacuum distillation units (VDU)	1–4
Crude swings	3–10 per week

plenty of storage. In Western Europe and processing refineries worldwide, the crude slate is very significant and logistics are heavily constrained.

Whenever the crude oils are received by pipelines, the refinery tools must be synchronized with the pipeline scheduling system to anticipate the batch deliveries and associated constraints of volumes and qualities, such as buffer zone tank allocation. The size of the problem can justify advanced optimization methods (Table 21.9).

The most difficult issues include

- The approximate knowledge of crude assays,
- The time periods for settling and dewatering,
- The flushing periods of shared pipelines,
- The uncertainty on ETAs for crudes delivered by tankers,
- The crude segregation requirements, including:
  - Sulfur content,
  - n-Paraffins content for arctic middle distillates,
  - Suitability for production of bitumen or base oils,
  - Hygroscopic crudes, and
  - Metal content for a delayed coker unit.

21.12.2 Blending Scheduling

Short-term scheduling of transportation fuel blends is also a major concern because it is closely related to the schedule of commercial product liftings. Here again, the objective is to have a minimal inventory but still meet all demands [45,47–51].

The use of advanced inline analytical technologies affects the product delivery business processes. In particular, inline certification of commercial products can reduce the level of inventory required to satisfy the market demands. The difficulty of short-term blending scheduling is dependent on the number of grades, the dynamics of the commercial contracts, and the number and capacity of tanks for blend components and commercial products.

21.12.3 Lube Oil Production

Lube oil production is a combination of continuous and batch processes and is therefore very complex from a scheduling viewpoint. MILP has been used in some lube plants [52].

21.13 COMMERCIAL SCHEDULING TOOLS

There are many commercial scheduling packages available on the market, but not all are suitable for precise continuous scheduling. As a matter of fact, there are more solutions for discrete manufacturing such as automobile or batch chemistry than for oil refining.

Several companies offer suitable scheduling software technologies with various degrees of complexity, from simple spreadsheet simulation to partial optimal scheduling. In particular, the selection criteria should include [53]

- Adequacy of the scheduling tool to the specific refinery problem(s),
- Maintainability of models by the refinery staff,
- Long-term support from the software vendor,
- Ease of integration to the refinery MIS and enterprise resources planning (ERP) to avoid manual entries, and
- Use of modern IT technology [39] to avoid short-term obsolescence:
  - Service-oriented architecture,
  - Web services, and
  - Object-oriented data model.

21.14 THE HUMAN FACTOR

The planning/scheduling department of oil refineries generally has a high profile in the organization [54]. Quite often regrouped with economic studies and performance monitoring staff, the schedulers of complex European refineries play a major role in day-to-day operations.

From a head-count viewpoint, the range is 4–10 schedulers, mostly depending on the complexity of operations. The optimal blend of skills is obtained by a team of

- Operational staff having a long experience of the refinery, especially oil movement, and
- Bright engineers with open minds to find new solutions and test new tools.

Even more than for any other computerized systems, the quality of the staff is the prime success factor, along with their ability to work as a single team. The staff comprises crude traders, marketers, logistics specialists, process engineers, laboratory chemists, and field and control room operators.

21.15 CONCLUSIONS

There is a huge potential for hard benefits capture when using optimal scheduling in process plants with high supply/demand dynamics, severe constraints, and large operational flexibility. The issue is complexity: Solving the optimal scheduling problem of an oil refinery from incoming crude to commercial product liftings is at the edge of the present mathematical programming technology.

No process plant can afford to keep a team of PhDs in mathematics to run the scheduling system; therefore, a compromise is required to have a manageable and robust solution to the optimal scheduling problem. Proper representation of constraints, concurrent use of different mathematical programming techniques, and integrations of scheduling subsystems are key prerequisites to success.

REFERENCES

[1] Pelham, R., and Pharris, C., “Refinery Operations and Control: A Future Vision,” *Hydrocarbon Processing*, July, 1996, pp. 89–94.

[2] Simon, J.D., and Azma, H.M., “Exxon Experience with Large Scale Linear and Nonlinear Programming Applications,” *Comp. Chem. Eng.*, Vol. 7, 1983, pp. 605-614.

[3] Hartmann, J.C.M., “Distinguish between Scheduling and Planning Models,” *Hydrocarbon Processing,* July, 1998, pp. 93–100.

[4] Grossmann, I.E., and Biegler, L.T., “Optimizing Chemical Processes,” *Chem. Tech*., December, 1995, pp. 27–35.

[5] Zhang, N., and Zhu, X.X., “Novel Modelling and Decomposition Strategy for Total Site Optimisation,” *Comp. Chem. Eng.*, Vol. 30, 2006, pp. 765–777.

[6] Shah, N., Saharidis, G.K.D., Jia, Z., and Ierapetritou, M.G., “Centralized-Decentralized Optimization for Refinery Scheduling,” *Comp. Chem. Eng.*, Vol. 33, 2009, pp. 2091–2105.

[7] Verheyen, W., and Zhang, N., “Design of Flexible Heat Exchanger Network for Multi-Period Operation,“ *Chem. Eng. Sci.*, Vol. 61, 2006, pp. 7730–7753.

[8] Kirkpatrick, S., Gelatt, C.D., Jr., and Vecchi, M.P., *Optimization by Simulated Annealing*, IBM Computer Science/Engineering Technology Report, IBM Thomas J. Watson Research Center, Yorktown Heights, NY, 1982.

[9] Dolan, W.B., Cummings, P.T., and Le Van, M.D., “Algorithmic Efficiency of Simulated Annealing for Heat Exchanger Network Design,” *Comp. Chem. Eng.*, Vol. 14, 1990, 1039–1050.

[10] Athier, G., Floquet, P., Pibouleau, L., and Domenech S., “Optimization of Heat Exchanger Networks by Coupled Simulated Annealing and NLP Procedures,” *Comp. Chem. Eng.*, Vol. 20 (Suppl.), 1996, pp. S13–S18.

[11] Ravagnani, M.A.S.S., Silva, A.P., Arroyo, P.A., and Constantino, A.A., “Heat Exchanger Network Synthesis and Optimization Using Genetic Algorithm,“ *Appl. Therm. Eng.*, Vol. 25, 2005, pp. 1003–1017.

[12] Lin, B., and Miller, D.C., “Tabu Search Algorithm for Chemical Process Optimization,” *Comp. Chem. Eng.*, Vol. 28, 2004, pp. 2287–2306.

[13] Chakrabhorty, S., and Ghosh, P., “Heat Exchanger Network Synthesis: The Possibility of Randomization,” *Chem. Eng. J.*, Vol. 72, 1999, pp. 209–216.

[14] Ahmad, M.I., Chen, L., Jobson, M., and Zhang, N., “Synthesis and Optimisation of Heat Exchanger Networks for Multi-Period Operation by Simulated Annealing,” *PRES 2008*, Prague, Czech Republic, August 2008.

[15] Briesen, H., and Marquardt, W., “New Approach to Refinery Process Simulation with Adaptive Composition Representation,” *AIChE J.*, Vol. 50, 2004, pp. 634–645.

[16] Aye, M.M.S., and Zhang, N., “A Novel Methodology in Transforming Bulk Properties of Refining Streams into Molecular Information,” *Chem. Eng. Sci.*, Vol. 60, 2005, pp. 6702–6717.

[17] Laaschuit, W., and Thijssen, N., “Supporting Supply Chain Planning and Scheduling Decisions in the Oil and Chemical Industry,” *Comp. Chem. Eng.*, Vol. 28, 2004, pp. 863–870.

[18] Pinto, J.M., Joly, M., and Moro, L.F.L., “Planning and Scheduling Models for Refinery Operations,” *Comp. Chem. Eng.*, Vol. 24, 2000, pp. 2259–2276.

[19] Shobrys, D.A., and White, D.C., “Planning Scheduling and Control Systems: Why Can’t They Work Together,” *Comp. Chem. Eng.*, Vol. 26, 2002, pp. 149–160.

[20] Neiro, S.M.S., and Pinto, J.M.A., “General Modeling Framework for the Operational Planning of Petroleum Supply Chains,” *Comp. Chem. Eng.*, Vol. 28, 2004, pp. 871–896.

[21] Valleur, M. and Grué, J.L., “Optimize Short-Term Refinery Scheduling,” *Hydrocarbon Processing*, June, 2004, pp. 46–49.

[22] Chryssolouris, G., Papakostas, N., and Mourtzis, D., “Refinery Short-Term Scheduling with Tank Farm, Inventory and Distillation Management: An Integrated Simulation-Based Approach,” *Eur. J. Oper. Res.*, Vol. 166, 2005, pp. 812–827.

[23] Cassio, R.T., *Oil Refinery Scheduling Optimization*, MSci Thesis, Cranfield University School of Engineering, Department of Process and System Engineering, Cranfield, United Kingdom, 2003, pp. 1–178.

[24] Leyffer, S., and Linderoth, J., *Integer Nonlinear Optimization*, Argonne National Laboratory, Lawrence Livermore National Laboratory, Livermore, CA, 2007.

[25] Lee, J., and Leyffer, S., *Mixed-Integer Nonlinear Optimization: Algorithmic Advances and Applications*, Institute for Mathematics and its Applications, University of Minnesota, St. Paul, MN, 2008.

[26] Pinto, J.M., *Scheduling Logistics, Planning, and Supply Chain Management for Oil Refineries*, Polytechnic University, Universidade de Sao Paulo, Sao Paulo, Brazil, 2008.

[27] Mouret, S., Grossmann, I., and Pestiaux, P., “Multi-Operations Time Slots, Model for Crude-Oil, Operations Scheduling,” in *18th European Symposium on Computer Aided Process Engineering*, B. Braunschweig and F. Joulia, Eds., Elsevier, Amsterdam, The Netherlands, 2008, pp. 593–598.

[28] Kallrath, J., “Introduction: Models, Model Building and Mathematical Optimization. The Importance of Modeling Languages for Solving Real World Problems,” 2003, available at http://www.gams.com/presentations/present_modlang.pdf.

[29] Rochart, G., Monfroy, E., and Jussien, N., *MINLP Problems and Explanation-Based Constraint Programming*, Département Informatique, Ecole des Mines de Nantes, Nantes, France, 2003.

[30] Bok, J.K., Lee, H., Chang, J.W., and Park, S., “Development of Refinery Scheduling System Using Mixed Integer Programming and Expert System,” *Korean J. Chem Eng.*, Vol. 19, 2002, pp. 545–551.

[31] Pountain, D., *Byte*, February, 1995.

[32] Simonis, H., “Cosytec,” 2000, available at http://www.cosytec.com.

[33] Grossmann, I.E., van den Heever, S.A., and Harjunkoski, I., *Discrete Optimization Methods and Their Role in the Integration of Planning and Scheduling*, Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, 2001, pp. 1–29.

[34] Biegler, L.T., and Grossmann, I.E., “Retrospective on Optimization,” *Comp. Chem. Eng.*, Vol. 28, 2003, pp. 1169–1192.

[35] Kallrath, J., “Mixed Integer Optimization in the Chemical Process Industry: Experience, Potential and Future,” *Chem. Eng. Res. Des.*, Vol. 78, 2000, pp. 809–822.

[36] Kelly, J.D., “Formulating Production Planning Models,” *Chemical Engineering Progress*, 2004a, pp. 43–50.

[37] Belotti, P., Lee, J., Liberti, L., Margot, F., and Waechter, A., “Branching and Bound Tightening Techniques for Non-Convex MINLP,” IBM Research Report RC24620 (2008), *Optimization Methods and Software* 24, 2009, pp. 597–634.

[38] Garey, M.R., and Johnson, D.S., *Computers and Intractability—A Guide to the Theory of NP-Completeness*, W.H. Freeman, New York, 1979.

[39] Agrawal, A., and Balasubramanian, K., “Consider Adopting Next-Generation Refinery Scheduling,” *Hydrocarbon Processing*, September, 2006, pp. 65–68.

[40] Girard, D., and Valentin, P., “Zonotopes and Mixtures Management,” *Int. Ser. Num. Math.*, Vol. 87, 1992, pp. 57–71.

[41] Kelly Dean, J., and Mann, J.L., “Crude Oil Blending Scheduling Optimization: An Application with Multimillion Dollar Benefits, Part 1,” *Hydrocarbon Processing*, June, 2003, pp. 47–79.

[42] Jia, Z., and Ierapetritou, M., “Refinery Short Term Scheduling Using Continuous Time Formulation: Crude-Oil Operations,” *Ind. Eng. Chem. Res.*, Vol. 42, 2003, pp. 3085–3097.

[43] Karuppiah, R., and Grossman, I., *Scheduling of Crude Oil Movements at Refinery Front-End*, CAPD Center, Carnegie Mellon University, Pittsburgh, PA, 2006.

[44] Saharidis, K.G., Minoux, M., and Dallery, Y., *Ordonnancement du Pétrole Brut*, Centrale Paris, Centrale Génie Industriel, Paris, France, 2006, pp. 1–44.

[45] Petit, A., *Constraint-Based Local Search for Crude Oil Scheduling*, INRIA Domaine de Voluceau Rocquencourt, France, 2006.

[46] Lee, H., Pinto, J.M., Grossmann, I.E., and Park, S., “Mixed-Integer Linear Programming Model for Refinery Short-Term Scheduling of Crude Oil Unloading with Inventory Management,” *Ind. Eng. Chem. Res.*, Vol. 35, 1996, pp. 1630–1641.

[47] Gruhn, G., Glismann, K., and Rutzen F., ”Integrated Planning and Scheduling for Blending Processes,” *Automatisierungstechnische Praxis atp*, 2000, pp. 1–8.

[48] Jia, Z., and Ierapetritou, M., “Mixed-Integer Linear Programming Model for Gasoline Blending and Distribution Scheduling,” *Ind. Eng. Chem. Res.*, Vol. 42, 2003, pp. 825–835.

[49] Glismann, K., and Gruhn, G., “Short-Term Planning of Blending Processes: Scheduling Nonlinear Optimization Recipes,” *Chem. Eng. Technol.*, Vol. 24, 2001, pp. 246–249.

[50] Hoshino, S., Furuya, N., and Seki, H., *Integrated Scheduling for Gasoline Blending Considering Storage Tanks and Pipe Network*, Tokyo Institute of Technology, Tokyo, Japan, 2007.

[51] Ferreira, A.C., *Modelos de Otimização na Produção de óleo Diesel: Uma Aplicação Industrial*, PhD Thesis, University of Campinas, Campinas, Brazil, 2008.

[52] Barbariol, S., Lusetti, M., Mantilli, M., and Scarioni, M., *Lube Production Scheduling Model at the AGIP Petroli Livorno Refinery*, Operational Research in Industry, Ichor Business Books, West Lafayette, IN, 1999.

[53] Rego, P., and Reichow, R., "Refinery Production Planning," *eptq.com,* Q1, 2005, pp. 99–105.

[54] Freyman, D.G., and Brumbaugh, M.A., "Identifying Roles, Responsibilities Optimizes Refinery Scheduling Process," *Oil Gas J.,* October, 2005, pp. 70–73.

APPENDIX

Abbreviations

CLP	Constraint logic programming
CMMS	Computerized maintenance management system
DFO	Derivative-free optimization
EOR	End of run
GA	Genetic algorithm
HEN	Heat exchanger network
LP	Linear programming
MILP	Mixed integer linear programming
MINLP	Mixed integer nonlinear programming
MIS	Management information system
MOR	Middle of run
NLP	Nonlinear programming
SA	Simulated annealing
SOR	Start of run
TAC	Total annualized costs
VGO	Vacuum gas oil

Indices

i	Hot process stream or hot utility
j	Cold process stream or cold utility
k	Stage number or temperature interval
p	Period of operation

Sets

CP	Set of a cold process stream j
HP	Set of a hot process stream i
PR	Set of an operation period, p = 1,…, NOP
ST	Set of a stage in the superstructure, k = 1,…, NOK

Parameters

	Units	
AF	-	Annualization factor
B	-	Exponent for area cost
C	€/unit	Area cost coefficient for heat exchanger
C_p	[kJ/kg·K]	Specific heat capacity
Ccu	€/unit	Per unit cost for cold utility
Cf	€/unit	Fixed charge for heat exchanger unit
Chu	€/unit	Per unit cost for hot utility
Cw	-	Weight parameter for decrease of areas
DOP(p)	-	Duration of period
DTup	[°C]	Upper bound on temperature difference
epsi	[°C]	Exchanger minimal approach temperature
Fi(i,p)	[kW/K]	Heat capacity flow rate of hot stream i
Fj(j,p)	[kW/K]	Heat capacity flow rate of cold stream j
HUup	[kW]	Upper bound on total hot utility available
MAXarea (i,j,k)	[m^2]	Upper bound on heat transfer area for exchanger connecting streams i and j in stage k
NOK	-	Number of stages
NOP	-	Number of periods
Qup	[kW]	Upper bound on heat exchange capacity
SplitC	-	Existence of split on cold stream j at stage k
SplitH	-	Existence of split on hot stream i at stage k
Tiin	[°C]	Inlet temperature of hot stream
Tiout	[°C]	Outlet temperature of hot stream
Tjin	[°C]	Inlet temperature of cold stream
Tjout	[°C]	Outlet temperature of cold stream
U	[kW/m^2K]	Overall heat transfer coefficient
z1(i,j,k)	-	Existence of match (i,j) in stage k
zcu1(j)	-	Existence of cold utility match for hot stream i

zhu1(i)	-	Existence of hot utility match for cold stream j

Variables

	Units	
A(i,j,k)	[m^2]	Maximal area for match of hot stream i and cold stream j in stage k
Acu(i)	[m^2]	Maximal area for match of hot stream i and cold utility
Ahu(j)	[m^2]	Maximal area for match of cold stream j and hot utility
dtcu(j,k,p)	[°C]	Temperature difference for match of hot stream i and cold utility in period p
dthu(i,k,p)	[°C]	Temperature difference for match of cold stream j and hot utility in period p
dt(i,j,k,p)	[°C]	Temperature difference for match (i,j) at temperature location k in period p
fc(i,j,k,p)	[kW/K]	Heat capacity flow rate of cold stream fraction related to exchanger i,j,k
fh(i,j,k,p)	[kW/K]	Heat capacity flow rate of hot stream fraction related to exchanger i,j,k
obj	-	Objective function, total annualized cost
q(i,j,k,p)	[kW]	Heat exchanged between hot stream i and cold stream j in period p
qcu(i,p)	[kW]	Heat exchanged between hot stream i and cold utility in period p
qhu(j,p)	[kW]	Heat flow exchanged between cold stream j and hot utility in period p
s(i,j,k,p)	-	Slack variable
smin(i,j,k)	-	Minimum of s (i,j,k,p) for match i,j,k
tcs(i,j,k,p)	[°C]	Temperature of cold stream fraction after exchanger i,j,k in period p
ti(i,k,p)	[°C]	Temperature of hot stream i at hot end of stage k in period p, exchanger inlet
ti(i,k+1,p)	[°C]	Temperature of hot stream i at hot end of stage k in period p, exchanger outlet
ths(i,j,k,p)	[°C]	Temperature of hot stream fraction after exchanger i,j,k in period p
tj(j,k,p)	[°C]	Temperature of cold stream j at hot end of stage k in period p, exchanger outlet
tj(j,k+1,p)	[°C]	Temperature of cold stream j at hot end of stage k in period p, exchanger inlet

Binary Variables

zcu(i)	Existence of cold utility match for stream i
zhu(j)	Existence of hot utility match for stream j
z(i,j,k)	Existence of match between i and j in stage k

22

Transportation of Crude Oil, Natural Gas, and Petroleum Products

Luis F. Ayala H.[1]

22.1 TRANSPORTATION OVERVIEW

On a daily basis, petroleum products are transported from source to market inland and across the oceans. The annual volume of petroleum fluids traded and transported worldwide is mind boggling. In 2008 alone, more than 19 billion bbl of crude oil and 28 trillion cubic feet of natural gas were traded across international boundaries [1]. The same year, the world consumed approximately 31 billion bbl of crude oil and 104 trillion cf of natural gas [2]. Transportation, as the economic activity that fixes the geographical imbalance between markets and producers, represents the backbone of international trade. Transportation also permeates every aspect of the daily life within the boundaries of countries, states, or municipalities. In fact, reliable and uninterrupted distribution of energy commodities to consumers is now taken as an implicit characteristic of any functional modern society.

Different methods of transportation are available depending on the type and quantity of transported fluid and distance of delivery. Not surprisingly, the main factor driving the selection of the appropriate transportation mode is cost. The most cost-effective mode of transportation for any given application is the one that can reliably move the commodity from source to destination with the minimum expense—which is a strong function of distance traveled and transportation volume.

Most of the transportation of oil and gas operates in one of two modes: pipeline transportation for inland and transcontinental trade and marine transportation (tankers) for international or intercontinental trade. Ocean tankers are the most common method of internationally moving petroleum products. Marine transportation systems, or tank fleets, are the primary option available for long-distance transportation of internationally traded energy commodities because they make use of a vast network of vessels and ports at a global scale. However, at some point the marine network relies on inland transportation systems for final distribution of goods to the markets. For the case of inland fluid transportation, one of the most effective and efficient means of transportation is the use of pipelines. Pipelines are convenient to manufacture and install and are typically characterized by a significantly long life span, better assurance of continuous delivery, and lower maintenance costs. Whenever distances are not prohibitive, pipeline transportation almost always turns out to be the most economical means of fluid transportation. This situation is illustrated in Figure 22.1 for the case of transportation of natural gas. In this figure, pipeline transportation always comes out ahead for transportation over short distances and can be used over relatively longer distances as long as larger volumes justify their installation. This is always the case for regional trade, in which pipelines remain unsurpassed as the most efficient means of transportation within continental boundaries. As transportation distances increase, pipelines can become uneconomical and marine transportation must be considered (oil tankers for crude oil; liquefied natural gas, compressed natural gas, and gas-to-liquid options for the case of natural gas). Transportation beyond a radius of 2000 km (1243 miles) would typically require marine transport.

An important factor for consideration when examining the cost-effectiveness of transportation is its energy efficiency, or the amount of energy able to be moved per unit volume of transportation capacity or per dollar of transportation expense. From this point of view, oil and liquid products typically have the upper hand over natural gas because they are able to pack the most amount of energy: 1 cf of crude oil can roughly contain as much energy as 1,000 scf of natural gas—this works out to a 1:1,000 energy ratio. This unfavorable energy ratio makes natural gas significantly more costly to transport compared with oil on a unit volume of transportation capacity basis. This also reinforces the selection of pipelines—the transportation mode with the least capital expense and associated maintenance overhead—as the method of choice for transportation of relatively small-to-medium volumes of petroleum products.

The key to economical transportation of large quantities of natural gas lies in the ability to compress it into significantly reduced volumes so that its transportation efficiency can be maximized. The largest volume reduction for natural gas can be obtained through outright liquefaction (LNG, or liquefied natural gas), which can realize a 1:600 reduction in volume. LNG currently dominates the market for maritime transportation of natural gas. Liquefaction is the most drastic reduction of volume that can be accomplished for any given natural gas volume, but it entails a significant capital expense. Such a significant expense can only be offset by the handling of significantly large gas volumes over long transoceanic distances—distances for which any other method would become unreasonably uneconomical. For this reason, Wang and Economides argue that, for smaller volumes of gas over shorter distances, compressed natural gas (CNG) can become economically more attractive than LNG for maritime transport, as shown in Figure 22.1 [3]. CNG technology can achieve up to a 1:200 reduction in volume with a significantly less capital investment

---

[1] The Pennsylvania State University, University Park, PA, USA

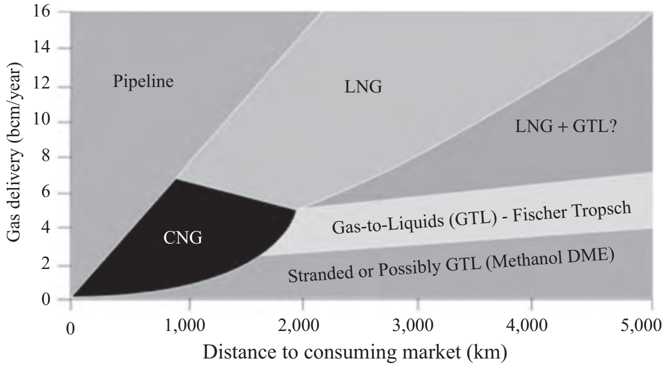


Figure 22.1—Transportation options for natural gas. *Source:* [4].

when compared with LNG. Other transportation options, such as gas hydrates and gas-to-liquids (GTL), have also been suggested. GTL entails a chemical transformation of natural gas molecules into larger hydrocarbon molecules that can be sold and transported as premium fuels, significantly increasing the underlying value of the fuel [5]. Alternative gas transportation options, such as LNG operations, are discussed elsewhere in this handbook. Another option that has received some attention is the transformation of natural gas into its hydrated form. It produces volume reductions of up to 1:180 and thus it has been studied as another potential means of natural gas transportation [6]. In comparison, pipeline applications can accomplish up to a 1:100 reduction in volume for high-pressure applications that use high-grade pipe materials with greater pipe thicknesses.

Among all of these transportation options, pipelining remains the most popular and customary method of moving petroleum fluids from source to destination for inland and near-shore applications. As such, they are the target of study in the transportation chapter of this handbook. In the petroleum industry, all producing wells are equipped with tubular fittings that bring wellstream fluids to the production facilities. For onshore and near-shore applications, pipelines are always the most recommendable option for transportation of fluids to the market. Pipelines are ubiquitous in all refineries and industrial facilities because they provide the connectivity that is needed among all process equipment. Pipeline transportation provides a versatility rarely found in other modes of transportation. Advances in pipeline engineering made it possible to place pipelines in many different environments, including deserts, ocean floors, forests, and mountain ranges. Some of the versatility can come with a strategic cost because pipelines are fixed in place and could be more readily vulnerable to deliberate acts of disruption, international disputes over right of ways and associated tariffs, and associated political risk.

22.2 PIPELINE SIZES AND STANDARDS

In the United States, pipes are manufactured in accordance to various specifications and standards set forth by American Society for Testing and Materials (ASTM International), American Petroleum Institute (API), ASME (American Society of Mechanical Engineers), and ANSI (American National Standards Institute). Table 22.1 shows some commonly specified piping materials used for pressure applications that typically require steel alloys. API specifications 5L and 5LX, common choices in the oil and gas industry along with ASTM A53 and A106, provide guidance for the manufacturing and testing of steel pipes for refinery and transmission service. Low-pressure water, oil, and gas service can use nonmetallic piping material whenever their use can be justified, which commonly leads to lower capital and maintenance overheads. However, steel pipes are required in any high-pressure application.

All commercial steel pipes, regardless of their material specification (Table 22.1), are manufactured with dimensions (diameter and thickness) that comply with standardized designators described by ASME standards B36.10M and B36.19M for welded/seamless wrought and stainless steel, respectively. Pipes used in industry must be dimensionally manufactured in compliance with these ASME standards as per the requirements of the various ASME B31 design codes, as discussed below. Pipe dimensions are set by the use of two nondimensional numbers: the nominal pipe size (NPS) and Schedule number (Sch). NPS is the dimensionless designator of standard pipe sizes and provides a rough, round indication of its outside diameter

TABLE 22.1—Common Pressure Piping Specifications

Specification	Pipe Type	Size Range (NPS)	Application
ASTM A53	Seamless/welded carbon steel	1/8 to 26	Ordinary use in gas, air, oil, water, steam
ASTM A106	Seamless carbon steel	1/8 to 48	High-temperature service
ASTM A369	Forged and bored carbon steel	Custom	High-temperature service
ASTM A335	Seamless carbon steel	Custom	High-temperature service
ASTM A333	Seamless/welded carbon steel	1/8 and larger	Service requiring excellent fracture toughness at low temperature
ASTM A671	Electric fusion welded carbon steel	16 and larger	Low-temperature service
ASTM A672	Electric fusion welded carbon steel	16 and larger	Moderate-temperature service
ASTM A691	Electric fusion welded carbon steel	16 and larger	High-temperature service
ASTM A312	Seamless/welded carbon steel	1/8 and larger	Low- to high-temperature and corrosive service
API 5L, 5LX	Seamless/welded carbon steel	1/8 and larger	Line pipe, refinery, and transmission service

Source: [7].

when measured in inches. Pipes with the same NPS share the same outside diameter; in particular, pipes NPS 12 and smaller have an outside diameter (measured in inches) greater than their NPS whereas pipes NPS 14 and larger have an outer diameter (in inches) exactly equal to their NPS. The inside diameter of a pipe depends on the pipe wall thickness specified by a dimensionless Schedule number. The Schedule number is a designation that varies from its lowest at 5 to its highest at 160 (e.g., 5, 5S, 10, 10S, 20, 20S, 80, 80S). Schedules of stainless steel pipe are followed by the letter S, as per the guidelines of ASME B36.19M. The higher the Schedule number, the thicker and heavier the pipe is made. NPS 12 Schedule 30 has an outside diameter of 12.75 in. and an inside diameter of 12.09 in., whereas NPS 12 Schedule 100 has an outside diameter of 12.75 in. but an inside diameter of 11.064 in. In the United States, thickness designators STD for standard weight (low pressure), XS/XH for extra strong/heavy (medium pressure), and XXS/XXH for double extra strong/heavy (high pressure) are not uncommon and are a legacy from the early years of the U.S. petroleum industry when the dimensional pipe system was known as iron pipe size (IPS). Diamètre nominal (DN) is the size designator in the SI system of units and is a dimensionless value numerically close to the pipe outside diameter expressed in millimeters. For thickness, the SI system uses the Schedule designator.

In terms of design and construction of piping systems, the body of codes and standards for high-pressure piping systems is contained within the ASME B31 pressure piping code, which consists of several sections identified as “B31.X.” For example, ASME standard B31.1 applies to steam piping systems, ASME standard B31.3 applies to process piping in petroleum refining and processing plants, ASME standard B31.4 applies to onshore pipeline transportation of liquid hydrocarbons, and ASME standard 31.8 applies to natural gas transmission and distribution systems. The understanding of these codes is necessary to design a project that meets recognized regulations (codes, standards, and specifications) for it to operate safely, obtain required operational licenses, and even obtain insurance for their operations [8–10].

The pipeline operator must select the most suitable and cost-effective pipe type for the specified service condition. Pipe material type is heavily dependent on operational environment, with steel alloys representing the most common selection for any high-pressure application in the petroleum industry. In turn, pipe dimensions are a function of the required transportation capacity and maximal allowable pressure of operation. The required transportation capacity fixes the minimum allowable internal pipe diameter, and the maximum allowable pressure of operation fixes the minimum allowable pipeline thickness. Pipe design (i.e., the selection of the proper pipe NPS and Schedule) is thus primarily based on the proper calculation of the minimal requirements of pipe diameter and thickness. These calculations are discussed in detail in this chapter for crude oil, petroleum products, and natural gas applications.

22.3 PIPELINE FLOW EQUATIONS

Fluid flow equations through pipes are derived from thermodynamic or energy balances. All fluid flow design equations can be traced back to the same basic energy balance combining the first and second laws of thermodynamics. Such a statement, for steady-state conditions and in its differential form, can be expressed as

$$\frac{dp}{\rho} + \frac{v\,dv}{g_c} + \frac{g}{g_c}dz + \delta lw = 0 \tag{22.1}$$

where:

δlw = compression energy (work) lost because of irreversibilities,

g = gravity acceleration, and

g_c = unit-dependent mass/force conversion constant.

Equation 22.1 recognizes that no work is considered to be done on or by the fluid in pipeline flow. This equation is then integrated between two points to yield the modified Bernoulli equation, or mechanical energy conservation statement, which relates elevation, pressure, and velocity head changes to energy losses. Alternatively, the equation can be recast as a pressure gradient equation by normalizing each of its terms on a per-unit-length of pipe (dx) basis as follows [11]:

$$\left(\frac{dp}{dx}\right)_T = \left(\frac{dp}{dx}\right)_e + \left(\frac{dp}{dx}\right)_a + \left(\frac{dp}{dx}\right)_{lw} \tag{22.2}$$

where:

$\left(\frac{dp}{dx}\right)_e = -\rho\frac{g}{g_c}\frac{dz}{dx}$, or the pressure gradient due to pipe elevation or potential energy changes,

$\left(\frac{dp}{dx}\right)_a = -\frac{\rho v}{g_c}\frac{dv}{dx}$, or the pressure gradient due to acceleration or velocity (kinetic energy) changes, and

$\left(\frac{dp}{dx}\right)_{lw} = -\rho\frac{\delta lw}{dx}$, or the pressure gradient due to irreversible energy losses.

Equation 22.2 allows rewriting the energy balance in terms of the relative contributions that elevation, acceleration, and irreversible losses have to pipeline total pressure drop. Both elevation and acceleration terms represent pressure losses of reversible nature because they are energy quantities retained by the fluid that can be converted back to pressure. Lost mechanical energy that cannot be transformed back into pressure represents an irreversible loss (δlw). In a flowing system, flow irreversibilities (δlw) consist largely of primary or major losses (δlw_f, losses due to frictional effects between the fluid and the pipe wall) and secondary or minor losses (δlw_K, losses due to flow obstacles, presence of fittings, valves, elbows, and sudden changes in diameter) where $\delta lw = \delta lw_f + \delta lw_K$. When considering flow in a straight section of pipe with no fittings where irreversibilities are only generated by wall shear stress (τ_w) between the moving fluid and the stationary pipe wall, $\delta lw = \delta lw_f$. For such a case, and for one-dimensional flow, wall shear stresses are customarily and conveniently calculated in terms of dimensionless friction factors, as shown in Eq 22.3:

$$\begin{aligned}\left(\frac{dp}{dx}\right)_{lw} &= -\rho\frac{\delta lw}{dx} = -\tau_w\frac{\pi d}{A} = -\left[f_F\cdot\frac{\rho v^2}{2g_c}\right]\frac{\pi d}{\pi d^2/4}\\ &= -f_F\frac{2\rho v^2}{g_c d} = -f_M\frac{\rho v^2}{2g_c d}\end{aligned} \tag{22.3}$$

Equation 22.3 embeds the definition of friction factor as the dimensionless ratio of wall shear stress (τ_w) to the fluid inertial force ($\rho v^2 / 2g_c$). In this equation, f_F represents the Fanning friction factor and f_M the Moody friction factor ($f_F = f_M/4$).

In most pipeline flow equations, the contribution of the kinetic energy term to the overall energy balance is considered insignificant compared with the much larger magnitudes of the friction loss and the potential energy terms. By invoking this simplification, Eq 22.2 is integrated over the entire pipe domain (from $x = 0$, $p = p_1$, and $z_1 = 0$ to $x = L$, $p = p_2$, and $z_2 = \Delta H$) to obtain

$$\int_{p_1}^{p_2} \rho\, dp = -\alpha \underbrace{\int_0^L dx}_{friction} - \beta \underbrace{\int_0^L \rho^2 dx}_{elevation} \tag{22.4}$$

where:
$\alpha = (32 \cdot W^2 f_F) / (\pi^2 g_c d^5)$,
$\beta = (g / g_c)(\Delta H / L)$, and
$dz = (\Delta H / L) \cdot dx$.

Equation 22.4 contains two density-dependent integrals: the pressure integral at the left-hand side of the equation and the elevation term contribution at its right-hand side. Because liquid and gas density behavior with pressure is markedly different, different flow equations for the flow of single-phase liquids and single-phase gases would result from the integration of this energy balance.

22.4 FLOW OF SINGLE-PHASE LIQUIDS

For the flow of liquids or nearly incompressible fluids, both density integrals in Eq 22.4 can be readily resolved. After integration, volumetric flow through a horizontal liquid pipe ($\Delta H = 0$) can be shown to be dependent on the difference of linear end pressures as follows:

$$q_L = \left(\frac{\pi^2 g_c}{32} \right)^{0.5} \frac{d^{2.5}}{\sqrt{\rho \cdot f_F \cdot L}} \cdot (p_1 - p_2)^{0.5} \tag{22.5a}$$

For liquid flow, it is customary to express flow equations in terms of pressure head (h_f)—or the equivalent height of the liquid fluid column for which the hydrostatic weight is equal to $p_1 - p_2$; that is, $h_f = (p_1 - p_2) / \gamma_L$ where $\gamma_L = \rho_L \cdot (g / g_c)$, or the liquid specific weight. Equation 22.5a alternatively becomes, when expressed in terms of a generalized short-form representation,

$$q_L = C_L \cdot h_f^n \tag{22.5b}$$

where:
$n = 0.5$ and
C_L = pipe conductivity to liquids, or $C_L = \sigma_L \dfrac{d^{2.5}}{\sqrt{f_F \cdot L}}$, which describes the dependency of pipe transport capacity on the properties of the fluid, flow, and pipe. σ_L is a constant $\left(\sigma_L^2 = \dfrac{\pi^2 g}{32} \right)$ for which the numeric value is clearly unit dependent: $\sigma_L = 3.15$ ft$^{0.5}$/s for the U.S. customary unit system and $\sigma_L = 1.74$ m$^{0.5}$/s for the SI system of units.

From Eq 22.5b, it follows that pressure head losses can be calculated explicitly in terms of flow rate using the following generalized expression for liquid flow:

$$h_f = R_L \cdot q_L^{1/n} \tag{22.6}$$

where:
R_L = pipe resistance to liquid flow, or $R_L = r_L \dfrac{L}{d^m}$, where r_L is the specific resistance to liquids $\left(r_L = \dfrac{f_F}{\sigma_L^2} = \dfrac{f_M}{4\sigma_L^2} \right)$, $m = 5$, and $n = 0.5$.

In direct analogy to electrical circuit theory, pipe resistance increases as pipe length increases and it decreases as the pipe cross-sectional area increases. Specific resistances capture the particularities of the fluid, flow, and pipe characteristics. It is clear from this development that pipe conductivities and resistances are readily related through the expression $C_L = \dfrac{1}{R_L^n}$.

Equations 22.5 and 22.6, derived from fundamental principles and for which $n = 0.5$ and $m = 5$, are collectively known as the Darcy-Weisbach equations for frictional head loss in a horizontal pipe carrying a single-phase liquid. This equation can be extended to flow in inclined liquid pipes by introducing the contribution of potential energy changes in Eq 22.4 in terms of elevation head ($\Delta H \neq 0$). Upon integration,

$$q_L = C_L \cdot \left(p_1 - p_2 - \gamma_L \cdot \Delta H \right)^n \tag{22.7}$$

or, equivalently,

$$h_f = R_L \cdot q_L^{1/n} + \Delta H \tag{22.8}$$

The implementation of Eqs 22.5–22.8 to practical problems requires the calculation of friction factor coefficients, discussed in Section 22.5.

22.5 FLOW OF SINGLE-PHASE GASES

For the isothermal flow of gases, fluid density dependency with pressure ($\rho = \varphi \cdot p$) introduces a much stronger influence of pressure into the makeup of the fluid flow equation. Substitution of this relationship into both density-dependent terms of Eq 22.4 yields, upon integration,

$$p_1^2 - e^s p_2^2 = \frac{2}{\varphi} \alpha L \frac{(e^s - 1)}{s} \tag{22.9}$$

where $s = 2\varphi\beta L$ and $\varphi = (SG_g M_{air}) / (Z_{av} R T_{av})$ with α, β defined previously for Eq 22.4. Equation 22.9 states the well-known fact that the driving force for gas flow through pipelines is the difference of the squared pressures. This is an unequivocal consequence of the now built-in dependency of fluid density on pressure ($\rho = \varphi \cdot p$) in the flow equation, which was assumed inexistent in the derivation of the liquid flow equations ($\rho = const$). In addition, Eq 22.9 also honors the $\rho \rightarrow p$ dependency during the integration of the potential energy or elevation term of Eq 22.4 as originally performed by J.W. Ferguson in 1936 [12]. However, it is not uncommon to find that the contribution of potential energy is alternatively evaluated using a constant average gas density ($\rho_{av} = \varphi \cdot p_{av}$), which simplifies the integration of the elevation term of Eq 22.4 to yield the following simplified version of the gas flow equation for inclined pipes:

$$p_1^2 - p_2^2 = \frac{2}{\varphi}\alpha L + 2\beta L\varphi \cdot p_{av}^2 \tag{22.10}$$

For horizontal flow, $\Delta H = 0,\ s = \beta = 0,\ (e^s - 1)/s \to 1$ and both design equations for gas flow naturally collapse to the same expression. In this case, both expressions can be solved for the gas flow rate evaluated at standard conditions (q_{Gsc}) by making the transformations $W = \rho_{sc} \cdot q_{Gsc}$ and $\rho_{sc} = (p_{sc} SG_g M_{air})/(R \cdot T_{sc})$ to obtain

$$q_{Gsc} = C_G \cdot (p_1^2 - p_2^2)^n \tag{22.11}$$

where $n = 0.5$ and C_G is the pipe conductivity to gas, defined as

$$C_G = \left(\frac{\pi^2 g_c R}{64 M_{air}}\right)^{0.5} \frac{T_{sc}/p_{sc}}{(SG_g T_{av} Z_{av})^{0.5}} \frac{d^{2.5}}{f_F^{0.5} L^{0.5}} \tag{22.12}$$

Pipe conductivity captures the dependency of the flow capacity of the pipe to gas as a function of friction factor, pipe geometry, and fluid properties. Equation 22.11 can also be recast in terms of pressure loss in the following generalized short-form representation:

$$p_1^2 - p_2^2 = R_G \cdot q_{Gsc}^{1/n} \tag{22.13}$$

where:

R_G = pipe resistance to gas,

$R_G = r_G \dfrac{L}{d^m}$,

r_G = pipe specific resistance to gas,

$r_G = \dfrac{SG_G T_{av} Z_{av}}{\sigma_G^2} f_F \left(\dfrac{p_{sc}}{T_{sc}}\right)^2$,

$m = 5$, and

$n = 0.5$.

In this relationship, $\sigma_G^2 = \dfrac{64 M_{air}}{\pi^2 g_c R}$, a dimensional constant for which the ultimate numeric value is dependent on the choice of units for the equation. For customary U.S. field units, σ_G = 2,818 SCF·ft$^{0.5}$ R$^{-0.5}$ in$^{-0.5}$ if q_{Gsc} (SCF/D), L (ft), d (in.), p (psia), and T (R). For SI units, σ_G = 574,901 sm^3/K$^{0.5}$ if q_{Gsc} (sm^3/d), L (m), d (m), p (kPa), and T (K). Again, gas pipe conductivities and resistances are clearly related through the expression $C_G = \dfrac{1}{R_G^n}$.

For flow in inclined gas pipes, Eqs 22.9 and 22.10 are rearranged to derive two versions of the same gas flow equation. If the potential energy evaluation is made based on the calculation of an average gas density value for the entire pipe, Eq 22.10 can be used to show

$$q_{Gsc} = C_G \cdot \left(p_1^2 - p_2^2 - \frac{g}{g_c}\varphi \cdot p_{av}^2 \Delta H\right)^n \tag{22.14}$$

or,

$$p_1^2 - p_2^2 = R_G \cdot q_{Gsc}^{1/n} + \frac{g}{g_c}\varphi \cdot p_{av}^2 \Delta H \tag{22.15}$$

where the definitions of C_G and R_G remain the same as for the horizontal case. Alternatively, when the evaluation of potential energy contribution is made using Ferguson's approach, Eq 22.9 is used to derive

$$q_{Gsc} = C_G \cdot \left(p_1^2 - e^s p_2^2\right)^n \tag{22.16}$$

or,

$$p_1^2 - e^s p_2^2 = R_G \cdot q_{Gsc}^{1/n} \tag{22.17}$$

where the definitions of C_G in Eq 22.12 and R_G in Eq 22.13 must be slightly modified to account for the concept of the equivalent pipe length (L_e):

$$C_G = \left(\frac{\pi^2 g_c R}{64 M_{air}}\right)^{0.5} \frac{T_{sc}/p_{sc}}{(SG_G T_{av} Z_{av})^{0.5}} \frac{d^{2.5}}{f_F^{0.5} L_e^{0.5}} \tag{22.18}$$

and,

$$R_G = r_G \frac{L_e}{d^m} \tag{22.19}$$

In Eqs 22.18 and 22.19, pipe equivalent length is a function of the s-elevation parameter defined above through the following relationship:

$$L_e = \frac{(e^s - 1)}{s} L \tag{22.20}$$

where:

$$s = 2\varphi\beta L = 2\left(\frac{SG_G M_{air}}{Z_{av} R T_{av}}\right)\left(\frac{g}{g_c}\right)\Delta H.$$

In Eq 22.20, $L_e = L$ for horizontal pipes [$(e^s - 1)/s \to 1$ as $s \to 0$]. For uphill flow, $L_e > L$ because $\Delta H > 0$ and $s > 0$. For downhill flow, $L_e < L$ because $\Delta H < 0$ and $s < 0$. In customary field English units, $s = 0.0375\left(\dfrac{SG_G \cdot \Delta H}{Z_{av} \cdot T_{av}}\right)$. The implementation of Eqs 22.11–22.19 to practical problems in natural gas pipeline engineering requires the calculation of friction factor coefficients to be discussed next.

22.6 FRICTION FACTOR CALCULATIONS

Frictional pressure losses are a direct function of wall shear stresses. Frictional losses are thus calculated in terms of the prevailing shear force (i.e., shear stress multiplied by pipe wall surface area) divided by the flow cross-sectional area as shown in Eq 22.3. Friction factors are the dimensionless quantities customarily used in the estimation of these wall shear stresses and are defined as the ratio of shear stress (τ_w) to kinetic energy ($\rho v^2/2g_c$),

$$f_F = \frac{\tau_w}{\rho v^2 / 2g_c} \tag{22.21}$$

for the case of the Fanning dimensionless friction factor. Dimensional analysis of the equations of change applied to flow in circular pipes demonstrates that such a definition of friction factor is directly dependent on Reynolds number for fully developed flows [13]. Reynolds number is the dimensionless parameter that quantifies the ratio of inertia forces to viscous forces and is defined as

$$\mathrm{Re} = \frac{\text{Inertia Forces}}{\text{Viscous Forces}} = \frac{\rho v^2/d}{\mu v/d^2} = \frac{\rho v d}{\mu} = \frac{v d}{\upsilon} = \frac{4q}{\pi d \upsilon} \tag{22.22}$$

where:
μ = fluid dynamic viscosity and
υ = fluid kinematic viscosity.

When viscous forces dominate over inertia forces (Re < 2,100), flow is said to be laminar and friction factors can be readily calculated from the analytical solution to the flow equation for circular pipes as

$$f_F = 16/\text{Re} \tag{22.23}$$

for the Fanning friction factor or, equivalently,

$$f_M = 64/\text{Re} \tag{22.24}$$

for the Moody friction factor. If one substitutes Eq 22.23 into the Darcy-Weisbach liquid flow equation (Eq 22.6), the result is the well-known Poiseuille's law for laminar liquid flow:

$$h_f = \frac{p_1 - p_2}{\gamma_L} = \frac{128 \cdot \mu_L}{\pi \cdot g_c \cdot \gamma_L} \frac{L}{d^4} \cdot q_L \tag{22.25}$$

An analogous expression is not extended to natural gas flow because gas pipe flows are highly turbulent due to the low viscosity of the gaseous phase and exhibit a more significant dependency of density on pressure, which is ignored by Eq 22.6.

When inertia forces overwhelm viscous forces, flow is said to be turbulent or transitional (Re > 2,100). For fully developed turbulent flow conditions, friction factors have been shown to be dependent not only on Reynolds numbers but also on relative pipe roughness (*e/d*) [13]. In this flow domain, dimensionless friction factors must be calculated from experimental data of pressure drop versus flow rates in pipes. In 1944, experimental results on pipe friction available at the time were masterfully consolidated by Lewis F. Moody in the form of the chart reproduced in Figure 22.2. Since then, Moody's chart has become an essential reference in pipe flow calculations. Moody's chart is based on the implementation of the Darcy-Weisbach equation for frictional loss (Eq 22.6) written in terms of Moody friction factors. Before the publication of Moody's chart, the smooth pipe, rough pipe, and transition flow behavior in the turbulent zone had been fully documented, but the selection of proper values of relative pipe roughness (*e/d*) for pipe materials of commercial interest had not been established. Moody's paper made the Darcy-Weisbach equation more readily applicable to engineering problems of interest not only because it aptly summarized the pipe friction data available at the time but also provided engineering guidance for the selection of appropriate values of relative pipe roughness (*e/d*) for pipe materials of commercial application such as riveted steel, concrete, cast iron, and wrought iron. Figure 22.2 provides Moody *f* values directly; thus, to calculate the associated "Fanning" friction factors, the equivalency $f_F = f_M/4$ must be used.

For computer applications, Figure 22.2 has been fitted to a myriad of empirical equations that numerically reproduce the data in the Moody diagram. One of the most

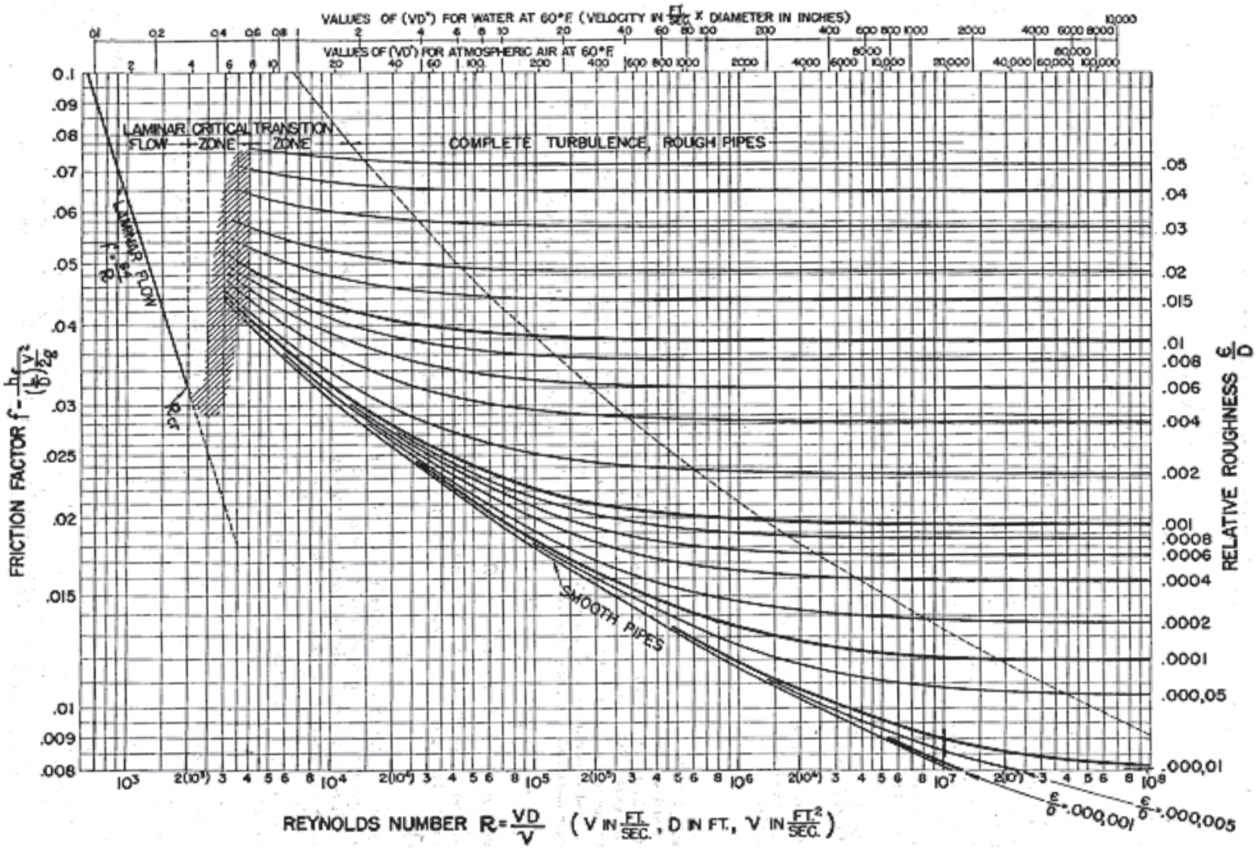


Figure 22.2—Moody friction factor (f_M) chart for the Darcy-Weisbach equation. *Source:* [14].

fitting choices for this purpose is the use of the Colebrook formula [15]:

$$\frac{1}{\sqrt{f_M}} = -2.0\log_{10}\left(\frac{e/d}{3.7}+\frac{2.51}{\mathrm{Re}\sqrt{f_M}}\right) = 1.74 - 2.0\log_{10}\left(\frac{2e}{d}+\frac{18.7}{\mathrm{Re}\sqrt{f_M}}\right) \qquad (22.26a)$$

It is to be noted that Colebrook's equation preceded the formulation of Moody's diagram. Moody's chart was actually drawn on the basis of Colebrook's equation, which combined experimental results of studies of turbulent flow in smooth pipes and rough pipes and allowed for a transition zone between the two limiting behaviors. Therefore, Colebrook's expression is bounded by (and thus can be collapsed to) these two widely known limiting pipe friction behaviors: the smooth pipe law ($e/d \to 0$) shown as Eq 22.26b and the Reynolds-independent rough pipe or fully turbulent equation ($Re \to \infty$) shown as Eq 22.26c.

$$\frac{1}{\sqrt{f_M}} = -2.0\log_{10}\left(\frac{2.51}{\mathrm{Re}\sqrt{f_M}}\right) = 2.0\log_{10}\left(\frac{\mathrm{Re}}{2.51\cdot\sqrt{1/f_M}}\right) \quad (\mathrm{e/d} \to 0) \qquad (22.26b)$$

$$\frac{1}{\sqrt{f_M}} = -2.0\log_{10}\left(\frac{e/d}{3.7}\right) = 2.0\log_{10}\left(\frac{3.7d}{e}\right) \quad (\mathrm{Re} \to \infty) \qquad (22.26c)$$

The point at which transition from smooth pipe law to fully turbulent or rough pipe law occurs can be determined by equating the above expressions to obtain

$$\mathrm{Re} = \frac{18.574d}{e}\log_{10}\left(\frac{3.7d}{e}\right) \qquad (22.26d)$$

A minor drawback in the implementation of the Colebrook equation is that it expresses the friction factor as an implicit function of itself, which requires the implementation of iterative equation-solving procedures. Although this is no longer a significant concern given the computational power available nowadays, several explicit friction factor expressions have been also proposed. One of such expressions is Chen's friction factor equation [16], claimed to present a maximal absolute deviation of 0.4651 % when compared with Colebrook's equation and reproduced as follows:

$$\frac{1}{\sqrt{f_M}} = -2.0\log_{10}\left[\frac{e}{3.7065d}-\frac{5.0452}{\mathrm{Re}}\log\left(\frac{(e/d)^{1.1098}}{2.8257}+\frac{5.8506}{\mathrm{Re}^{\,0.8981}}\right)\right] \qquad (22.27)$$

For the calculation of Fanning friction factors, the equivalency $\frac{1}{\sqrt{f_M}} = \frac{1}{2}\cdot\frac{1}{\sqrt{f_F}}$ must be substituted into these equations. The left-hand side of these equations, when written as $F = \frac{1}{\sqrt{f_F}} = \frac{2}{\sqrt{f_M}}$, is known as the transmission factor of the pipe (F).

22.7 SPECIALIZED EQUATIONS FOR LIQUID FLOW

As already established, pipeline equations for liquid flow can be conveniently written in the following general short-form representation, previously presented as Eq 22.6:

$$h_f = R_L \cdot q_L^{1/n} = r_L \frac{L}{d^m}\cdot q_L^{1/n} \qquad (22.6)$$

This generalized expression captures the dependency of pressure head loss on total pipe resistance to liquid flow (in terms of length, diameter, and specific resistance r_L) and flow rate. This equation requires the definition of the appropriate flow exponent (n) and diameter exponent (m) and the calculation of pipe specific resistance (r_L).

The most rigorous approach for the calculation of frictional losses for single-phase incompressible flow of fluids in pipelines is the application of the Darcy-Weisbach equation, which is derived from first principles and for which $m = 5$ and $n = 0.5$. However, this entails the calculation of friction-factor dependent r_L values by using the Moody chart or any of its associated empirical equation fittings. This calculation invariably requires the availability of a good estimate for pipe roughness and an iterative procedure for the calculation of pipe diameter or flow rate. Some users would rather avoid this. This is why, despite the stated generality of the Darcy-Weisbach equation, the use of alternative, iteration-free, empirical pressure loss equations continues to be common. These empirical equations are always much more limited in terms of range of applicability; however, they remain popular in many applications because of the shear convenience of their ease of use and simpler formulation. Another factor that contributes to the familiarity and repeated use of empirical substitutes is that many were widely available even before the development of the Moody diagram, and many successful designs have since been made on their account.

Table 22.2 lists the most commonly used equations for liquid flow, their inherent assumption for friction factor calculation, and the resulting exponents n and m in terms of the generalized functional form. The Darcy-Weisbach equation is the first equation shown in Table 22.2. As previously demonstrated, the Darcy-Weisbach equation collapses to Poiseuille's law for laminar flow conditions, which is shown as the second entry in the table. All equations for liquid flow can be written in terms of the generalized functional form shown at the top of Table 22.2, including the empirical choices. Empirical correlations just replace Moody-based friction factor calculations by alternative, simpler expressions of friction factor, which are limited in their scope.

By far, one of the most widely known empirical equations for liquid flow is the Hazen-Williams correlation. The Hazen-Williams correlation was originally developed for the study of the flow of water in turbulent flow conditions [17] and provides an empirically derived relationship between water volumetric flow and pressure (or head) losses. Table 22.2 shows the implied friction factor functional relationship when the Hazen-Williams correlation is implemented. In this expression, the parameter C_{HW} is

TABLE 22.2—Summary of Specialized Equations for Liquid Flow

$$h_f = R_L \cdot q_L^{1/n} = r_L \frac{L}{d^m} \cdot q_L^{1/n} \quad \text{[Eq 22.6]}$$

Equation	Friction Factor	r_L	n	m
Darcy-Weisbach (generalized)	Moody chart	$r_L = \frac{f_F}{\sigma_L^2} = \frac{f_M}{4\sigma_L^2}$	0.50	5.0
Poiseuille's law (laminar flow)	$f_F = \frac{16}{\text{Re}}$	$r_L = \frac{128 \cdot \mu_L}{\gamma_L \cdot \pi \cdot g_c}$	1.0	4.0
Hazen-Williams	$f_F = \frac{\kappa_{HW}}{C_{HW}^{1.852}} \frac{d^{0.13}}{q_L^{0.148}}$	$r_L = \frac{1}{\sigma_{L,HW}^2 \cdot C_{HW}^{1.852}}$	0.54	4.87
Manning	$f_F = \frac{\kappa_M \cdot n_M^2}{d^{0.33}}$	$r_L = \frac{n_M^2}{\sigma_{L,M}^2}$	0.50	5.33

C_{HW} = Hazen-Williams dimensionless roughness coefficient and n_M = Manning dimensionless roughness parameter; C_{HW} = 150, and n_M = 0.009 for polyvinyl chloride (PVC); C_{HW} = 140 and n_M = 0.011 for smooth metal pipes and cement-lined ductile iron; C_{HW} = 130 and n_M = 0.014 for new cast iron and welded steel; C_{HW} = 120 and n_M = 0.016 for wood and concrete; C_{HW} = 110 and n_M = 0.017 for clay and new riveted steel; C_{HW} = 100 and n_M = 0.020 for old cast iron and brick; and C_{HW} = 80 and n_M = 0.035 for badly corroded cast iron [18]. Values above assume the flow of water. Suggested values of C_{HW} for refined petroleum products as a function of temperature have also been reported [19]. κ_{HW}, κ_M = unit-dependent constant in the friction empirical equation. κ_{HW} = 46.9334 and κ_M = 46.2388 for d (ft), q_L (ft^3/s); κ_{HW} = 33.977 and κ_M = 105.6732 for d (in.), q_L (ft^3/s); and κ_{HW} = 32.3045 and κ_M = 31.154 for SI units. σ_L, $\sigma_{L,HW}$, and $\sigma_{L,M}$ = unit-dependent constants for specific resistance calculations. For q_L (ft^3/s), L (ft), d (ft), σ_L = 3.15, $\sigma_{L,HW}$ = 0.4598, and $\sigma_{L,M}$ = 0.46324. For q_L (ft^3/s), L (ft), d (in.), $\sigma_L = 6.3148 \cdot 10^{-3}$, $\sigma_{L,HW} = 1.08335 \cdot 10^{-3}$, and $\sigma_{L,M} = 6.143 \cdot 10^{-4}$. For SI units, σ_L = 1.74, $\sigma_{L,HW}$ = 0.30614, and $\sigma_{L,M}$ = 0.31174.

the Hazen-Williams dimensionless roughness coefficient, which attempts to capture the change in roughness associated with different pipe materials. Table 22.2 shows some typical values of C_{HW} for common pipe materials. There is no explicit dependency of friction factor on Reynolds number; thus, the resulting calculations are arguably insensitive to fluid properties and fluid type. In practical applications, the selection of the Hazen-Williams roughness coefficient (C_{HW}) has largely relied on the user's experience with the system under investigation and has been tuned accordingly to account for different fluid types and even viscosity changes with temperature. Albeit its significant limitations, the Hazen-Williams correlation remains popular in the design of water hydraulic systems in the United States, and its use has been documented and recommended even for calculations of pressure drop for refined petroleum products such as gasoline, kerosine, and diesel with properly tuned values of C_{HW} (see, e.g., [18,20]).

Figure 22.3 presents a friction factor prediction comparison between the Hazen-Williams correlation versus

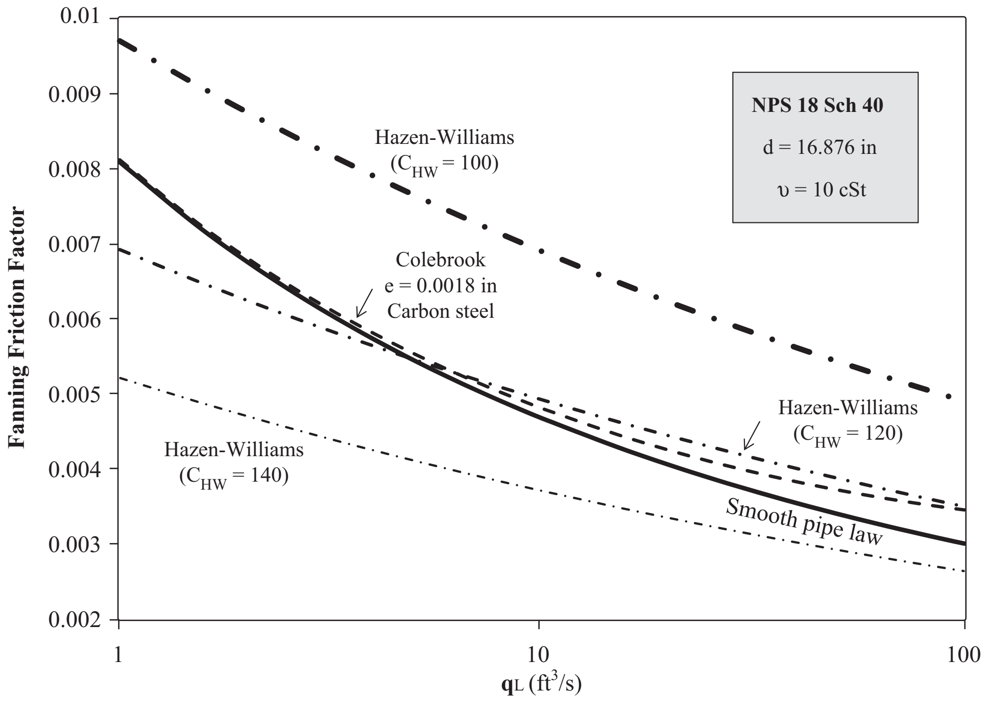


Figure 22.3—Friction factor comparison for the specialized liquid equations.

the more rigorous Colebrook prediction for the case of the transportation of a petroleum product (kinematic viscosity = 10 Sct) through a NPS 18 Sch 40 carbon steel pipe (e = 0.0018 in.). This figure reveals that a Hazen-Williams coefficient of $C_{HW} = 120$ is able to approximately capture the overall friction factor behavior with increasing flow rate with a somewhat underestimated slope at low flow rates. Other C_{HW} choices have the potential of grossly overestimating or underestimating friction losses, as shown. This figure demonstrates that whether Hazen-Williams predictions can be trusted or not is basically dependent on whether the user of the equation can rely on experience or expert advice for the proper value of C_{HW} that should be used. The user could potentially reconstruct a plot such as Figure 22.3 for the particular application and "tune" the value of C_{HW} to the one that best captures the overall Colebrook trend. This would entail some iterative calculations and beg the question of why Darcy-Weisbach was not used in the first place.

The Manning correlation is another correlation empirically developed for the study of flow of liquids in open channels that became popular in the late 19th century [21]. It continues to be widely used in the design of water sewer systems—where fluid channels do not typically flow at full capacity [17]. For the Manning correlation, $n = 0.5$ (flow exponent) and $m = 5.33$ (diameter exponent) whereas r_L is made a function of a dimensional constant and a material-dependent dimensionless roughness coefficient (n_M) alone, as shown in Table 22.2. In Manning's expression, the dimensionless parameter n_M has the same purpose as the C_{HW} parameter had for the Hazen-Williams equation, which is to attempt to capture the change in roughness associated with different pipe materials. One of its shortcomings is that it offers a flow-rate independent friction factor calculation; thus, it would display as a straight horizontal line in Figure 22.3. Interestingly, Manning and Hazen-Williams correlations were used by the reviewers of Moody's paper [14] when evaluating the merits of the then recently proposed Moody's method—an observation that highlights the deeply engrained reliance on such empirical correlations before the publication of Moody's chart. Other empirical flow equations for liquids are also available for specialized purposes. For example, Menon presents a summary of liquid empirical equations used for liquid pipeline flow calculations that includes the Shell-MIT equation for the calculation of pressure drop in heavy crude oil and heated liquid pipelines, the B. Miller equation for the calculation of pressure losses in crude oil pipelines, and the T.R. Aude equation for the calculation of head losses in pipelines transporting refined petroleum products [20]. All of these equations can be written in terms of the general liquid pipeline functional form, $h_f = r_L \dfrac{L}{d^m} \cdot q_L^{1/n}$, where the appropriate values of r_L, n (flow exponent), and m (diameter exponent) must be defined.

22.8 SPECIALIZED EQUATIONS FOR GAS FLOW

As before, the fundamental difference among specialized formulas available for natural gas flow resides in how friction factors are evaluated. These gas equations for pipe flow can be conveniently written in terms of the generalized short-form representation previously presented as Eq 22.13:

$$p_1^2 - p_2^2 = R_G \cdot q_{Gsc}^{1/n} = r_G \frac{L}{d^m} \cdot q_{Gsc}^{1/n} \tag{22.13}$$

Table 22.3 presents a list of well-known choices available for gas pipe calculations, along with their associated definitions of n, m, and pipe specific resistance (r_G). Average compressibility factors (Z_{av}) in this table are calculated as a function of p_{av} and T_{av} using any standard gas compressibility factor correlation. A popular choice for the calculation of the average pipeline pressure (p_{av}) in gas systems is to use the expression $p_{av} = \dfrac{2}{3}\left(\dfrac{p_1^3 - p_2^3}{p_1^2 - p_2^2}\right)$ or any of its equivalent versions. This p_{av} expression results from applying the standard average pressure definition $\left(p_{av} = \dfrac{1}{V}\int_0^V p dV = \dfrac{1}{L}\int_0^L p dx\right)$ to the expected parabolic pressure profile for isothermal gas pipes $\left(p^2(x) = p_1^2 - \dfrac{x}{L}(p_1^2 - p_2^2)\right)$. In turn, values of T_{av} are typically taken as the arithmetic average between the pipe inlet and outlet temperatures for conditions when expected temperature changes in the pipe are not significant. Please refer to Section 22.13 for a discussion about the additional calculations required when fluid temperatures are expected to significantly change along the pipe.

The most rigorous approach for the calculation of frictional losses in single-phase compressible fluid flow in pipelines is the application of the general gas equation—shown first in Table 22.3 and for which $m = 5$ and $n = 0.5$. The general gas equation, derived from first principles, captures the dependency of squared pressure loss with respect to gas flow rate and total pipe resistance flow on the basis of length and diameter, and calculates specific resistances (r_G) rigorously from Moody's chart. The implementation of Moody's friction factor equations requires an iterative numerical procedure given the dependency of friction factor on flow rate and pipe diameter.

Since the early 1900s, and much before the formulation of Moody's diagram, many empirical approaches were already in place to describe gas flow [22]. Many of these equations, and their successors, were formulated on the basis of matching field data obtained from operating or experimental gas pipeline systems. One noteworthy example is the Weymouth equation, developed by Thomas R. Weymouth in the early 1910s by matching compressed air test data flowing through small diameter pipes (0.9–11.8 in.) at low pressures [23]. Decades later, in the 1940s, the Panhandle-A equation (the "original" Panhandle equation) was proposed by matching field pressure drop test data performed in 24-in. transmission lines operated by the Panhandle Easter Pipe Line Company [24,25]. Panhandle equations were developed with the intention of proposing flow equations suitable for larger diameter pipes because the Weymouth equation was known to overestimate pressure losses for those systems. The Panhandle-B equation (the revised or "modified" Panhandle equation) was published in 1952 when more operating data at higher pressures and flow rates became available from other Panhandle pipelines [24,25]. Friction factor assumptions

TABLE 22.3—Summary of Specialized Equations for Gas Flow

$$p_1^2 - p_2^2 = R_G \cdot q_{Gsc}^{1/n} = r_G \frac{L}{d^m} \cdot q_{Gsc}^{1/n} \quad [\text{ Eq } 22.13 \text{]}$$

Equation	**Friction Factor**	r_G	n	m
General gas equation	Colebrook equation	$r_G = \frac{SG_g T_{av} Z_{av}}{\sigma_G^2} f_F \left(\frac{p_{sc}}{T_{sc}}\right)^2$	0.50	5.0
Weymouth	$f_F = \frac{\kappa_W}{d^{1/3}}$	$r_G = \frac{SG_g T_{av} Z_{av}}{\sigma_{G,W}^2} \left(\frac{p_{sc}}{T_{sc}}\right)^2$	0.50	5.333
Panhandle-A (original panhandle)	$f_F = \frac{\kappa_{PA}}{\left(\frac{q_{Gsc} \cdot SG_g}{d}\right)^{0.1461}}$	$r_G = \frac{SG_g^{0.854} T_{av} Z_{av}}{\sigma_{G,PA}^{1.854}} \left(\frac{p_{sc}}{T_{sc}}\right)^2$	0.5394	4.854
Panhandle-B (modified panhandle)	$f_F = \frac{\kappa_{PB}}{\left(\frac{q_{Gsc} \cdot SG_g}{d}\right)^{0.03922}}$	$r_G = \frac{SG_g^{0.961} T_{av} Z_{av}}{\sigma_{G,PA}^{1.961}} \left(\frac{p_{sc}}{T_{sc}}\right)^2$	0.510	4.961
AGA (partially turbulent)	$\frac{1}{\sqrt{f_F}} = 4F_D \log_{10}\left(\frac{\text{Re}\sqrt{f_F}}{1.41}\right)$	$r_G = \frac{SG_g T_{av} Z_{av}}{\sigma_G^2} f_F \left(\frac{p_{sc}}{T_{sc}}\right)^2$	0.50	5.0
AGA (fully turbulent)	$\frac{1}{\sqrt{f_F}} = 4.0\log_{10}^{\left(\frac{3.7d}{e}\right)}$	$r_G = \frac{SG_g T_{av} Z_{av}}{\sigma_G^2} f_F \left(\frac{p_{sc}}{T_{sc}}\right)^2$	0.50	5.0

$\kappa_W, \kappa_{PA}, \kappa_{PB}$ = unit-dependent constant in friction empirical equations. κ_W = 0.008 for d (in.) or 0.002352 for d (m); κ_{PA} = 0.01923 for d (in.), q (SCF/D) or 0.01954 for d (m), q (sm³/d); κ_{PB} = 0.00359 for d (in.), q(SCF/D) or 0.00361 for d (m), q (sm³/d). σ_G, $\sigma_{G,W}$, $\sigma_{G,PA}$, $\sigma_{G,PB}$ = unit-dependent constants for specific resistance calculations. For q_{Gsc} (SCF/D), L (ft), d (in.), p (psia), T (R): $\sigma_G = 2{,}818$; $\sigma_{G,W} = 31{,}508$; $\sigma_{G,PA} = 44{,}400$; $\sigma_{G,PB} = 58{,}328$. For q_{Gsc} (SCF/D), L (miles), d (in.), p (psia), T (R): $\sigma_G = 38.784$; $\sigma_{G,W} = 433.618$; $\sigma_{G,PA} = 435.98$; $\sigma_{G,PB} = 736.77$. For SI units in q_{Gsc} (sm³/d), L (m), d (m), p(kPa), T (K): $\sigma_G = 574{,}901$; $\sigma_{G,W} = 11.854 \cdot 10^6$; $\sigma_{G,PA} = 13.656 \cdot 10^6$; $\sigma_{G,PB} = 13.196 \cdot 10^6$.

of these popular gas equations are presented in Table 22.3. Weymouth, Panhandle-A, and Panhandle-B represent an enduring legacy of this early modeling period and they have outlived many of their empirical predecessors and remain the most well-known equations for gas pipeline flow. These equations continue to be used nowadays for applications clearly far beyond the scope of their original formulation. Many users like the simplicity of their formulation and their noniterative nature. Many others cannot justify their use given the availability of rigorous approaches (i.e., the Colebrook equation coupled with the general gas flow equation) and the computer power to implement it.

In the 1960s, the American Gas Association (AGA) proposed the AGA equation, which uses the general gas equation with simplified, limiting forms of the Colebrook equation [26–28]. The AGA method calculates two friction factor estimates using Colebrook's limiting behaviors (i.e., modified versions of Eqs 22.26b and 22.26c) and selects the highest value between the two. A first friction factor estimate is calculated on the basis of the empirically modified smooth pipe approximation (i.e., Eq 22.26b for $e/d \rightarrow 0$) via the introduction of a "drag factor" (F_D) multiplier. This smooth pipe law empirical modification was renamed the AGA partially turbulent equation and is shown as such in Table 22.3. AGA's version of the smooth pipe law uses a slightly different numerical coefficient within the logarithmic argument, as shown in Table 22.3, combined with the use of empirical drag factors (F_D), which can take values from 0.90 to 0.97—effectively increasing friction factor estimations when compared against the original smooth pipe law. A second AGA friction factor estimate is obtained from the fully turbulent (rough pipe) form of the Colebrook equation (i.e., Eq 22.26c for $Re \rightarrow \infty$). This is known as the AGA fully turbulent equation and is shown as such in Table 22.3. Friction factor calculations in fully turbulent regimes are known to be Reynolds independent and solely dependent on pipe roughness; thus, the fully turbulent AGA equation is frequently recommended for the design of a high-flow system, especially when roughness estimations are reliable. However, given its implicit nature, the application of the partially turbulent AGA equation requires as much iterative work as the direct application of the Colebrook equation does, and it would additionally require the empirical estimation of a drag factor based on AGA guidelines [26–28].

Empirical correlations, albeit convenient to use, are limited in their scope of application and should be used with caution. Figure 22.4 displays the typical performance of gas equations in terms of their Fanning friction factor predictions. This plot is analogous to the one presented by Boyd (1983) in terms of transmission factors [29]. This figure displays friction factor predictions from all empirical correlations in Table 22.3 and compares them against the more rigorous Colebrook prediction for the case of transportation of a natural gas ($SG_G = 0.70$ and $\mu_g = 0.012$ cP) through a NPS 18 Sch 40 carbon steel pipe (e = 0.0018 in.). It is important to keep in mind that, in Figure 22.4, all models are supposedly predicting the same variable—namely friction factor—however, predictions can be seen to be wildly different from each other. For example, Weymouth

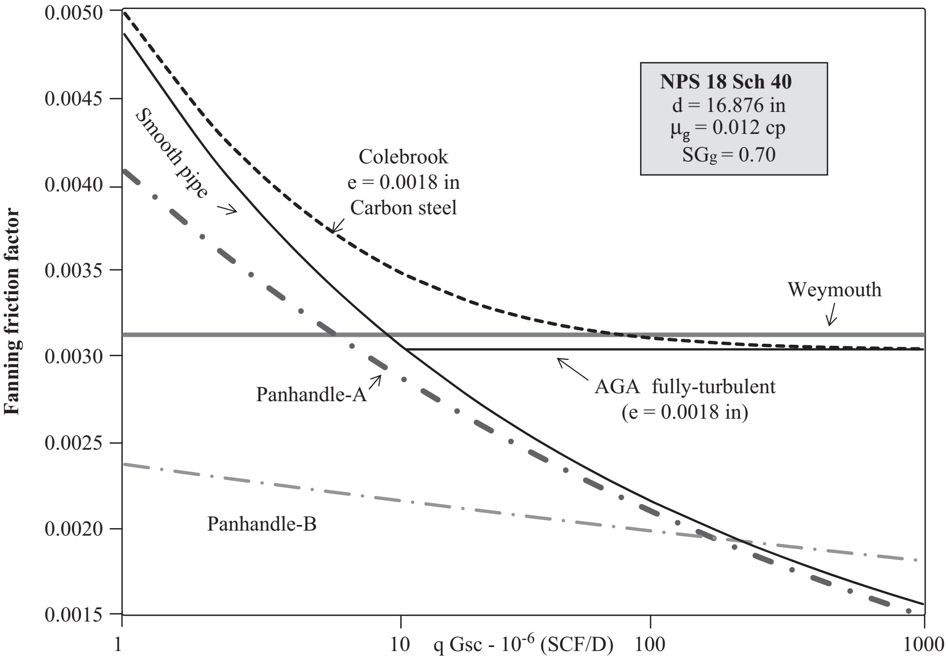


Figure 22.4—Friction factor comparison for the specialized gas equations.

values tend to obviously overestimate friction losses at high flow rates, which would lead to conservative pipe designs. For some users, this friction overestimation by Weymouth is not necessarily seen as a problem but rather as a potentially desirable built-in safety factor in high-volume gas piping design. The flow-rate independent nature of the Weymouth friction factor prediction identically matches the behavior of fully turbulent predictions of the Colebrook equation but only for pipes with roughness equaling $e = 3.7 \cdot d \cdot 10^{0.25 \cdot d^{1/6} / \sqrt{\kappa_W}}$, which corresponds to e = 0.0021 in. for the scenario presented in Figure 22.4—a larger value than expected for carbon steel pipes. In direct contrast to the flow rate independent nature of the Weymouth prediction, the Panhandle-A (original Panhandle) equation tends to rather track the smooth-pipe law prediction and thus does a better job at lower Reynolds numbers (partially turbulent region) at which friction factors tend to be less dependent on pipe roughness. While Weymouth is able to track fully turbulent behavior and Panhandle-A smooth-pipe behavior, the Panhandle-B (modified Panhandle) equation does quite a poor job of mimicking any Colebrook trend. This "modified" Panhandle equation was intended to be applicable to high-flow pipes, which results in its flatter slope in Figure 22.4. Because of these different slopes and Reynolds dependencies, Panhandle-A always predicts larger friction factors than those of Panhandle-B when used at low to moderate flow rates. At high flow rates, the situation reverses. This Panhandle crossover point takes place at flow rates equal to $q_{Gsc} = \left(\frac{\kappa_{PA}}{\kappa_{PB}}\right)^{9.35} \left(\frac{d}{SG_g}\right)$, above which Panhandle-B would predict larger, higher friction factors, although still significantly lower than Colebrook's and Weymouth's in Figure 22.4. To bring Panhandle-B friction factor predictions in line with fully turbulent Colebrook predictions at high flow rates, the Panhandle-B prediction would have to be "displaced" upward by multiplying it with a suitable factor. This is the effect accomplished by the introduction of "efficiency factors" into gas flow equations.

The concept of efficiency factors (E_f) has found widespread use in the implementation of gas specialized equations of empirical nature. These parameters empirically adjust transmission factor values with the ultimate purpose of matching field observations by increasing the effective friction factor embedded into the gas equation. Tuned transmission factors become $F = E_f \cdot \frac{1}{\sqrt{f_F}}$ and effective friction factors hence become $(f_F)_{eff} = \frac{f_F}{E_f^2}$. From this definition, larger effective friction factors and pressure losses are generated by the gas equations for any $E_f < 1$ (note that the use of $E_f = 0.7071$ actually doubles the friction factor prediction of the equation). Throughout the years, the successful applications of empirical gas flow equations to field problems have been largely tied to this artificial tuning of their prediction capabilities via the use of these adjustable factors. In Figure 22.4, all calculations assumed $E_f = 1$ for all equations. However, the implementation of adjustable and less-than-unity E_f values ($E_f < 1$) would force the upward displacement of the empirical curves in Figure 22.4, which with careful selection can result in making them more closely follow Colebrook's predictions and trends. This discussion is analogous to the one pertaining the "proper" selection of C_{HW} values in the empirical Hazen-Williams liquid equation in the sense that values of E_f (empirical gas equations) and C_{HW} (liquid Hazen-Williams equations) need "tuning" for the equation to match field data or Colebrook's trends, or both. However, different equations would require the use of different E_f values to match a common Colebrook or field data target. Such E_f

values are thus likely to be rate dependent. When evaluating empirical equations, a comparison plot analogous to the one presented in Figure 22.4 can be used as a useful tool for assessing the suitability of an empirical equation for a given particular application. The reliability of an empirical equation can be measured in terms of how well it is able to track the corresponding Colebrook prediction for the expected transportation volumes and pipe sizes. It is important to point out that the direct use of the general gas equation coupled with the Colebrook equation would not be completely free of uncertainty because proper values of roughness of a pipe need to be determined and they are known to evolve with time.

Beyond the popular Weymouth and Panhandle equations, many other empirical gas flow equations have been proposed. Menon presents a summary of other empirical equations that have been proposed for gas pipeline flow, such as the IGT, Splitzglass, Mueller, and Fritzsche equations [30]. All of these equations can be similarly written in terms of the same generalized short form $p_1^2 - p_2^2 = r_G \dfrac{L}{d^m} \cdot q_{Gsc}^{1/n}$ once the appropriate values of r_G, n (flow exponent), and m (diameter exponent) have been defined.

22.9 PIPELINE DESIGN: NPS AND SCHEDULE SELECTION

Liquid and gas equations can be written in an analogous short-form notation, as shown by Eq 22.28:

$$\Delta p^* = R_K \cdot q_K^{1/n} = r_K \frac{L}{d^m} \cdot q_K^{1/n} \tag{22.28}$$

In Eq 22.28, the subscript K denotes either L for liquids or G for gases and $\Delta p^* = (p_1 - p_2)/\gamma_L = h_f$ for liquids or $\Delta p^* = p_1^2 - p_2^2$ for gases. The internal diameter requirement of a pipeline can thus be calculated as

$$d = \left(r_K \cdot L \cdot \frac{q_K^{1/n}}{\Delta p^*} \right)^{1/m} \tag{22.29}$$

Equation 22.29 demonstrates that the pipeline internal diameter requirement is a function of desired transportation capacity (q_K), available pressures (Δp^*), transportation distance (L), and specific pipe resistance (r_K). For rigorous calculations, r_K is an implicit function of diameter through the friction factor; thus, this calculation would require an iterative procedure unless a suitable diameter-independent empirical correlation is used for the calculation of specific resistance (r_K). Note that flow and diameter-dependent friction-factor empirical frictions do not necessarily lead to flow and diameter-dependent specific-resistance calculations because of the adjusted values of n and m (for example, refer to the simplified forms of the Hazen-Williams and Panhandle equations in Tables 22.2 and 22.3). Because pipeline diameters come in discrete finite sizes, the nearest larger pipeline internal diameter is selected from a table of available nominal sizes. This selection needs to take into consideration the required pipe wall thickness, which is discussed below.

Although pipe internal diameter is a direct function of its desired transportation capacity, the selection of wall thickness (and thus pipe schedule) is based on the minimal mechanical strength required for the pipe to safely operate. The calculation of pipe internal diameter that is based on the use of the flow equations discussed above combined with the estimation of the minimum wall thickness provide all of the information engineers need to select the proper NPS and schedule of the required pipe for the given application.

For a safe operation, pipe walls must be made thick enough so that pipeline stresses do not to exceed the minimal yield strength of its construction material. In other words, pipes must be designed with sufficient mechanical strength so they can withstand the stresses associated with their operating environment and hence avoid initiation of fractures that can lead to pipe failure. Conditions that lead to pipeline failure include excessive internal pressure, thin pipe walls, and low yield strength of the pipeline manufacture material. Relating these three variables and finding the safest operational combination among the three is the key driving force behind pipe stress analysis.

In stress analysis, pipes are visualized as cylindrically shaped containers. The stress state in these containers is characterized by the stress tensor (S), written, in cylindrical coordinates, in terms of a radial (r), axial (z), and circumferential (θ) component. In the analysis of failure due to excessive internal pressure, the initiation of cracks is said to be controlled by the magnitude of the largest component of the internal-pressure-induced stress tensor (S). The stress component recognized to be the largest in magnitude is the one that acts on the circumferential or tangential direction, which is known as the hoop stress (S_h). The hoop stress derives its name from being the component of the stress tensor that directly counteracts the bursting force of the internal pressure (P_{in}), just as steel hoops prevent wooden barrels from bursting. In a free-body diagram of a half segment of the cylindrical body, hoop stresses are found at both ends of the cylindrical cavity acting perpendicularly to the cross-sectional pipe thickness areas ($t \cdot L$) found along the pipe axis. When the hoop stress force component $[S_h \cdot 2(t \cdot L)]$ counteracts the bursting force created by the internal pressure $[P_{in} \cdot (d_o \cdot L)]$, the following relationship can be written:

$$S_h = \frac{p_{in} \cdot d_o}{2 \cdot t} \tag{22.30}$$

where

t = pipe wall thickness,

d_o = pipe outside diameter, and

P_{in} = pipe design or internal pressure.

Equation 22.30 is known as the thin-wall approximation for the hoop stress in cylinders and is only valid when the diameter of the cylinder (pipe) is several times larger than the wall thickness—at least 10 times, $d/t > 10$. When pipes cannot be considered thin-walled, a more rigorous form of the three stress components, known as Lamé's equation, needs to be considered [8].

For safe pipeline operation, the largest stress component in the pipe (hoop stress, or S_h) must be found below the specified minimum yield strength of the pipe material (SMYS or S_y; i.e., $S_y > S_h = \dfrac{p_{in} d_o}{2t}$). This limitation can be restated in terms of the minimum value of wall thickness required for any given value of minimum strength S_y, as follows:

$$t > \frac{p_{in} \cdot d_o}{2 \cdot S_y} \tag{22.31}$$

The calculation of pipe wall thickness also includes additional safety factors that are prescribed by codes, standards, and regulations and apply to the geographic location where the project is located. The basic equation for the determination of wall thickness thus becomes

$$t = \frac{p_{in} \cdot d_o}{2S_y \cdot F \cdot E \cdot T} \tag{22.32}$$

where:

P_{in} = maximal operating pressure to which the pipe can be subjected (psia);

F, E, and T = dimensionless safety factors;

S_y = specified minimum yield strength of the pipe (psi) or "SMYS," which depends on pipe material and grade;

F = a design derating factor;

E = the weld joint derating factor; and

T = the temperature derating factor.

The most typical values used for each of these parameters are discussed below. The calculation in Eq 22.32 fixes the required wall thickness, hence the Schedule, of the pipe required for the operation. Because Eq 22.32 requires the knowledge of outside diameter, few trials may be needed with different plausible NPS and Schedule selections that are consistent with minimum internal diameter and thickness requirements.

The SMYS, or specified minimum yield strength of a pipe, refers to the specified minimum yield strength of a pipe manufactured according to the corresponding pipe material specification. As a result, the SMYS of a pipe depends on its type of material specification (Table 22.1) and grade. For pipes manufactured according to API 5LX guidelines, the grade designation uses the letter X and the first two digits of the specified minimum yield strength. The pipe specification API 5LX Grade X46 corresponds to the grade having a specified minimum strength SMYS of 46,000 psi, X60 implies a SMYS of 60,000 psi, X80, 80,000 psi, etc. API 5L Grade A has one of the lowest SMYS values (30,000 psi) whereas Grade B has a SMYS of 35,000 psi. In high-pressure applications, it is common to prefer higher-grade pipes (X52, X60, X65) because significantly less wall thickness would be required with associated lighter weights and lower cost [31].

For wall thickness calculations, ASME Standard B31.4 for onshore liquid transportation recommends $F = 0.72$ to be used for all locations in Eq 22.30, does not implement temperature derating factors ($T = 1$), and recommends weld joint derating factors (E) that depend on the welded pipe class. For instance, $E = 1$ for seamless pipes and electric resistance welded (ERW) pipes; $E = 0.80$ for electric fusion arc and electric fusion welds; and $E = 0.60$ for furnace butt welded pipes. ASME Standard B31.8, used for gas transportation, implements similar weld joint derating factors (E) but recommends temperature-dependent derating factors (T) that range from $T = 0.867$ for high temperatures (approximately 450°F) to $T = 1$ for lower temperatures up to 250°F [32]. The design factor F for gas lines is made location dependent and primarily a function of how close the pipeline is found to structures with significant human occupancy. ASME-recommended design factors range from $F = 0.40$ for densely populated areas with heavy traffic and multistory buildings (Class 4 locations) to $F = 0.80$ for deserts, wastelands, farmlands, and sparsely populated areas (Class 1 locations) [32]. ASME Standard B31.8 can be seen as somewhat more stringent or conservative than Standard B31.4 because of the potential additional hazards that gas pipeline failures create compared with crude oil pipelines.

When ASME Standards B31.4 and B31.8 are compared to ASME Standard B31.3, it is clear that the latter leads to more conservative designs. This is because of the higher levels of hazard associated with process piping found in petroleum refineries and processing plants when compared with crude oil and natural gas transmission systems. In the United States, most onshore facilities are designed in accordance to B31.4 and B31.8, depending on fluid type, whereas offshore facilities are mandated by regulation to follow ASME Standard B31.3 [31]. ASME Standard B31.3 uses a modified form of Eq 22.30 for wall thickness calculations, which include corrosion and thread allowances with more severe derating factors.

There are some other considerations that also influence the selection of recommended wall thickness and steel grade of the pipe. For example, for offshore applications, F derating design factors are typically made less than 0.80, which makes offshore pipeline thicker and heavier than pipelines used for inland applications. ASME B31.8 Chapter VIII covers the calculation of allowable pipe stresses in these environments. Design factors of 0.72 and 0.50 are recommended for offshore pipe wall thickness calculations, with the latter used for pipe sections such as risers that are subjected to the most stress during offshore operations. When small diameter pipes are used offshore, they might not be able to sink in low-density saltwater environments. This can be compensated by deploying concrete weight coatings or using even thicker wall pipe that can make the pipe heavier [31,33]. In inland and offshore application, piping should also be designed to support the bending stress induced by thermal expansion or contraction and the movement of air or marine currents along the pipe path. High-strength, high-grade pipes are typical in offshore applications for pipes to be able to support not only the internal pressure readily taken into account in this section, but also the external crushing force of the water column on top of the line and associated bending stresses induced by undulations of the seabed and marine currents. For inland applications, if pipe thermal expansion or contraction cannot be fully absorbed by the pipe material, additional flexibility should be provided by deploying bends, expansion loops, and offsets [18].

22.10 DESIGN CONSTRAINTS

Pipe design must additionally consider the examination of the associated economics, resulting pressure drops, and prevailing flow velocities. Fluid flow velocities, for example, must always be found within recommended minimal and maximal values, especially when flow of entrained particulate matter with the oil or gas or both phases is a real possibility. Velocity constraints are usually an important consideration because strict single-phase pipe operation or clean service can be a rare occurrence. Leading concerns when constraining the velocity of a fluid inside of a pipe are to control noise, vibration, erosion, corrosion, water hammer, and fluid carrying capacity.

Pipe design can be velocity constrained to avoid excessive noise production and pipe vibration during clean single-phase pipe service and multiphase flow. Noise control is an important aspect of health and safety policies for industry workers and can become an important concern for communities living along pipeline right of ways. In addition, excessive vibration is a cause for material fatigue of the pipe material that could lead to catastrophic failure. Flow-induced vibration and associated noise are indeed studied as a coupled problem. Norton and Karczub explain that noise and vibration in pipelines is a multistep process that starts with the internal generation of random acoustic pressure fluctuations typical of turbulent (high velocity) flow, followed by the excitation (vibration) of the pipe wall in response to the fluctuating pressure signal closest to the wall, and finally the radiation of noise from the vibrating pipe wall [34]. The presence of pipeline fittings (valves, bends, and junctions) can significantly increase the intensity of the vibration and noise in the system because of the significantly increased pressure and flow disturbance they introduce. Sound waves generated by these localized disturbances at fittings are able to propagate undiminished through the pipe system [34]. Flow-induced noise and vibration are thus controlled by reducing turbulence and fluid disturbances; this is typically accomplished by placing maximal allowable fluid velocities in the system. Gas flows are more prone to noise and vibration problems because of the higher associated Reynolds numbers and turbulence that characterize these systems.

Other problems associated with excessive fluid velocity are pipe wall erosion, ineffective corrosion inhibition, and water hammer. These are problems that, when not controlled, can significantly reduce the life span of the pipe. Pipe erosion can be caused by large fluid velocities and turbulence when particulate matter (e.g., liquid particles or sand) impinges the pipe wall, causing it to erode with time. The higher the fluid velocity, the more exposed the metal becomes to fluid-induced erosion. Excessive velocities are also responsible for increased erosion at fittings and for the ineffective action of corrosion inhibitors. In liquid systems, another concern with large fluid velocities is the higher likelihood of water hammer problems. Water hammer is the violent pressure surge that can be generated by sudden changes in fluid inertia (e.g., valve closings) and that is especially problematic in nearly incompressible fluid systems. Water hammer can lead to pipe rupture because of its potentially destructive force and the presence of repeated stress that can weaken the pipe material to its point of failure. The first line of attack in the prevention of water hammer damage is the control of liquid inertia through lower design velocities.

In liquid-dominated systems, maximal velocities of 15 ft/s are suggested to minimize erosion and water hammer damage [31,35]. In gas lines, fluid velocities are typically recommended to be limited to 60–80 ft/s to prevent excessive noise and vibration during clean service [31,35]. Kelkar quotes maximal recommended gas velocities of 50 ft/s for production tubing of natural gas wells and a maximum of 90 ft/s for natural gas pipe transport but less than 25 ft/s if corrosion inhibitors are used [36]. He further indicates that for completely dry gas wells, no limit is necessary to be placed on gas velocities [36], implying that noise and vibration would not be of concern in gas well applications.

For two-phase systems, the API RP14E recommends the use of Eq 22.33, the erosional velocity equation, as the maximal allowable velocity in carbon steel pipes,

$$v_e = \frac{C}{\sqrt{\rho}} \tag{22.33}$$

where:

v_e = limiting erosional velocity (ft/s),

ρ = flowing mixture density (lb/ft^3), and

C = erosional empirical constant typically taking values anywhere in between 80 and 350 ft$^{2.5}$/lb$^{0.5}$-s.

The lower the selected value of C, the more constrained the design and allowable velocities or flow rates. Although somewhat conservative values of $C = 100$ for continuous service (and lower for sand-laden fluids) and $C = 125$ for intermittent service were originally recommended by the API, less stringent values of $C = 150–200$ for continuous service and $C = 200–250$ for intermittent service have also been suggested for systems in which chemical corrosion is actively controlled [31,35]. Brill and Mukherjee describe the topic of fluid-induced erosional velocity prediction as rather controversial [11]. They point out some important limitations of Eq 22.33, such as its lack of compliance with experimental observations for sand-laden fluids, and discuss alternative models available for the estimation of erosional velocity in petroleum applications. On the basis of observations by Shirazi et al. [37], the authors point out that although Eq 22.33 implies that erosional velocities decrease when the density of the fluid increases, experience shows that sand in higher-density liquids actually causes less erosion than sand in a lower density gas. The authors also discuss the models of Shirazi et al. [37] and McLaury and Shirazi [38], which account for the effect of pipe material and particle (sand) size, density, and sharpness and allow for the evaluation of various acceptable wall penetration (erosion) rates. Despite these well-known weaknesses, Eq 22.33 remains popular because of its simplicity—the very attribute that can actually make it potentially misleading and too constraining for realistic estimates. McLaury and Shirazi [38] argue that the existence of such a wide range of recommended C values ($C = 80–350$ ft$^{2.5}$/lb$^{0.5}$-s—more than a 4-fold difference between lower and upper predictions without clear-cut selection criteria) is the very proof of the inadequacy of the equation. The use of Eq 22.33 is so widespread that it is even recommended for the calculation of maximal allowable velocities for single-phase flow—although it was originally proposed by API on the basis of two-phase flow experimental data. For example, Mohitpour et al. [18] recommend constraining the gas velocity in transmission gas lines to approximately 40–50 % of the erosional value obtained from Eq 22.33 while using of $C = 100$, which is equivalent to calculating a maximal allowable velocity using $C = 45$ and can work out to be severely more constraining than applying the typical limit of 60–80 ft/s used for noise and vibration control. Kelkar [36] indicates that Eq 22.33 is used in natural gas applications with values of *C* that vary between 100 and 150. Arnold and Steward [35] indicate that Eq 22.33 is consistent with the typically recommended maximum of 15 ft/s for liquid flow when the equation is used with $C = 125$, which works out to be the case for fluids with liquid specific gravities of approximately 1.11.

Pipeline flow can be velocity constrained at a lower bound as well. The main concern here is to ensure enough fluid carrying ("sweeping") capacity and prevent the settling, deposition, slugging, or surging of heavier phases (liquids or solids) flowing with the fluid. A minimal velocity of 3 ft/s is the typical recommendation for liquid-dominated pipe systems. In gas-dominated systems with flowing liquids, minimal velocities should be at least 10–15 ft/s to ensure that liquids will flow [31,35]. Increasing fluid velocities to satisfy minimal velocity constraints for a given pipe throughput entails considering smaller pipe sizes with increased pressure losses. Conversely, reducing fluid velocity to satisfy a maximal flow velocity constraint implies considering larger pipe diameters. The design equation presented as Eq 22.29 provides the minimal diameter that satisfies the given transportation requirement. Any larger diameter adjusted not to surpass the maximal allowable fluid velocity would still satisfy the transportation requirement, additionally yielding reduced wall friction losses. However, larger diameters could be problematic in terms of increased pipe costs and in two-phase operations, where the highly undesirable slug flow pattern becomes more likely as pipe diameter increases.

Another way of constraining pipe design and fluid velocities, or to determine if an ongoing pipeline operation is suboptimal or not, is through the control of allowable/desirable pressure drop during pipe operations. For example, in the case of gas transportation, pressure drop in pipes is typically constrained to reduce the load on compressors and compressor fuel costs. A maximal permissible pressure drop in gas lines is typically placed at 15 psi/mile, and gas velocity is adjusted so that the resulting pressure drop is found below this value. Mohitpour et al. suggest that a pipe design that is based on resulting pressure drops between 3.5 and 5.85 psi/mile is optimal [17]. They argue that excessive pressure drops induce greater potential for operating problems and increased compressor load. Pressure drops below 3.5 psi/mile indicate suboptimal use of available pipe capacity and facilities. When designing a pipe based on a maximal pressure drop constraint, pipe equations can be solved for downstream pressure on the basis of a given flow capacity and available upstream pressure by testing different commercially available finite pipe sizes until the target pressure drop and velocity are attained. This protocol circumvents the iterations typically needed when trying to directly solve for pipeline diameter.

A restriction in maximal allowable pressure drops in a system is essentially an economic constraint. When there are no significant economic restrictions, such as in the case of freely available motive power from the fluid source or reservoir, the smallest diameter pipe that satisfies the flow rate requirement is usually favored regardless of resulting pressure drop. However, this is hardly the case. Motive power provided by pumps and compressors can become a significant operational expense over time. Ongoing operating expenses (OPEX) can easily overcome any savings in initial capital expenditures (CAPEX) obtained by selecting smaller and least costly pipe diameters. CAPEX in pipeline projects does include pipe purchase cost and its installation, both of which can appreciably increase as larger pipeline diameters are considered, plus the cost of peripheral components such as compressors, pumps, valves, and monitoring equipment. OPEX in pipeline projects considers the annual capital outlays driven by overall system maintenance and motive power generation. Because CAPEX in pipeline project increases with pipeline diameter whereas OPEX tends to decrease with increasing pipe diameters, an optimal or most economical pipe size can be defined when the sum of these two is minimized. This is a constrained optimization problem because the velocity restrictions discussed above must also be satisfied. The optimization problem can also be construed in terms of the maximization of the project's present value based on discounted cash flows and estimated future revenues associated with the operation of the pipeline. The optimal diameter calculation would also yield the optimal pressure drop that should be pursued for the pipeline project under consideration. Economics drives pipeline design and thus informed pipeline design decisions should be made by looking at the effect that they have over the lifetime span of the pipe operation. For example, the selection of higher grade line in exchange for smaller pipe thicknesses is also an economic-driven design constraint.

22.11 MULTIPHASE FLOW CONSIDERATIONS

Multiphase flow is very common in industrial processes. Many industrial processes rely on multiphase phenomena for the transport of energy and mass or for material processing. Since the last century, the nuclear, chemical, and petroleum industries have propelled an intense research activity in this area. Their effort has been aimed at the demystification of the mechanisms taking place during this complex flow situation. Two-phase flow can be found in various situations. Gas-liquid, liquid-liquid, solid-liquid, and solid-gas flows are the different two-phase flow permutations that can have the three more commonly encountered fluids in the petroleum industry (oil, natural gas, and water). A solid phase can be found with the production fluids from the reservoir itself (because of drilling activities or sand formation during production) or from the formation of complex solid structures because of the prevailing production conditions (hydrates in natural gas flow or asphaltenes in oil flow).

Oil and natural gas transportation typically deals with gas-liquid systems of flow. Because of the deformable nature of the simultaneously flowing fluids, flow of gas and liquid in pipes represents a much more complex process than single-phase flow. As a consequence of this deformable nature, gases and liquids may adopt a wide variety of spatial flowing configurations known as flow patterns. Figure 22.5 illustrates typical gas/liquid spatial distributions that can take place in horizontal flow in pipes. Pressure loss predictions for each of these flow patterns are significantly more complex than the single-phase flow predictions previously discussed. The prediction of the type of flow pattern taking place under the given operational conditions is typically a primary consideration because the mechanistic model and empirical correlation that needs to be used to describe pressure losses are dependent on it.

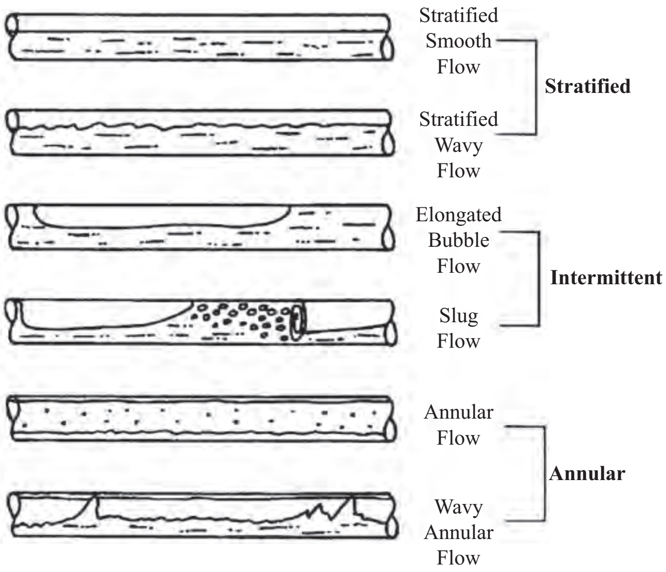


Figure 22.5—Two-phase flow patterns in horizontal flow. *Source:* [39].

Flow pattern condition is a strong function of pipe inclination and relative amounts and velocities of the gas and liquid flowing in the pipe. One of the distinguished features of modern multiphase prediction models is the need for a reliable tool for the prediction of flow pattern transitions for a given set of operational conditions. Baker introduced what is considered the first useful attempt to creating a flow regime map for flow pattern determination [40]. One of the earliest attempts that introduced a fully phenomenological description of how transitions occur among the different flow patterns was the work developed by Taitel and Dukler [41], which focused on horizontal and near-horizontal pipes. This work led the way for the subsequent research in the area, and most of their transition criteria are still in use in more recent two-phase flow models. A few years after that initial work, Taitel et al. proposed the model for the vertical and near-vertical case [42]. Afterward, Barnea extended the phenomenological approach to the whole range of pipe inclinations [43]. These three works are commonly referenced among researchers in the area and are the basis of numerous subsequent attempts for prediction improvement.

Brill and Arirachakaran presented an overview of how multiphase flow development was undertaken by the petroleum industry during the second half of the past century [39]. They clearly divided this development into three partially overlapping periods: the empirical period, the awakening years, and the modeling period. During the empirical period, all of the efforts were focused on correlating data from laboratory and field facilities in an attempt to encompass the widest range of operational conditions possible. One of the earliest attempts to empirically predict two-phase flow pressure drops is the well-known work of Lockhart and Martinelli for horizontal pipes [44]. This correlation was followed by an innumerable number of new ones, which claimed to be progressively more applicable for a wider range of operational conditions. Being the first quantitative approach to two-phase flow modeling, Lockhart- Martinelli's correlation became a classic against which subsequent correlations were compared. The fact is that most correlations were always best applicable for the conditions for which they were derived from. One of the best well-known empirical correlations from the period is the one developed by Beggs and Brill for two-phase flow behavior prediction in inclined pipes [45]. Along with several modifications applied to it, Beggs and Brill's correlation has become one of the most extensively used empirical correlations in the petroleum industry. The correlation considers horizontal, vertical, and inclined pipes, and the basic correlating parameter was the Froude number—the dimensionless number quantifying the relative influence of gravitational forces to inertial forces. Reliability of empirical approaches is limited by the uncertainty of their application to systems operating under different conditions than those from which the correlations were originally proposed. However, design of flow lines in multiphase production facilities that is based on empirical correlations was the norm until well into the 1980s and continues to be popular. Brill and Mukherjee presents a complete review of the tools available for pressure-gradient prediction of multiphase flow in oil wells, which is composed of a diverse set of empirical correlations and more recent mechanistic developments [11].

The advent of the personal computer during the 1980s dramatically enhanced the capabilities of handling progressively more complex design situations, which Brill and Arirachakaran called "the awakening years." Much of the petroleum research on multiphase flow during these years and the subsequent modeling period was enriched by the progress already made by the nuclear industry [39]. Although the nuclear industry dealt with simpler fluids (water and steam), it led the way toward more involved two-phase flow analysis in the petroleum industry. The work of Taitel and Dukler is considered one of the classical papers in multiphase predictions that began to incorporate more physical insight into the analysis in the petroleum industry and spearheaded phenomenologically based modeling efforts [41]. The modeling period, extending up to the present day, refers to the growing tendency of introducing more physically based (mechanistic or phenomenological) approaches into multiphase flow calculations. The main goal remains at attempting to reduce the dependency on empirical correlations during multiphase predictions. This has been achieved through the implementation of two-fluid models, in which separate equations of mass and momentum conservation are written for each flowing phase. Mechanistic modeling has since evolved as a compromise between the use of empirical correlations and two-fluid models. In mechanistic modeling, physical laws from the two-fluid model approach are applied and empirical relationships are used to achieve mathematical closure of the model. The studies of Xiao et al. [46], Ansari et al. [47], and Kaya et al. [48] proposed steady-state comprehensive mechanistic models for two-phase flow in horizontal pipes, vertical wells, and deviated wells, respectively. Brill and Mukherjee present a review of some of the steady-state mechanistic models available for the case of multiphase flow in vertical wells [11]. Hasan and Kabir provide a complete review of multiphase model developments for vertical, deviated, and horizontal wells [49]. More recently, Shoham presented a comprehensive review of the mechanistic modeling of multiphase flow in pipelines, wellbores, and inclined pipes [50].

Expected pressure drops in gas-liquid pipes can be much higher than in single-phase pipes and much more sensitive to pipe elevation and relative amounts and velocities of flowing phases. Significantly increased pressure losses can take place because of the interaction between the phases across their interface and the interaction of each of the phases with the pipe wall. In various applications, increased pressure drops have been accounted for by extending the application of single-phase models and assuming the flow of a single homogeneous pseudophase in the pipe. This can be shown to result in poor predictions because it oversimplifies the multiphase flow problem. The use of single-phase equations for multiphase flow applications forces the use of artificially inflated values of single-phase friction factors. For example, in natural gas applications, the use of low "efficiency factors" (E_f) is typically "recommended" when liquids are expected in the line. For such cases, efficiency factors of $E_f = 0.80$ are not uncommon, and what this value does is to artificially increase friction factor prediction of the gas equation by 54 %. The use of efficiency factors in the order of $E_f = 0.70$ would more than double the friction factor prediction of the equation. It is a better practice to implement special purpose multiphase flow correlations. Proper pipeline design must account for the effect of concurrently flowing phases on the performance of the line, and for the purpose of more reliable predictions, readers are referred to the mechanistic references and correlations discussed above.

22.12 PIPELINE NETWORKS AND TRANSPORTATION MODELING

Most practical situations involve systems of pipelines that are interconnected forming a network. Typical networks can be made up of pipes in series, pipes in parallel, branching pipes, and looped pipes. In complex network analysis, it is not uncommon to reduce the complexity of the system as much as possible based on the concept of the equivalent pipe. On the basis of this and under certain conditions, it usually proves convenient to replace a system of pipelines by single pieces of pipe of equivalent length or diameter. A single pipe is considered to be equivalent to another system of pipes when it is capable of transporting the same fluid volume under the same pressure drop requirement.

For pipelines in series, flow rate is the same in all pipe sections and total pressure drop equals the sum of all partial pressure drops per section; thus,

$$(\Delta p^*)_T = \sum_i (\Delta p^*)_i \tag{22.34a}$$

or,

$$R_{eq} \cdot q_K^{1/n} = \sum_i R_i \cdot q_{Ki}^{1/n} \tag{22.34b}$$

Because flow rates are the same in all sections, we end up with the well-known relationship for calculation of equivalent resistance in an electrical circuit in series:

$$R_{eq} = \sum_i R_i \tag{22.34c}$$

which can be re-expressed, on the assumption of same specific resistances for all pipelines (when applicable), as

$$\frac{L_{eq}}{d_{ref}^m} = \frac{L_{ref}}{d_{eq}^m} = \sum_i \frac{L_i}{d_i^m} \tag{22.34d}$$

The calculation of equivalent diameter for a system in series entails the selection of a reference length (usually total length), or, alternatively, the selection of a reference diameter (usually the most common in the system) for the calculation of an equivalent length. For the case of Hazen-William equation for liquid flow ($m = 4.87$), equivalent pipe calculations are thus expressed as

$$L_{eq} = d_{ref}^{4.87} \cdot \sum_i \frac{L_i}{d_i^{4.87}} \tag{22.34e}$$

$$d_{eq} = \frac{L_{ref}^{0.20534}}{\left(\sum_i \frac{L_i}{d_i^{4.87}}\right)^{0.20534}} \tag{22.34f}$$

For pipelines in parallel, pressure drop is the same in all pipe sections and total flow capacity equals the sum of all flow rates transported for each line in the system. Thus, one writes

$$(q_K)_T = \sum_i (q_K)_i \tag{22.35a}$$

or,

$$(C_{eq} \cdot \Delta p^{*n})_T = \sum_i (C_K \cdot \Delta p^{*n})_i \tag{22.35b}$$

Because all pipe sections share the same pressure drop, one readily derives the well-known relationship for calculation of equivalent resistance and conductivity in an electrical circuit in parallel:

$$C_{eq} = \sum_i C_{Ki} \quad \rightarrow \quad \frac{1}{R_{eq}^n} = \sum_i \frac{1}{R_{Ki}^n} \tag{22.35c}$$

On the assumption of same specific resistances for all pipelines (when applicable), the above equation can be expressed in terms of pipe dimensions as follows:

$$\frac{d_{ref}^{m \cdot n}}{L_{eq}^n} = \frac{d_{eq}^{m \cdot n}}{L_{ref}^n} = \sum_i \frac{d_i^{m \cdot n}}{L_i^n} \tag{22.35d}$$

Therefore, and contingent on the definition of a reference dimension (length or diameter), pipe equivalent diameters or lengths in circuits in parallel can be defined by applying Eq 22.35d. For example, for the case of the Weymouth equation for gas flow ($m = 16/3$; $n = 0.5$), equivalent pipe calculations are readily expressed as

$$d_{eq} = \left[L_{ref}^{0.5} \cdot \sum_i \frac{d_i^{8/3}}{L_i^{0.5}}\right]^{3/8} \tag{22.35e}$$

$$L_{eq} = \frac{d_{ref}^{16/3}}{\left(\sum_i \frac{d_i^{8/3}}{L_i^{0.5}}\right)^2} \tag{22.35f}$$

A well-known application of parallel pipe systems is the implementation of pipeline looping, which is the most widely used way of increasing system capacity in natural gas gathering system and transmission lines. It consists of the use of a parallel, additional pipe of equal or larger diameter and equal or shorter length that runs parallel to the original existing line. Using the above equations, it can be shown that the length of loop (x) needed to increase system capacity from $q_{K\text{-}orig}$ to $q_{K\text{-}new}$ is given by

$$\frac{x}{L} = \frac{1 - \left(\dfrac{q_{K-orig}}{q_{K-new}}\right)^{1/n}}{1 - \left(\dfrac{d_{orig}^{m \cdot n}}{d_{orig}^{m \cdot n} + d_{new}^{m \cdot n}}\right)^{1/n}} \tag{22.36}$$

Equation 22.36 implies that, on the basis of predictions from Panhandle-B in a gas system, 40 % of an existing pipeline should be looped to increase the overall capacity of the system by 20 % if a new parallel line of equal diameter is to be installed.

Systems where the majority of the pipelines are interconnected forming a network are the prevailing situation in fluid transmission and distribution. Pipeline systems that form a connected net or network are composed of two basic elements: nodes and node connecting elements (NCEs). NCEs can include pipe legs, compressor or pumping stations, valves, and pressure and flow regulators, among other components. Nodes are the points where two pipe legs or any other connecting elements intercept or where there is an injection or offtake of fluid. Modeling and understanding the behavior of a network system is not a matter of studying the performance of a single constituent component; but rather one must undertake a comprehensive study of the consequences of interconnectivity on the system.

It is not uncommon for network systems to have at least one closed pipe circuit or pipe loop. The presence of pipe loops increases the reliability of delivery of the transported fluid because certain network nodes can be reached simultaneously by more than one pipe. In network problems, all physical features of the network are assumed to be known and the analysis consists in determining resulting flow through each pipe and associated nodal pressures. The steady-state assumption is typically embraced, although transient flow analysis is also possible at a much greater computational load. A steady-state network problem can be formulated in several ways. In general, it consists of a system made up of N nodes, B pipe branches or bridges (edges or arcs), and LP loops, as shown in Figure 22.6. Network theory shows that these three quantities are mathematically related through the expression B = (N − 1) + LP, where LP represents the number of independent loops that can be defined in a network graph with N nodes and B branches. In Figure 22.6, B = 7, N = 6, and thus LP = 2. Network analysis typically entails the calculation of flow capacity of each pipeline segment (B-segments) and pressure at each pipe junction (N-nodes) in a network. This can be accomplished by either making pipe flows the primary unknowns of the problem (i.e., the q-formulation, consisting of B unknowns) or by making nodal pressures the primary unknowns (i.e., the p-formulation, with N − 1 unknowns). In both cases, to achieve mathematical closure, the number of available equations must match the number of unknowns in the problem.

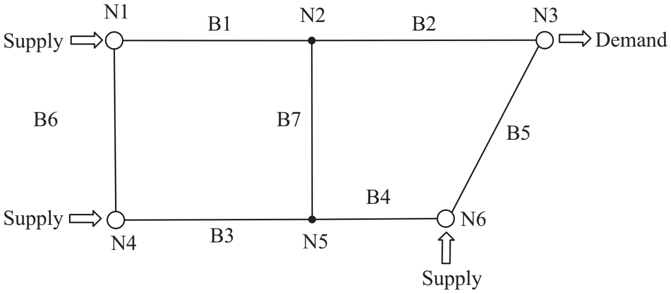


Figure 22.6—A pipeline network schematic.

In the q-formulation, network equations are formulated based on the principles of mass conservation or continuity and energy conservation to solve for B unknowns (individual pipe flow rates). N equations of mass conservation can be written at each nodal junction in the system. In nodal mass conservation, the algebraic sum of flows entering and leaving the node must be equal to zero. In other words,

$$\sum_i q_{ki}^{in} - \sum_i q_{ki}^{out} + S - D = 0 \tag{22.37}$$

written for each node and for all flows converging to it.

Equation 22.37 is recognized as the first law of Kirchhoff of circuits, in direct analogy to the analysis of flow of electricity in electrical networks. S and D represent any external supply or demand (sink/source) specified at the node. For gas networks, this equation is actually a mass conservation statement although it is written in terms of volumetric rates. For liquids, mass conservation and volumetric conservation go hand in hand because densities are nearly constant. For gases, volumetric flow rates are always expressed at a common standard condition reference (SCF), in which one unit of standardized volume contains a fixed number of molecules (1 SCF = 379.4 lbmol). Equation 22.37 provides (N − 1) admissible equations because only (N − 1) nodal equations are linearly independent. In a network model, an overall mass balance must be always in place when network problems are proposed because demand and supply nodes are balanced. Therefore, one out of the N nodal conservation equations can be inferred by subtracting the (N − 1) nodal equations from the overall demand and supply balance. As a consequence, LP additional equations would be needed to exactly balance the number of unknowns B [B = (N − 1) + LP] and achieve mathematical closure of the q-formulation. These equations can be formulated by applying the second law of Kirchhoff to every independent loop. In any loop in the system, the algebraic sum of all pressure drops must be equal to zero. This is true of any closed path in a network because the value of pressure at any point of the network must be the same regardless of the path followed to reach the point. The signs of the pressure drops are taken with respect to a consistent sense of rotation around the loop, and the loop equation is written as

$$\sum_i (\Delta p^*)_i = 0 \tag{22.38}$$

written for each loop and each pipe belonging to it. Loop equations must be rewritten in a q-formulation in terms of flow rates using the short form of the flow equation written in terms of pipe resistances:

$$\sum_i R_i \cdot q_{ki}^{1/n} = 0 \tag{22.39}$$

Equation 22.37 provides (N + 1) equations and Eq 22.39 the additional LP equations required to solve for B flow pipe unknowns. Note that these equations are valid for liquid and gas flow networks and can be readily applied to any specialized flow equation provided that the proper values of R_K, n, and m are applied.

In the p-formulation, network equations are formulated based on the principles of nodal mass conservation (continuity) to solve for N – 1 unknowns (i.e., nodal pressures). One nodal pressure is assumed to be known in the system and the rest are calculated as a function of it. Because only N – 1 equations are required, nodal mass continuity equations are all that is required by this formulation. However, Eq 22.37 must be written in terms of nodal pressures using the short form of the flow equation written in terms of pipe resistances:

$$\sum_i C_{Ki} \cdot (\Delta p^*)_i^n + S - D = 0 \tag{22.40a}$$

In Eq 22.40, fluid flowing into the node is assumed positive and fluid leaving the node is given a negative sign. External supplies and demands (sink/sources) specified at the node must also be considered. Again, these network equations are equally applicable to liquid and gas networks and can be readily applied to any specialized flow equation when the proper values of C, n, and m are applied. For liquids, the equation is written in terms of pressure heads (see Eq 22.4c):

$$\sum_i C_{Li} \cdot (h_f)_i^n + S - D = 0 \tag{22.40b}$$

For gases, the use of Eq 22.11 yields

$$\sum_i C_{Gi} \cdot (p_1^2 - p_2^2)_i^n + S - D = 0 \tag{22.40c}$$

Whether it is the q-formulation with B simultaneous equations or the p-formulation with N – 1 simultaneous equations, a network problem is finally expressed in terms of a set of nonlinear equations that must be solved simultaneously for the desired target unknowns. The larger the network, the more complex the resulting system of equations becomes. Throughout the years, several protocols for the simplified solution of network equations have been proposed, most notably, the Hardy Cross method [51] and the Linear Theory method [52]. The Hardy Cross method, originally proposed for the analysis of frames in structural engineering by moment distribution, became widely popular for the analysis of fluid networks because it implemented an iterative scheme readily suitable for hand calculations that circumvented the significant labor of solving the simultaneous set equations. The advent of modern computer power has rendered the application of these early approaches unnecessary, although they continue to be an important reference and the basis of early computer software. Nowadays, the application of the multivariate Newton-Raphson method is rather the norm for the simultaneous solution of the large systems of nonlinear equations typically involved in network applications. The most significant and widely known limitation of Newton-Raphson methods is that it has the unfortunate tendency of diverging hopelessly if it is not started sufficiently close to the actual solution ("local convergence"). As a result, only globally convergent Newton-Raphson methods should be implemented while solving complex network problems. In these methods, the quadratic local convergence of Newton-Raphson is coupled with a globally convergent strategy that can better guarantee progress and convergence toward the solution regardless of the starting point (see, for example, Press et al. [53]).

To circumvent Newton-Raphson convergence problems and its potentially costly implementation, Ayala and Leong recently proposed a robust linear-pressure pipe analog for the solution of highly nonlinear natural gas transportation networks [54]. The method consists in defining an alternate, analog system of pipes that obey the simpler linear-pressure analog flow equation $q_{gSC} = C'_G \cdot (p_1 - p_2)$. When gas pipe flows are written in terms of such linear analog, nodal mass balance in Eq 22.40c collapses to very simple algebraic equations in linear pressures shown in Eq 22.41:

$$\sum_i C'_{Gi} \cdot (p_1 - p_2)_i + S - D = 0 \tag{22.41}$$

which can be used to simultaneously solve for all nodal pressures in the network using any standard method of solution of linear algebraic equations. Ayala and Leong demonstrate that all that is needed to create the linear-pressure analog is to adjust actual pipe conductivities according to the following transformation [54]:

$$C'_G = C_G \cdot \sqrt{1 + \frac{2}{r-1}} \tag{22.42}$$

where:

C'_G = conductivity of the linear-pressure analog pipe,

C_G = the actual pipe conductivity conforming to the generalized gas flow equation $q_{gSC} = C_G \cdot (p_1^2 - p_2^2)^{0.5}$ shown in Table 22.3, and

r = the pipe pressure ratio $r = p_1 / p_2 > 1$.

Because pipe pressure ratios are always higher than unity ($p_1 > p_2$ for gas to flow), the transformation in Eq 22.42 indicates that linear-pressure analog conductivities are consistently (and sometimes significantly) higher than actual pipe conductivities. Because these pressure ratios cannot be known in advance, the implementation of Eq 22.42 requires solving the nodal balances in Eq 22.41 for $C'_G \approx C_G$ for the first iteration. Once a nodal pressure solution is available, pressure ratios and linear-analog conductivities in Eq 22.42 are updated. Successive iterations will follow until calculated nodal pressures do not significantly change within a prescribed tolerance. Actual C_G values are also updated at every iteration using the appropriate friction factor functional form in Table 22.3 that corresponds to the gas flow equation being implemented.

The linear-pressure pipe analog method is fundamentally different than the Linear Theory method [52] in the

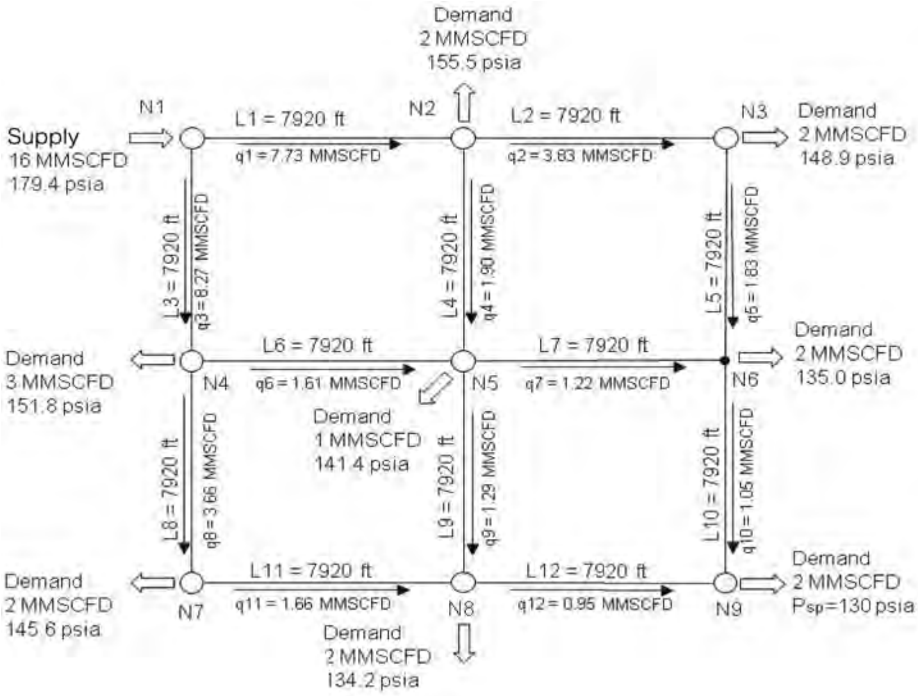


Figure 22.7—A natural gas network distribution scenario.

sense that it always relies on exact solutions to well-behaved linear-analog fluid flow problems for each of its iterations, which makes it quite stable and reliable. The Linear Theory method instead relies on solving approximate sets of linearized equations that do not necessarily correspond to physically constrained systems and thus are susceptible to spurious numerical oscillations. In addition, the linear-analog method does not require the formulation of loop equations (which eases its implementation), solely relies on nodal balance information, and does not need initial pressure guesses to initiate the protocol. When compared with Newton-Raphson iterations, linear-analog iterations are inexpensive in implementation and execution. However, the convergence of the linear-pressure analog is nonquadratic. Because of the unfortunate Newton-Raphson tendency of diverging hopelessly if not started sufficiently close to the actual solution, a hybrid approach can be devised in which the linear-analog method is first implemented to inexpensively and reliably advance the pressure solution to a point where the quadratic convergence of the Newton-Raphson protocol can be fully taken advantage of.

Figure 22.7 presents a fully converged natural gas ($SG_g = 0.69$) network distribution scenario that is based on the implementation of the generalized gas equation and Colebrook-based friction factor calculations. The network solution depicted in Figure 22.7 was independently attained using a globally convergent Newton-Raphson method and the linear-pressure pipe analog method. The average compressibility factor was calculated implicitly using the Dranchuk and Abou-Kassem correlation at each pipe average pressure [55]. An average flowing temperature of 75°F was assumed for the entire system. All pipes are carbon steel ($e = 0.0018$ in), horizontal, 7920 ft long, and NPS 4 Sch 40, except for pipes 1, 2, 3, and 8, which are NPS 6 Sch 40. In terms of the implementation of the linear-pressure pipe analog method, the proposed gas network in Figure 22.7 generates the following linear system of algebraic equations in nodal pressures:

$$\begin{bmatrix} -O_1 & C'_{G1} & 0 & C'_{G3} & 0 & 0 & 0 & 0 & 0 \\ C'_{G1} & -O_2 & C'_{G2} & 0 & C'_{G4} & 0 & 0 & 0 & 0 \\ 0 & C'_{G2} & -O_3 & 0 & 0 & C'_{G5} & 0 & 0 & 0 \\ C'_{G3} & 0 & 0 & -O_4 & C'_{G6} & 0 & C'_{G8} & 0 & 0 \\ 0 & C'_{G4} & 0 & C'_{G6} & -O_5 & C'_{G7} & 0 & C'_{G9} & 0 \\ 0 & 0 & C'_{G5} & 0 & C'_{G7} & -O_6 & 0 & 0 & C'_{10} \\ 0 & 0 & 0 & C'_{G8} & 0 & 0 & -O_7 & C'_{G11} & 0 \\ 0 & 0 & 0 & 0 & C'_{G9} & 0 & C'_{G11} & -O_8 & C'_{G12} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} p_1 \\ p_2 \\ p_3 \\ p_4 \\ p_5 \\ p_6 \\ p_7 \\ p_8 \\ p_9 \end{bmatrix} = \begin{bmatrix} -16 \\ 2 \\ 2 \\ 3 \\ 1 \\ 2 \\ 2 \\ 2 \\ 130 \end{bmatrix}$$

where O_i represents the summation of all off-diagonal entries for the ith row. For example, $O_1 = C'_{G1} + C'_{G3}$; $O_5 = C'_{G4} + C'_{G6} + C'_{G7} + C'_{G9}$; and $O_8 = C'_{G9} + C'_{G11} + C'_{G12}$. All pipe conductivities (C_G and C'_G) are assumed in MMSCFD/psi. The resulting linear-pressure analog system of equations can be solved quite inexpensively by exploiting the symmetric nature of the resulting matrix that does not use the p-specified node constraint. Successive iterations are implemented until the linear-analog conductivities (C'_G) and resulting nodal pressure converge to a final solution.

One of the most important applications of pipe network analysis such as the one applied to the system in Figure 22.7 is its ability to perform network-wide sensitivity analysis. Sensitivity analysis is used to prioritize what changes in network components are the most important for the improvement of overall network performance. This can be especially critical when the demands or supplies in the system change in time and the network adjustments are required. The quantification of how sensible flow variables are to changes in one variable or several design variables can provide a much deeper understanding of network performance. This analysis typically leads to the identification of the network component for which adjustment or replacement is most likely to help overcome deficiencies in network performance. Larock et al. present an excellent description of recommended sensitivity analysis for operating liquid networks, easily extendable to the analysis of gas networks, and extending the network discussion to transient modeling [17]. Szilas [56] and Osiadacz [57] also review computational details of the numerical calculation of network systems typical of gas transportation for steady-state and transient modes.

Extension of network analysis to multiphase flow is not straightforward. In fact, the issue of two-phase flow in the analysis of complex pipeline networks is yet to be comprehensively addressed by currently available pipe network models. The most common approach of two-phase pipeline network analysis is the development of pseudo two-phase network models. These models attempt to use single-phase network analysis equations coupled with empirical two-phase correlations that account for the augmented pressure loss caused by multiphase condition (e.g., through the introduction of efficiency factors or multiphase flow pressure drop correlations). However, this generation of models is handicapped. Although they attempt to account for the increased pressure losses in the system, such approaches cannot predict liquid and gas distribution within the network, identify preferential routes, and thus generate reliable pressure or temperature profiles. One of the critical problems here is the uneven phase split that takes place at network nodes (T-junctions). During two-phase flow operation, liquid splitting at locations of pipeline branching is known to have a profound effect on the fluid distribution and behavior of the network response. Liquid preferential routing at these locations determines bottleneck locations and affects the quality and quantity of fluid that the network is able to deliver at demand nodes. Splitting mechanisms in two-phase flows at pipe junctions have been shown to be a strong function of junction geometry and relative kinetic energy of the incoming phases. Although junction effects are yet to be fully incorporated in the context of traditional network analysis, Alp recently discussed the issue and presented a finite-volume based numerical algorithm that can be applied for the prediction of fluid migration in such a complex multiphase environment [58].

Pipes are not the only components present in complex network transportation systems. There are other important components that make up a network system and that are essential to operation of the system. Some of these are pumps, compressors, meters, valves, elbows, tees, and various fittings. Pumps and compressors primarily input additional energy to the network system to make fluid transportation possible. All other fittings would actually cause additional pressure losses. Depending on the scale of the pipe network system, the so-called minor, local, or secondary irreversible losses experienced by these fittings might need to be accounted for. As shown in previous sections, pipeline equations only consider irreversible primary losses ($\delta lw = \delta lw_f$; see Eq 22.3). Minor or secondary losses (δlw_K) encompass any compression energy loss that takes place at fittings (elbows, valves, etc.) and that adds to the primary or major losses taking place at the straight portions of pipe in the system. In Eq 22.1, full accountability of primary and secondary irreversible losses requires considering

$$\delta lw = \delta lw_f + \delta lw_K \tag{22.43}$$

where primary losses (δlw_f) are determined by using the dimensionless friction factor concept (Eq 22.3) and secondary losses due to fittings are determined using the concept of local loss or minor loss coefficient (K), also known as the resistance coefficient. The minor loss coefficient (K) is a dimensionless coefficient that is heavily dependent on experimental data and allows the calculations of minor losses as follows:

$$\delta lw_K = K \cdot \frac{v^2}{2g_c} \tag{22.44}$$

where v is typically taken as the velocity downstream of the fitting. Minor loss coefficients are heavily dependent on the type of fitting, and can take values anywhere in between 0.1 to more than 10. Minor losses caused by 45° elbows, for example, are characterized by coefficients $0.3 < K < 0.4$, whereas secondary losses caused by 90° elbows typically show $0.4 < K < 0.9$. Loss coefficients for individual devices, valves, and fittings are tabulated in reference books in fluid mechanics and industry handbooks (e.g., Bird et al. [13]; GPSA [25]; Stevens and May [31]). The use of loss coefficients (K) for the estimation of minor losses is common in process system piping design, and it has become customary to express minor (secondary) losses in terms of an equivalent pipe length. The additional loss caused by fittings is expressed in terms of an additional equivalent length of straight pipe that would have the same pressure drop as the one caused by the fitting for the same flow rate. The equivalent pipe length calculation is based on equating the definitions of δlw_K (Eq 22.44) and δlw_f (Eq 22.3) to obtain

$$f_M \cdot \frac{v^2}{2g_c d}(L_e) = K \cdot \frac{v^2}{2g_c} \tag{22.45a}$$

or,

$$L_e = K \cdot \frac{d}{f_M} = K \cdot \frac{d}{4f_F} \tag{22.45b}$$

Equation 22.45b provides the means for the calculation of the additional length of pipe that should be added to the actual pipe length to come up with an equivalent system in terms of pressure loss. In large-scale pipeline networks, these minor losses are largely ignored because most of the pressure drop takes place at the straight pipe sections. However, in some other applications, these secondary losses can become quite significant and accounting for them may become critical. For example, pressure drops caused by the presence of chokes and constrictions (such as partially closed valves) in production facilities can be significantly larger than those experienced by the straight portions of piping.

For long-distance transportation, the installation of pumps and compressors is essential. Fluid compression energy gets lost as fluid flows through the pipe, and available fluid compression energy can get easily exhausted in long-distance transportation. Pumps and compressors are the mechanical devices in charge of increasing fluid motive power (pressure) at prescribed locations in the network so that the fluid can get delivered at the contracted rates and delivery pressures. The presence of pumps or compressors must be acknowledged by the network equations used in transportation modeling. These devices are treated as additional NCEs with their own set of $q_K = f$ (*nodal pressure or head increase*) constitutive rate-pressure relationship. Constitutive relationships for pumps and compressors are derived from manufacturer-provided performance data. In gas transportation, compressor performance can be approximated by the following $q_{gSC} = f$ (*nodal pressure increase*) functional relationship:

$$q_{Gsc} = \frac{HP}{k_a \left(\frac{p_2}{p_1} \right)^{k_b} + k_c} \tag{22.46}$$

This functional relationship between compressor horsepower (HP) and compressor throughput (q_{Gsc}) can be derived from a thermodynamic balance applied to a compression process. Coefficients k_a, k_b, and k_c can be related to fluid properties when using the thermodynamic ideal compression equation, but they are typically calculated to match actual compressor performance data and compressor characteristics as provided by the manufacturer. In liquid transportation, the pump characteristic curve is expressed in terms of liquid head produced by the pump (h_p) expressed as a polynomial function of pump discharge [17]:

$$h_p = k'_a q_L^2 + k'_b q_L + k'_c \tag{22.47}$$

Equation 22.42 provides the basis for the typical $q_L = f$ (*nodal head increase*) functional relationship used for pumps, which can be explicitly derived by applying the quadratic formula. The coefficients k'_a, k'_b, k'_c of this polynomial are determined from an empirical fitting of manufacturer-provided pump-curve data.

Fluid supplies in network analysis (S) can be treated as known and constant if there is enough certainty about the amount of fluid that can be withdrawn from the supply source. However, available fluid supplies at a node might vary with changes in the transportation network. In general, as the network provides more resistance to flow, the less fluid can be withdrawn from a supply node. Fluid withdrawal from above-ground reservoirs/tanks and production from underground reservoirs are examples of supply sources with variable fluid delivery capacity, which can be dependent on the prevailing conditions at the connection node. In water transportation and distribution systems, reservoir discharge from above-ground water reservoirs is a function of water surface elevation with respect to a datum. Flow occurs out of the upper reservoirs into lower reservoirs when connected through a system of pipes. For the modeling of these supply sources, the point where the reservoir is connected to the network is modeled as a node where the liquid head (h_p) is specified, and the resulting discharge is calculated by coupling it with the rest of the network system. In production from underground reservoirs, fluid discharge is a function of the pressure imposed at the wellhead (p_{wh}) and reservoir and well tubing characteristics. This requires coupling reservoir performance with tubing performance and to postulate a $q_K = f$ (*wellhead pressure*) functional relationship. For example, production of gas wells from an underground reservoir can be characterized by the following rate-pressure relation:

$$q_{Gsc} = C_{wr}(p_{shut}^2 - p_{wh}^2)^n \tag{22.48}$$

where:
C_{wr} = the well/reservoir performance coefficient;
n = the flow exponent ($0.5 < n < 1$); and
p_{shut} is the wellhead pressure specification (p_{wh}) for which $q_{Gsc} = 0$, which corresponds to the no-flow static reservoir pressure corrected by the weight of the hydrostatic gas column between the wellhead and reservoir depth.

The C_{wr} well/reservoir performance coefficient is a function of tubing pipe resistance (R_K) and reservoir properties such as permeability, formation thickness, and drainage area. In network analysis, wells are connected through a nodal point that represents wellhead pressure (p_{wh}), and the variable supply from the gas well is calculated by implementing the rate-pressure relation in Eq 22.48.

22.13 TEMPERATURE PROFILES IN PIPE FLOW

Most pipeline flow analysis is largely done based on the assumption of isothermal flow—i.e., by largely neglecting temperature variations along the pipeline. An average flow temperature assumption is reasonable when fluid inlet temperature is close to ambient temperature surrounding the pipeline and heat transfer effects with the environment can be neglected. However, significant changes in fluid temperature should be expected when the heat transfer with the surroundings is large and when energy transformations induced by fluid flow cannot be neglected (e.g., kinetic or potential energy changes and Joule-Thomson effects). Heat transfer can be significant for gas pipes leaving compressor stations, where inlet temperatures can be significantly above ambient temperature; in the flow of high viscosity oils, which are heated for viscosity control before they are sent to a pipeline; or during fluid flow in wellbores, where the pipe traverses the geothermal gradient and reservoir fluid temperature cools as it is brought to the surface. Fluid properties are temperature–dependent, and temperature-driven property changes along the pipe can have an important effect on pressure drop calculations.

Even when kinetic, potential, and heat transfer effects are not considered significant, pipeline temperature can change with distance. In this case, pipeline flow is said to be adiabatic and isoenthalpic as demonstrated by the thermodynamic balance presented in Eq 22.52. Isenthalpic natural gas pipelines tend to cool with distance (effect commonly called Joule-Thomson cooling) whereas oil lines heat. The reason for such energetic inversion is directly related to the sharply different volumetric behavior of liquids when compared to gases. For isoenthalpic pipe flow, Eq 22.2 yields

$$\vartheta dp = \frac{dp}{\rho} = -\delta lw_f = f_F \frac{2v^2}{g_c d} dx \tag{22.49}$$

Equation 22.49 indicates that compression energy ϑdp is continuously being lost during pipeline flow because of frictional or irreversible effects and that this loss of compression energy is what is being quantified through the use of friction factor coefficients. Katz and Lee argue that, because of the constant enthalpy constraint, the ϑdp compression energy lost through the frictional process is merely being internally converted into Tds heat energy within the flow system (since $dh = \vartheta dp + Tds$, it follows that $\vartheta dp = -Tds$ for isenthalpic flow) [59]. This internal conversion of energy is inherently irreversible because the process cannot be reversed to convert the newly created Tds heat energy back into ϑdp compression energy. In other words, the end result of friction between two surfaces is not heat generation but rather a transformation or conversion of one type of internal fluid energy into another. In pipeline flow, this internal swap of $\vartheta dp/Tds$ fluid energy can result in a lower or higher downstream fluid temperature depending on the substance's volumetric behavior. Because volumetric behavior is controlled by intermolecular forces, it follows that thermal behavior during the $\vartheta dp/Tds$ swap is controlled by the prevailing intermolecular force field in the fluid. This is the effect quantified by the Joule-Thomson coefficient (η), which is the thermodynamic property that measures fluid temperature responses during isenthalpic changes of pressure. Thermodynamics show that Joule-Thomson coefficient behavior closely tracks volumetric behavior through the changes in fluid compressibility factor (Z) with temperature as shown:

$$\eta = \left(\frac{\partial T}{\partial p}\right)_H = \frac{RT^2}{pc_p}\left(\frac{\partial Z}{\partial T}\right)_p \tag{22.50}$$

where:

c_p = constant pressure heat capacity of the fluid.

Because all other variables in this expression are always positive, the sign of the Joule-Thomson coefficient is directly dependent on the sign of the volumetric derivative $\left(\partial Z/\partial T\right)_p$. From this definition, cooling occurs during an isenthalpic process when η is positive ($\eta > 0$, which means $\left(\partial Z/\partial T\right)_p > 0$), and heating occurs when η is negative ($\eta < 0$, implying $\left(\partial Z/\partial T\right)_p < 0$). Equation 22.50 also shows that the condition $\left(\partial Z/\partial T\right)_p = 0$ directly defines the energetic inversion locus where $\eta = 0$. Figure 22.8 illustrates this point. This figure displays how the Z-factor of methane—the most predominant component in natural gases—changes as a function of reduced pressure ($p_r = p/p_c$) and reduced temperature ($T_r = T/T_c$) as calculated by the Peng-Robinson EOS. Figure 22.8 effectively describes the fluid energetic inversion. All transition points where $(dZ/dT)_p$ takes a zero value define the energetic inversion curve depicted by the dome in this figure. Cooling occurs when $(dZ/dT)_p$ (i.e., η) is positive—that is, inside of the inversion envelope—and heating occurs when $(dZ/dT)_p$ (i.e., η) is negative—outside of the inversion envelope.

Figure 22.8 shows that when the $\vartheta dp/Tds$ isenthalpic-energy swap takes place in a predominantly attractive molecular force field (i.e., inside of the inversion envelope), cooling takes place. However, when the isenthalpic swap takes place in a predominantly repulsive molecular force field (i.e., outside of the inversion envelope), heating takes place. Liquids have p-ϑ-T properties that cause them to rise in temperature when expanded adiabatically whereas gases usually show the opposite effect. Liquid systems typically operate above the vapor-pressure curve and far below its critical conditions (i.e., within the heating region that is found to the left of the inversion curve). Therefore, liquid systems would typically heat upon adiabatic expansion because $(dZ/dT)_p$ is negative for such conditions. In contrast, most natural gas systems operate at $T_r > 1$ and inside of the inversion curve; their volumetric behavior would consequently cause them to drop their temperature upon isenthalpic expansion (i.e., Joule-Thomson cooling). The transition from cooling to heating, represented by the inversion envelope, starts around $0.80 < T_r < 0.90$ and can be used to distinguish liquid-like from gas-like thermodynamic behavior around critical conditions. An alternate visualization of the energetic inversion line was proposed by Katz and Lee [59]. They contend that because $T = -\vartheta dp/ds$ for isenthalpic processes, the effect of pressure on fluid entropy is what defines the energetic inversion. For gases, entropy increase with pressure decline is so large that it overwhelms the denominator in the $\vartheta dp/ds$ ratio and induces self-cooling to take place. In contrast, entropy change with pressure decline for oils is so small that the exchange of ϑdp

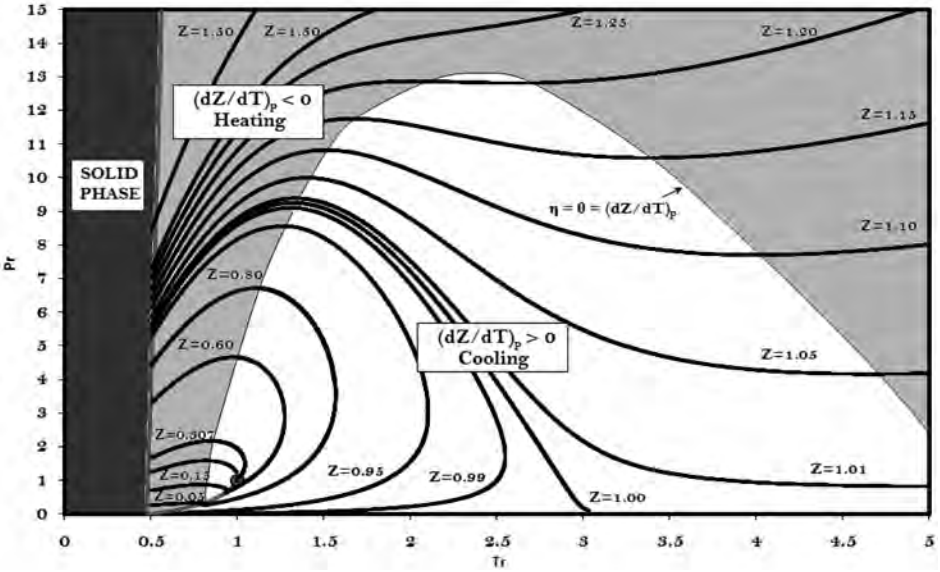


Figure 22.8—Volumetric behavior of methane based on Peng-Robinson EOS predictions highlighting its Joule-Thomson energetic inversion.

compression energy into *Tds* heat energy causes heating instead. Because the effect of pressure on entropy is controlled by volumetric behavior $[(\partial s / \partial p)_T = -(\partial \vartheta / \partial T)_p]$, and $(\partial \vartheta / \partial T)_p$ and $(\partial Z / \partial T)_p$ are directly related to each other through the fluid thermal expansion coefficient, their argument closely tracks the $(\partial Z / \partial T)_p$ discussion above.

More often than not, pipe flow cannot be considered fully isenthalpic and the effect of energy exchange with the environment and kinetic and potential energy changes must be also quantified. For the case of single-phase flow in pipelines, Coulter [60] proposed an explicit expression for the prediction of flowing temperature in gas pipelines that can be easily extended to liquid pipelines with the use of the appropriate fluid properties. The development of the Coulter [60] equation represented an extension of the previously published Coulter and Bardon [61] equation. These studies brought important improvements to the pioneering work of Shorre [62] and the review of Forrest [63] for pipeline temperature profiling. For the case of temperature profile predictions in wellbores, Ramey [64] presented what is considered the classical paper on the subject in the 1960s. In the 1990s, Alves et al. [65] presented a unified equation for flowing temperature prediction applicable to pipelines and wellbores applicable to the entire range of inclination angles. In the 2000s, Hasan and Kabir [49] have presented a comprehensive review of available wellbore fluid temperature models, including predictions for two-phase flow. In general, pipe and wellbore flowing temperature equations are derived by postulating the following enthalpic balance that is based on the first law of thermodynamics:

$$\left(\frac{dh}{dx}\right)_T = \left(\frac{dh}{dx}\right)_a + \left(\frac{dh}{dx}\right)_e + \left(\frac{dq}{dx}\right) \tag{22.51}$$

or, equivalently,

$$\frac{dh}{dx} = -\frac{v}{g_c J}\frac{dv}{dx} - \frac{g}{g_c J}\frac{dz}{dx} + \frac{dq}{dx} \tag{22.52}$$

where the heat transfer exchange (*dq/dx*) with the environment is typically written in terms of the overall heat transfer coefficient, *U*, as follows:

$$\frac{dq}{dx} = \frac{\pi U d (T_s - T)}{W} \tag{22.53}$$

where:

U = overall heat transfer coefficient,

d = pipe internal diameter,

T = flowing gas temperature,

T_s = surrounding temperature, and

W = total mass flow rate.

In Eq 22.48, q is considered positive when heat enters the pipe $(T_s > T)$ and negative if heat is leaving the pipe $(T_s < T)$. The heat transfer coefficient (U) in this equation characterizes the heat interaction between the flowing fluid and the environment (i.e., materials surrounding the pipeline). Use of accurate values for U becomes crucial when fluid flowing temperature changes are mainly driven by heat transfer with the surroundings. In an analogous way to the determination of U-coefficients in heat exchangers, the best way of estimating U-coefficients in pipe flow is the availability of actual flow tests when possible. In noninsulated pipes, pipe walls are considered infinitely conductive because they do not pose any significant heat flow resistance because of the typically large conductivity of steel and not very large wall thicknesses. In such situations, U basically equals the effective convective coefficient between the external side of the pipe and the environment. Values of U ultimately depend on the environmental conditions around the pipe and, for example, whether the pipe is buried or not. For a buried pipe, typical values of U are 0.1–2 Btu/ft²·h·°F. In these buried cases, U ends up being more or less equal to the conductivity of the surrounding ground or soil, which is formally true when the soil (surrounding) temperature is prescribed at a unit distance measured from the pipe external diameter because $U = k / L$ for approximately constant heat flow areas. Thermal conductivities of earth materials are found around k = 1.4 Btu/ft·h·°F, with values changing as a function of soil type, soil density, moisture content, and salt concentration, among others. Soil thermal science literature provides correlations for the calculation of conductivity as a function of soil properties, but reasonable values of U are most typically determined from known values used for old lines placed in similar soil conditions. In general, an average value of 1 Btu/ft·h·F is largely used for preliminary calculations for buried pipes. When pipelines are directly exposed to the atmosphere, the value of U can significantly increase to anywhere between 2 and 20 Btu/ft·h·°F or more. In cases of direct atmospheric exposure, U becomes practically equal to the convection heat transfer coefficient between the pipe external surface and the air surrounding it. A pipe can be exposed to natural (free) convection or forced convection in windy environments. For reliable estimations of U for pipes under external forced convection, one should use correlations for convective heat transfer coefficients for heat flow across cylinders found in standard heat transfer books. Typical values of heat transfer coefficients for forced convection can be approximately 2–50 Btu/ft·h·F. When pipes go across a water body (i.e., river or bottom of the ocean), U values can be much greater than 20 because heat transfer coefficients for forced convection in liquid bodies can be easily found anywhere within the range of 2–2,000 Btu/ft·h·°F.

By substituting the thermodynamic identity $dh = C_p dT - C_p \eta dp$ into Eq 22.52, an explicit expression for the fluid temperature gradient can be derived in terms of pressure drop as follows:

$$\frac{dT}{dx} = -\phi_u \left[(T - T_s) - \frac{\eta}{\phi_u}\frac{dp}{dx} + \frac{\phi_{ea}}{\phi_u} \right] \tag{22.54}$$

where:

ϕ_{ea} = elevation and acceleration factor $= \dfrac{1}{g_c J \cdot C_P}\left(v\dfrac{dv}{dx} + g\dfrac{dz}{dx} \right)$

and

ϕ_u = heat transfer factor $= \dfrac{\pi U d}{W C_P}$.

The integration of this equation yields

$$\int_{T_1}^{T} \frac{dT}{\left(T - T_s - \dfrac{\eta}{\phi_u}\dfrac{dP}{dx} + \dfrac{\phi_{ea}}{\phi_u} \right)} = -\int_0^x \phi_u dx \tag{22.55}$$

where:

T_1 = fluid inlet temperature.

This equation yields, upon integration and assuming a constant dp/dx within the integration interval,

$$T(x) = T_s + (T_1 - T_s)\,e^{-\phi_u x} + (1 - e^{-\phi_u x})\left(\frac{\eta}{\phi_u}\frac{dp}{dx} - \frac{\phi_{ea}}{\phi_u}\right) \tag{22.56}$$

Equation 22.56 gives the explicit dependency of temperature on pressure drop (dp/dx) as proposed by Coulter [60]. This expression considers the dependency of this relationship on Joule-Thomson coefficients, potential and kinetic changes (ϕ_{ea}), and heat transfer with the environment (ϕ_u). If potential and kinetic energy changes are neglected ($\phi_{ea} = 0$), Eq 22.56 collapses to the original Coulter and Bardon [61] equation:

$$T(x) = T_s + (T_1 - T_s)\,e^{-\phi_u x} + (1 - e^{-\phi_u x})\frac{\eta}{\phi_u}\frac{dp}{dx} \tag{22.57}$$

When one further assumes that Joule-Thomson effects can be neglected (i.e., Joule-Thomson coefficient is close to zero, which can be a reasonable assumption for liquids), Eq 22.57 is rendered pressure drop independent and can be further simplified to

$$T(x) = T_s + (T_1 - T_s)\,e^{-\phi_u x} \tag{22.58}$$

Equation 22.58 considers that the dominant contribution to fluid temperature changes is heat transfer with the surroundings and it is frequently used in oil transportation. The exponential term in this equation tends to approach zero as distance from the inlet increases; thus, fluid temperature ultimately equals surrounding temperature (atmospheric or soil temperature), especially for long pipes.

Equations 22.56–22.58, as applicable, must be coupled with the appropriate pressure drop equation when the flow of liquid and gases cannot be well represented by an isothermal model. This would especially be the case when fluid inlet temperature greatly differs from ambient temperature, which forces nonadiabatic conditions throughout the length of the pipe. For simultaneous prediction of pressure and temperature changes along a pipeline, one may resort to using specialized flow equations for dp/dx calculations and the analytical dT/dx equation for temperature calculations working concurrently. Caution is needed to fully account for the combined effect that pressure and temperature changes can have on fluid properties such as density and viscosity. Fluid properties should be updated accordingly, and iterations are likely to be needed.

REFERENCES

[1] "Statistical Review of World Energy," 2009, British Petroleum, www.bp.com.

[2] "EIA—Energy Information Administration," 2010, http://www.eia.doe.gov/.

[3] Wang, X., and Economides, M., "Advanced Natural Gas Engineering," *Gulf Publishing Company*, Houston, Texas, 2009.

[4] Wood, D.A., Mokhatab, S., and Economides, M.J., "Technology Options for Securing Markets for Remote Gas," *Proceedings of the 87th Annual Convention of the Gas Producers Association*, March 2–5, 2008, Gas Producers Association, Grapevine, TX.

[5] Shah, P., and Durr, C., "Monetizing Stranded Gas," in *Petroleum Engineering Handbook, Vol. VI*, H.R. Warner and Larry Lake, Eds., Society of Petroleum Engineers Publications, Richardson, TX, 2007.

[6] Makogon, Y.F., Holditch, S.A., and Makogon, T.Y., "Natural Gas-Hydrates—A Potential Energy Source for the 21st Century," *J. Petrol. Sci. Eng.*, Vol. 56, 2007, pp. 14–31.

[7] Geiger, E.L., "Piping Components," in *Piping Handbook*, 7th ed., M.L., Nayyar, Ed., McGraw Hill, New York, 2000.

[8] Antaki, G.A., *Piping and Pipeline Engineering*, Marcel Dekker, New York, 2003.

[9] Ellenberger, J.P., *Piping Systems & Pipeline: ASME Code Simplified*, McGraw Hill, New York, 2005.

[10] Smith, P., *The Fundamentals of Piping Design*, Gulf Publishing Company, Houston, TX, 2007.

[11] Brill, J.P., and Mukherjee, H., "Multiphase Flow in Wells," *SPE Monograph*, Vol. 17, Henry L. Doherty Series, Richardson, TX, 1999.

[12] Ferguson, J.W., "A Mathematical Analysis of the Effect of Differences on Flow Formulae for Gas Pipe Lines," *Gas Age*, Vol. 78, 1936, pp. 72–76.

[13] Bird, R.B., Steward, W.E., and Lightfoot, E.N., *Transport Phenomena*, 2nd ed., John Wiley & Sons, New York, 2002.

[14] Moody, L.F., "Friction Factors for Pipe Flow," *Trans. ASME*, Vol. 66, 1944, pp. 671–684.

[15] Colebrook, C.F., "Turbulent Flow in Pipes, with Particular Reference to the Transition Region between Smooth and Rough Pipe Laws," *J. Inst. Civil Eng. London*, Vol. 12, 1939, pp. 133–156.

[16] Chen, N.H., "An Explicit Equation for Friction Factor in Pipe," *Ind. Eng. Chem. Fund.*, Vol. 18, 1979, p. 296–297.

[17] Hazen, A., and Williams, G.S., *Hydraulic Tables*, 3rd ed., John Wiley & Sons, New York, 1933.

[18] Larock, B.E., Jeppson, R.W., Watters, G.Z., *Hydraulics of Pipeline Systems*, CRC Press, Boca Raton, FL, 2000.

[19] Mohitpour, M., Golshan, H., and Murray, A., *Pipeline Design and Construction*, 3rd ed., ASME Press, New York, 2007.

[20] Menon, E.S., *Liquid Pipeline Hydraulics*, Marcel Dekker, New York, 2004.

[21] Manning, R., "On the Flow of Water in Open Channels and Pipes," *Trans. Inst. Civil Eng. Ireland*, Vol. 20, 1891, pp. 161–207.

[22] Johnson, T.W., and Berwald, W.B., "Flow of Natural Gas through High-Pressure Transmission Lines," Monograph 6, U.S. Department of Interior, Bureau of Mines, Washington, DC, 1935.

[23] Weymouth, T.R., "Problems in Natural Gas Engineering," *Trans. ASME*, Vol. 34, 1912, pp. 185–206.

[24] Boyd, O.W., "Petroleum Fluid Systems," Campbell Petroleum Series, Norman, OK, 1983.

[25] GPSA—Gas Processors Suppliers Association, "Fluid Flow and Piping," in *GPSA Engineering Data Book*, 12th ed., Gas Processors Association, Tulsa, OK, 2004.

[26] AGA—American Gas Association, *Steady Flow in Gas Pipelines: Testing/Measurement/Behavior/Computation*, Institute of Gas Technology Technical Report 10, New York, 1965.

[27] Uhl, A.E., "Steady Flow in Gas Pipelines," *Pipe Line Industry*, Vol. 25, Part 1, pp. 41–44 (August); Part 2, pp. 48–54 (September), 1966.

[28] Uhl, A.E., "Steady Flow in Gas Pipelines," *Pipe Line Industry*, Vol. 26, 1967, Part 3: No 1, p. 45–48 (January); Part 4: No. 3, p. 56-58 (March); Part 5: No. 4, p. 74 (April).

[29] Boyd, O.W., "Petroleum Fluid Systems," Campbell Petroleum Series, Norman, OK, 1983.

[30] Menon, E.S., "Gas Pipeline Hydraulics," Taylor and Francis Group, Boca Raton, FL, 2005.

[31] Stevens III, R.S., and May, D., "Piping and Pipelines," in *Petroleum Engineering Handbook, Vol. III*, K.E. Arnold and L. Lake, Eds., Society of Petroleum Engineers Publications, Richardson, TX, 2007.

[32] ASME, *B31.8—2007 Gas Transmission and Distribution Piping Systems*, American Society of Mechanical Engineers, New York, 2007.

[33] Braestrup, M., Andersen, J.B., Andersen, L.W., Bryndum, M., Christensen, C.J., and Nielsen, N.R., *Design and Installation of Marine Pipelines*, Blackwell Science and ASME Press, Fairfield, NJ, 2005.

[34] Norton, M., and Karczub, D., *Fundamentals of Noise and Vibration for Engineers*, 2nd ed., Cambridge University Press, Cambridge, United Kingdom, 2003.

[35] Arnold, K., and Steward, M., *Surface Production Operations: Vol. 1: Design of Oil Handling Systems and Facilities*, 2nd ed., Gulf Professional Publishing, Houston, TX, 1999.

[36] Kelkar, M., *Natural Gas Production Engineering*, Penn Well Corporation, Tulsa, OK.

[37] Shirazi, S.A., McLaury, B.S., Shadley, J.R., and Rybicki, E.F., "Generalization of the API RP 14E Guideline for Erosive Services," *J. Petrol. Technol.*, August, 1995, pp. 693–698.

[38] McLaury, B.S., and Shirazi, S.A., "Generalization of API RP 14E for Erosive Service in Multiphase Production," SPE Paper 56812 presented at the SPE Annual Technical Conference and Exhibition, October 3–6, 1999, Houston, TX.

[39] Brill, J.P., and Arirachakaran, S. J., "State of the Art in Multiphase Flow," SPE Paper 23835, *J. Petrol. Technol.*, Vol. 44, 1992, pp. 538–541.

[40] Baker, O., "Simultaneous Flow of Oil and Gas," *Oil & Gas J.*, Vol. 53, 1954, p. 185.

[41] Taitel, Y., and Dukler, A.E., "A Model for Predicting Flow Regime Transitions in Horizontal and Near Horizontal Gas Liquid Flow," *AIChE J.*, Vol. 22, 1976, pp. 47–55.

[42] Taitel, Y., Barnea, D., and Dukler, A.E., "Modeling Flow Pattern Transitions for Steady Upward Gas-Liquid Flow in Vertical Tubes," *AIChE J.*, Vol. 26, 1980, pp. 345–354.

[43] Barnea, D., "A Unified Model for Predicting Flow-Pattern Transitions for the Whole Range of Pipe Inclinations," *Int. J. Multiphase Flow*, Vol. 13, 1987, pp. 1–12.

[44] Lockart, R.W., and Martinelli, R.C., "Proposed Correlations of Data for Isothermal Two-Phase Two-Component Flow in Pipes," *Chem. Eng. Prog.*, Vol. 45, 1949, pp. 39–48.

[45] Beggs, H.D., and Brill, J.P., "A Study of Two-Phase Flow in Inclined Pipes," SPE Paper 4007, *J. Petrol. Technol.*, Vol. 25, 1973, pp. 607–617.

[46] Xiao, J.J., Shoham, O., and Brill, J.P., "A Comprehensive Mechanistic Model for Two-Phase Flow in Pipelines," SPE Paper 20631 presented at the SPE Annual Technical Conference and Exhibition, September 23–26, 1990, New Orleans, LA.

[47] Ansari, A.M., Sylvester, N.D., Sarica, C., Shoham, O., and Brill, J.P., "A Comprehensive Mechanistic Model for Upward Two-Phase Flow in Wellbores," SPE Paper 20630, *SPE Prod. Facil. J.*, Vol. 9, 1994, pp. 143–151.

[48] Kaya, A.S., Sarica, C., and Brill, J.P., "Mechanistic Modeling of Two-Phase Flow in Deviated Wells," SPE Paper 72998, *SPE Prod. Facil. J.*, Vol. 16, 2001, pp. 156–165.

[49] Hasan, A.R., and Kabir, C.S., *Fluid Flow and Heat Transfer in Wellbores*, Society of Petroleum Engineers Publications, Richardson, TX, 2002.

[50] Shoham, O., *Mechanistic Modeling of Gas-Liquid Two-Phase Flow in Pipes*, Society of Petroleum Engineers Publications, Richardson, TX, 2006.

[51] Cross, H., "Analysis of Continuous Frames by Distributing Fixed-End Moments," *Trans. ASCE*, Vol. 96, 1932, pp. 1–10.

[52] Wood, D., and Carl, O.A., "Hydraulic Network Analysis Using Linear Theory," *J. Hydraul. Div. ASCE*, Vol. 98, 1972, pp. 1157–1170.

[53] Press, W.H., Teukolsky, S.A., Vetterling, W.T., and Flannery, B.P., *Numerical Recipes in Fortran: The Art of Scientific Computing*, 3rd ed., Cambridge University Press, Cambridge, United Kingdom, 2007.

[54] Ayala H., L.F., and Leong, C.Y., "A Robust Linear-Pressure Analog for the Analysis of Natural Gas Transportation Networks," *J. Nat. Gas Sci. Eng.*, manuscript submitted, 2012.

[55] Dranchuk, P.M., and Abou-Kassem, J.H., "Calculation of Z-factors for Natural Gases Using Equations of State," *Can. J. Petrol. Technol.*, Vol. 14, 1975, pp. 34–36.

[56] Szilas, A.P., *Production and Transport of Oil and Gas—Part B, Developments in Petroleum Science*, Vol. 18B, 2nd ed., Elsevier Science Publishers, Amsterdam, The Netherlands, 1986.

[57] Osiadacz, A.J., "Simulation and Analysis of Gas Networks," Gulf Publishing Company, Houston, TX, 1987.

[58] Alp, D., "Numerical Modeling of Natural Gas Two-Phase Flow Split at Branching T-Junctions with Closed-Loop Network Applications," PhD Dissertation, Pennsylvania State University, University Park, PA, 2009.

[59] Katz, D.L., and Lee, R.L., "Natural Gas Engineering: Production and Storage," McGraw Hill Publishing Company, New York, 1990.

[60] Coulter, D.M., "New Equation Accurately Predicts Flowing Gas Temperature," *Pipeline Ind.*, Vol. 50, May, 1979, pp. 71–73.

[61] Coulter, D.M., and Bardon, M.F., "Revised Equation Improves Flowing Gas Prediction," *Oil & Gas J.*, Vol. 70, February, 1979, pp. 107–108.

[62] Shorre, C.E., "Flow Temperature in a Gas Pipeline," *Oil & Gas J.*, Vol., 53, September, 1954, pp. 64–68.

[63] Forrest, J.A., "Interpreting the Schorre Gas Temperature Equation," *Pipeline Ind.*, Vol. 48, 1978, pp. 58–60.

[64] Ramey, H.J., Jr., "Wellbore Heat Transmission," *J. Petrol. Technol. Trans. of AIME*, Vol. 14, 1962, pp. 427–435.

[65] Alves, I.N., Alhanati, F.J.S., and Shoham, O., "A Unified Model for Predicting Flowing Temperature Distribution in Wellbores and Pipelines," SPE Paper 20632, *SPE Prod. Eng.*, Vol. 7, 1992, pp. 363–367 .

NOMENCLATURE

A = pipe cross sectional area [L^{2}]
B = number of pipe branches in a pipe network [–]
C = erosional empirical constant [$L^{2.5}\ m^{-0.5}\ t^{-1}$]
C_p = fluid specific heat at constant pressure [$L^{2}\ t^{-2}\ T^{-1}$]
C_L = pipe conductivity to liquids [$L^{3-n}\ t^{-1}$]
C_G = pipe conductivity to gas [$L^{3+2n}\ m^{-2n}\ t^{4n-1}$]
C_{wr} = well/reservoir performance coefficient [$L^{3+2n}\ m^{-2n}\ t^{4n-1}$]
D = fluid demand at a node in a pipe network [$L^{3}\ t^{-1}$]
d = pipe internal diameter [L]
E = ASTM weld joint derating factor in pipe thickness calculations [–]
E_f = gas pipe efficiency factor [–]
e = pipe roughness [L]
F = pipe transmission factor [–]; or ASTM design derating factor in pipe thickness calculations [–]
F_D= AGA's gas equation drag factor [–]
f_F = Fanning friction factor [–]
f_M = Moody friction factor [–]
g = acceleration of gravity [$L\ t^{-2}$]
g_c = mass/force unit consistency/conversion constant [$m\ L\ F^{-1}\ t^{-2}$ where $F = m\ L\ t^{-2}$] (32.174 lbm ft lbf^{-1} s^{-2} in Imperial units; 1 Kg m N^{-1} s^{-2} in SI)
H = elevation with respect to datum [L]
HP = compressor horsepower [$F\ L\ t^{-1} = m\ L^{2}\ t^{-3}$]
h = fluid enthalpy per unit mass [$L^{2}\ t^{-2}$]
h_f = liquid pressure head [L]
J = mechanical energy conversion factor (778 lbf-ft/BTU in Imperial units; 1 Kg m^{2} s^{-2}/joule in SI) [–]
K = local loss or minor loss coefficient for fittings [–]
k = thermal conductivity of the material [$m\ L\ t^{-3}\ T^{-1}$]
k_a, k_b, k_c = compressor performance constants [$m\ L^{-1}\ t^{-1}$, –, $m\ L^{-1}\ t^{-1}$]
k_a', k_b', k_c' = pump performance constants [$L^{-5}\ t^{2}$, $L^{-4}\ t$, L]
L = pipe length [L]
L_e = pipe equivalent length [L]
LP = number of independent loops in a pipe network [–]
$1lw$ = irreversible energy losses, lost compression energy, or lost work [$L^{2}\ t^{-2}$]
M = molecular mass [$m\ n^{-1}$]
m = diameter exponent [–]
N = number of nodes in a pipe network [–]
n = flow exponent [–]
n_M = Manning dimensionless roughness parameter [–],

O_i = summation of off-diagonal entries in the i-th row for the linear analog method [$L^4\,m^{-1}\,t$]
p = pressure [$m\,L^{-1}\,t^{-2}$ or $F\,L^{-2}$ where $F = m\,L\,t^{-2}$]
p_r = reduced pressure [–]
p_{shut} = gas well shut-in wellhead pressure [–]
p_{wh} = gas wellhead pressure [–]
q = pipe heat exchange with the surroundings per unit mass [$L^2\,t^{-2}$]
q_L = liquid flow rate [$L^3\,t^{-1}$]
q_{Gsc} = gas flow rate at standard conditions [$L^3\,t^{-1}$]
R = universal gas constant [$m\,L^2\,T^{-1}\,t^{-2}\,n^{-1}$] (10.7315 psia-ft^3 lbmol^{-1} R^{-1} in English units or 8.314 m^3 Pa K^{-1} gmol^{-1})
Re = Reynolds number [–]
R_L = pipe total resistance to liquids [$L^{n^*n-3n}\,t^n$]
R_G = pipe total resistance to gases [$L^{-3n-2n^*n}\,m^{-2n^*n}\,t^{n-4n^*n}$]
r = radial component [L], or pressure ratio in the linear-pressure analog method [–]
r_L = pipe specific resistance to liquid [$L^{n^*n-3n+m-1}\,t^n$]
r_G = pipe specific resistance to gas [$L^{-3n-2n^*n+m-1}\,m^{-2n^*n}\,t^{n(1-4n)}$]
S = stress tensor [$m\,L^{-1}\,t^{-2}$ or $F\,L^{-2}$ where $F = m\,L\,t^{-2}$]; or supply at a node in a pipe network [$L^3\,t^{-1}$]
S_h = hoop stress [$m\,L^{-1}\,t^{-2}$ or $F\,L^{-2}$ where $F = m\,L\,t^{-2}$]
S_Y = specified minimum yield strength of the pipe material or SMYS [$mL^{-1}\,t^{-2} = F\,L^{-2}$ where $F = m\,L\,t^{-2}$]
SG = fluid specific gravity [–]
s = elevation parameter in the gas equation [–]; or entropy per unit mass [$L^2\,t^{-2}\,T^{-1}$]
T = absolute temperature [T]; or ASTM temperature derating factor in pipe thickness calculations [–]
T_r = reduced temperature [–]
t = pipe wall thickness [L]
U = Overall heat transfer coefficient [$m\,t^{-3}\,T^{-1}$]
v = velocity [$L\,t^{-1}$]
v_e = erosional velocity [$L\,t^{-1}$]
W = mass flow rate [$m\,t^{-1}$]
x = pipe axial axis [L]
Z = fluid compressibility factor [–]
z = pipe elevation axis; or axial component [L]

Greek

α = rate-dependent integration term in the energy balance [$m^2\,L^{-5}\,t^{-2}$]
β = elevation-dependent integration term in the energy balance [$L\,t^{-2}$]
ϕ_u = heat transfer factor in fluid temperature calculations [L^{-1}]
ϕ_{ae} = elevation and acceleration factor in fluid temperature calculations [$T\,L^{-1}$]
Δp^* = standardized pressure drop, $\Delta p^* = h_f$ for liquids and $\Delta p^* = p_1^2 - p_2^2$ for gases [L, or $m^2\,L^{-2}\,t^{-2}$]
γ_L = liquid specific weight [$m\,L^{-2}\,t^{-2}$, or $F\,L^{-3}$ where $F = m\,L\,t^{-2}$]
μ = fluid dynamic viscosity [$m\,L^{-1}\,t^{-1}$]
υ = fluid kinematic viscosity [$L^2\,t^{-1}$]
φ = gas density dependency on pressure [$t^2\,L^{-2}$]
η = Joule-Thomson coefficient [$T\,L\,t^2\,m^{-1}$]
π = ratio of the circumference of a circle to its diameter = 3.14159265… [–]
ρ = fluid density [$m\,L^{-3}$]
σ_L = unit-dependent constant for the liquid flow equation [$L\,t^{-2}$]
σ_G = unit-dependent constant for the gas flow equation [$T\,t^2\,L^{-2}$]
τ_w = wall shear stress [$m\,L^{-1}\,t^{-2}$ or $F\,L^{-2}$ where $F = m\,L\,t^{-2}$]
θ = circumferential component [–]
ϑ = fluid specific volume $(1/\rho)$ [$L^3\,m^{-1}$]

Subscripts

1 = pipe entrance
2 = pipe exit
a = acceleration
av = average through the pipe
e = elevation
f = friction
G = gas
h = hoop
in = internal
K = phase (L or G); or *secondary* or *minor* loss subscript
L = liquid
o = outside or external
r = reduced condition
s = surroundings
sc = standard conditions (60 F or 520 R and 14.696 psi in English units; 288.71 K and 101.325 KPa in SI)
T = total

23

Introduction to Trading, Pricing, and Valuation of Crude Oils and Petroleum Products

Cheng Seong Khor[1], Luis A. Ricardez-Sandoval[2], Ali Elkamel[2], and Nilay Shah[1]

ABBREVIATIONS

$ (or USD)	United States' dollar currency
APPI	Asian Petroleum Price Index
ARA	Amsterdam, Rotterdam, and Antwerp
BL	Bill of lading (a document that provides a detailed list of a ship's cargo in the form of a receipt given by the master of the ship to the person consigning the goods) (Oxford English Dictionary)
BFO	Brent, Forties, Oseberg
CDU	Crude distillation unit
CIF	Cost, insurance, and freight
FCC	Fluidized/fluid catalytic cracking unit
FO	Fuel oil
FOB	Free on board
GO	Gas oil
GPW	Gross product worth
GSP	Government selling price
LPG	Liquefied petroleum gas
IOC	International oil company/corporation
IPE	International Petroleum Exchange at London
LOR	London Oil Report
LP	Linear programming
Mogas	Motor gasoline (or petrol)
MOPS	Means of Platts Singapore
MOPAG	Means of Platts Persian (Arabian) Gulf
NOC	National oil company/corporation
NEW	North-West Europe
NYMEX	New York Mercantile Exchange
OSP	Official selling price
OTC	Over-the-counter
RGV	Refinery gate value
RON	Research octane number
SIMEX	Singapore International Mercantile Exchange

23.1 INTRODUCTION

Trading, costing, pricing, and valuation of crude oils and petroleum products in the refining industry are fairly well-treated subjects, but perhaps the presentation in most published materials has been tailored mostly to an advanced audience with prior exposure to the field. Largely on the basis of the excellent expositions by Long [1] and Favennec [2] as well as the classic *The Petroleum Handbook* by the Royal Dutch/Shell group of companies [3], our goal in this chapter is to provide a systematic explanation intended for novice readers or those fairly new to the subject. As far as possible, we strive to ensure that all fundamental concepts, particularly terms and industry jargon introduced, are adequately explained while not compromising on sufficient coverage of more modern and up-to-date materials through extensive use of tables to summarize the pertinent points. As such, the materials are covered in sufficient clarity and depth for a newcomer to the subject yet still cater to readers interested in current developments in the related issues.

The systematic exposition that we use throughout offers an interesting snapshot of how the refining industry has developed from purely physical trading to a sophisticated financial market. For a complete treatment, we also briefly review how oil markets have historically operated and evolved. In the final section, we explain the concepts of capital and operating costs as well as profit margins in the context of the refining industry before culminating with some concluding remarks.

23.2 PHYSICAL MARKETS FOR CRUDE OIL AND PETROLEUM PRODUCT TRADING

Crude oil has become the world's biggest commodity market in the last 25 years or so, and its trading is also the most complicated. The industry has therefore developed a complex set of interconnecting markets not only to establish prices across the entire spectrum of crude and product qualities, but also to enable purchasers and sellers to accommodate changes in relative prices or price differentials. Thus, oil trading has evolved from a primarily physical activity into a sophisticated financial market.

The physical oil markets exist for the sole purpose of delivering and receiving physical oil, termed as the wet (or prompt) oil markets and the spot markets. Many types of crude oil and refined products are traded, and the relative values of each grade are continually shifting in response to changes in supply and demand on global and local scales. The contracts involved are normally nonstandard, in which the title and the risk in the oil commodity are transferred from one party to another at a specified time and location. Before the 1980s, these contracts were mostly long-term

---

[1] Chemical Engineering Dept., Universiti Teknologi PETRONAS, Malaysia

[2] Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

contracts, usually simply referred to as “term contracts,” but today, most are spot contracts, Tables 23.1 and 23.2 delineate the features of the trading methods practiced. The international physical markets involve crude oil trading that includes Russian Urals and Colombian crudes as well as crudes produced from the geopolitically distressed regions of Nigeria and Iran. In general, a high-quality crude clearly sells for more than a low-quality crude. For refined product trading, the physical markets mainly comprise gasoline, naphtha, jet-grade kerosine, burning kerosine, diesel (gas oil or heating oil), and high-sulfur fuel oil [1].

23.3 PAPER INSTRUMENT MARKETS FOR CRUDE OIL TRADING

To optimize crude oil trading operations, a trading entity should not be tied to a term contract nor be exposed to the spot market at the time the oil is required. A potential purchaser requires a certain quantity of oil, not now but in the future (e.g., next month). On the other hand, a producer (i.e., seller) wants to lock purchasers ahead of time and needs to arrange for shipping of the cargoes [2].

International oil trading prices have been set by the spot market since the end of the 1980s. This trend has

TABLE 23.1—Crude Oil Trading Methods

Agreement Type	Feature
Long-term contracts (fixed-price)	• Typical of period between the two oil shocks • Used to make up ~50 % of fixed-price internationally traded volume but no longer with new trading methods developed • Typically agreed upon for ≥1 year • Prices and volumes reviewed and renewed periodically • Guaranteed crude outlets for producers • Refiners assured that certain crude quality is available, thus avoiding many spot purchases • Used by most buyers to cover most requirements—optimize balance through spot and best combination of crude price and quality • Contractual price negotiation is key during volatile spot prices • Producers (including national oil companies [NOCs]) want prices as fixed as possible to plan budgets
Spot contracts (single cargo sales)	• More oil became available on a spot basis as market moved away from term supplies • Make up ~30 % of internationally traded volume but has greater impact because determines selling price for ~80 % of term contracts • Involve purchases and sales for short-term delivery, often within days and the following month • Actual prices are set daily by market forces • Oil companies profiting from refining margins want pricing reflecting daily spot markets as much as possible, hence determine oil market value • Used by private companies (international oil companies [IOCs]) and NOCs as main reference for cargo prices • Although negotiations center on a single cargo (or variable volumes in the U.S. pipeline market) rather than several loadings over a time period, loading date might still be in future • Some delay or risk inevitable (because of cargo loading, tanker availability, or vessel speed) • Different regional markets operate similarly: purchasers seeking cargoes within next month contact various producers or traders within the area by telephone and agreement is confirmed by telex or fax • Price differentials between crudes and products are more important for margins than absolute crude prices • Market prices could still move dramatically; thus purchasers and sellers increasingly turn to floating pricing approaches
Barter agreements	• Still have important role—presently account for >15 % of traded volume • Typically involve exchanges of crudes or oil products for other commodities, services, plants, or equipment

TABLE 23.2—Term Versus Spot Contract Sales in Crude Oil Trading

	Term Contract	Spot Contract
Contract period	Long term (>3 months), typically 1 year	Short term (1–3 months only)
Crude oil delivery	Typically a series of cargoes or deliveries over a period usually up to 1 year or more	• Typically one cargo in the international market • One-time transactions for a single cargo or delivery
Pricing mechanism	• Possibly established as a result of tenders • Floating	Fixed (typically) or floating
Restrictions on resale	Possible	Typically none
Market share of international trade	~50 %	~30 % but has greater impact because determines selling price for ~80 % of term contracts
Price transparency	May not be publicly acknowledged	Frequently reported to trade publications

subjected the petroleum industry to the additional risk of price volatility. To hedge against this price risk, oil companies have established forward markets, in which future production can be locked and delivery of crude oil cargoes at a defined later date (in the future) can be bought for a fixed price. The forward markets are the ancestor of the present futures markets. Collectively, they form the paper instrument oil markets, providing an avenue to reduce price fluctuation risk by hedging, although they are also widely used for speculation [4,5].

A paper oil deal represents a promise to purchase or sell a contractual volume of a petroleum commodity at a specified time and price. Paper instruments are categorized as follows:

- Oil forward contracts;
- Oil futures contracts;
- Contracts for difference (CFD; or more popularly known as swaps);
- Options, in which the right to buy is termed a "call option" and the right to sell is termed a "put option"; and
- Crack spreads.

Futures and forward papers are standard contracts for the purchase and sale of a standard quantity and quality of oil that is traded for future delivery at a specified time, price, and place. Swaps and options form the derivatives markets. Crack spreads replicate the refinery margin in the paper market, thus representing the refiner's position to allow for hedging exposure to the difference (i.e., "crack") between products and crude oil prices [6,7].

Paper markets are subjected to similar price fluctuations as the physical markets but at different levels. After a turbulent and rapid development, these increasingly maturing instruments are now an integral part of world oil trading systems that have radically changed in the last 30 years or so. Tables 23.3 and 23.4 summarize the characteristics of these instruments. For a comprehensive treatment

TABLE 23.3—Paper Instrument Markets [1,2,9,10]

Instrument	Feature	Example of Commodity
Forward	• Involve single transactions resembling spot market but for delivery up to 6 months ahead, usually for full crude cargoes • Often used before spot trading period • Physical version of futures markets but involve over-the-counter (OTC) or bilateral deals between purchasers and sellers directly with nonstandard contract specifications and nonguaranteed performance (typical of physical markets) • Outcome usually results in physical delivery or single final cash settlement at nomination date • Quantities subject to volume tolerances • Regulated by oil industry itself (not under a particular body's rules)	• Brent, Forties, Oseberg (BFO) • Dubai
Futures	• Traded on highly standardized regulated exchanges (e.g., NYMEX) • Hedging tool against price volatility risk • Outcome not intended to be physical (although linked to it) but cash settlement only (except for NYMEX crude, IPE gas oil, and SIMEX fuel oil or gas oil) • Has standard number of available months for trading • Last day of trading for each contract month stipulated	Intercontinental Exchange (ICE): Brent crude, gas oil
Options	• Contract gives holder the right but not obligation to trade; gives writer the obligation but not the right to trade; therefore option holder can exercise option to purchase or sell • Exchange traded or OTC traded (i.e., settled against published price indices)	• ICE: Brent crude, gas oil • NYMEX: West Texas Intermediate, heating oil, gasoline, crack spread
Swaps or CFD	• Contract with two parties swapping price of an asset, which is fixed at signature time, for asset's market price on a settlement date also decided at signature time • Purchaser to buy at fixed price and resell at market price whereas seller to sell at fixed price and repurchase at market price on settlement date • Market price is generally taken as Platts mean quotation over settlement period • Outcome: no physical delivery—only cash settlement; if market price is higher (respectively, lower) than fixed price, then purchaser (seller) receives the difference • OTC traded • Adds further pricing flexibility because offers possibility to physical oil purchaser to continue to take oil from supplier at floating price, yet ensure against later adverse price movements • Purchaser may have long-standing relationship with a reliable supplier (e.g., a major oil company); therefore asking this kind of supplier for fixed price might jeopardize relationship with a supplier used to more established floating price basis • Purchaser may elect to offload price risk onto a third party, who will provide (swap) a fixed pricing against the floating pricing agreement • Third party typically does not make any oil delivery but provides insurance against risk by fixing price—in turn, will often hedge risk in futures or options markets	All grades of crudes and products

TABLE 23.4—Comparison between Forward and Futures Oil Paper Contract Markets

Attribute	Forward Contract	Futures Contract
Trading mode	OTC traded	Exchange traded
Regulation	Nonregulated (decentralized and unmonitored)	Regulated
Terms of contract	Flexible	Standardized
Credit risk	Exposed	Near zero
Number of crude oils and oil products	Limited to small number of crudes and products	Standard number of crudes and products
Number of players in market	Small: about 15 for Brent forward and 10 for Dubai forward	Large: because contracts are traded without direct purchaser–seller contact
Cargo size	Practical sizes, e.g., 500,000 bbl for Brent	In small lots, e.g., 1000 bbl, 100 t
Contract size	On order of $10 million	Smaller than forward
Number of cargoes per month (approximate)	75 for Brent forward; 55 for Dubai forward (mostly Oman)	Not applicable because not intended to involve physical oil
Liquidity	4 months	3 months
Nomination	Known purchaser and seller, e.g.: • Brent forward: seller at 21 days in advance • Dubai forward: buyer at 30 days from bill of lading (BL)	Do not have to identify purchaser or seller to mutually agree on contract (exchange is responsible for matching buying and selling requirements)

of contracts in the paper markets, the interested reader is referred to Battley [8].

23.4 REFERENCE PRICING OF MARKER CRUDE OILS

With numerous individual crude oil grades traded on a regular basis, it is difficult to know the daily price of each of them. The difficulty is compounded because some crudes are not traded daily. However, there are certain crudes that are widely traded in significant volumes daily and for which prices are transparent (i.e., publicly known and available) that are used to price other crude oil grades. A few of these crudes have become so well known that they have been considered as price leaders or benchmark crude oils, known as "marker" crudes. There are now four crude oils serving as a reference on the basis of which other crudes are priced against, as detailed in Table 23.5. This means that the prices of the Brent, WTI, Dubai, and Tapis crude oils are assessed directly whereas all other prices are set as differentials to one of these according to trading in the market. The price movements of these marker crudes are carefully studied because of their influence on pricing as price indexes. Two thirds of the world's internationally traded crude supply volumes are priced using the Brent marker. In general, marker crudes display the criteria in Table 23.6 [11].

TABLE 23.5—The Four Main Marker Crudes (That Are Traded at a Fixed Price)

Marker Crude Oil	Region Covered	Price Publisher	Oil Trading Mode	Crude Oil Quality
Brent or BFO (comprises Brent Crude, Brent Sweet Light Crude, Ecofisk, Forties, Oseberg)	***Europe, Africa, and the CIS*** (Commonwealth of Independent States): Western Europe, North Sea, West and North Africa, Mediterranean, Arab Gulf (AG) to Europe[a]	IPE or Platts (dated)[b]	Physical, forward, futures	Light sweet (i.e., low sulfur content)
West Texas Intermediate (WTI)	***Western Hemisphere***: North and South America, Persian Gulf to United States (Gulf Coast)	Platts or NYMEX	Physical, forward, futures	Light sweet (low sulfur)
Dubai (also Oman[c])	***East***: Middle East, East of Suez (Arab Gulf, Red Sea)	Platts or APPI	Physical, forward	High sulfur
Tapis (also Miri[c] and Minas[c])	***Far East***	Platts or APPI	Physical, forward	Light sweet (low sulfur)

[a] A less common marker is Urals (medium sour quality) for the Eastern Europe region (mainly Russia).
[b] Dated Brent (e.g., refers to a forward Brent cargo with loading dates).
[c] Oman, Miri, and Minas are relatively less widely used as marker crudes.

TABLE 23.6—Criteria of a Global Marker Crude Oil

- Large and stable markets with decent production rates providing sufficient supply
- Traded in large volumes that are representative of trading in general (as demonstrated by its transparency of trades and accurate price assessments in publications)
- Disparate and broad range of equity ownership
- Robust and accessible logistics
- Stable quality
- Ease of entry or exit into a market
- Reasonable balance of power between purchasers and sellers
- High liquidity
- Possesses price transparency
- Narrow bid–ask spread
- No politically influenced trading limitations

To illustrate how this system works, we consider the instance of Arabian crude oils that are priced according to the Dubai and Oman marker crudes, with the addition of a premium for Eastern customers and the subtraction of a discount that is based on the Brent marker crude for European customers. It is noteworthy that increasing controls are placed on marker crudes to ensure their continued suitability for purpose. Although Dubai is currently adopted as the marker crude for Asia and the Middle East, no crude oil has been successful as a marker for this region, either because the production level has been too low or the market is too susceptible to manipulation [12]. Therefore, Dubai and Tapis are relatively less widely used as marker crudes compared with Brent and WTI.

23.5 INTERNATIONAL CRUDE OIL SUPPLY, TRADING, AND PRICING IN HISTORICAL PERSPECTIVE

The oil industry operated in an integrated manner under 40 years of prolonged price stability and long-term contracts from 1930 to 1970. It was the heyday of the Seven Sisters, vertically integrated companies with almost complete collective control over global oil output via participation in key producing consortia, from exploration and production to product marketing. They internally handled the bulk of crude oils and products among themselves, leaving virtually no crudes and only a limited amount of products to be traded outside. Thus, international oil trading was limited to minimal exchanges among these organizations that mainly took place only in the western hemisphere [13]. Table 23.7 summarizes the pertinent events in crude oil price evolution history with Figure 23.1 graphically depicting the relative rise and fall of crude oil price from 1970 onward.

23.6 CRUDE OIL TRADING, PRICING, AND VALUATION

23.6.1 Pricing of Crude Oils

Crude oil by itself possesses no value because it derives its value from the products produced from the oil refining processes at refineries, and refineries are the only major market for crude oils. A contract for the sale of a crude oil cargo must specify the following elements:

- Basic price;
- Delivery time (specified in terms of availability date range);
- Delivery location, which is specified in terms of where the cargo is available;
- Grade (i.e., guaranteed quality);
- Agreed price adjustment in terms of premium or discount to account for grade or quality deviations;
- Taxes and duties (if relevant); and
- Inclusion of freight and insurance.

Although there are other factors that can influence the actual cost of a crude oil cargo, the seven elements above adequately specify the general components that determine pricing of crude oil as well as that of petroleum products. Most, if not all, of these elements apply regardless of whether a mechanism of fixed pricing or floating pricing is adopted (as elucidated later in Section 23.6.5). The next section explains the general factors governing these elements in determining crude oil pricing [1].

23.6.2 Factors Determining Pricing of Crude Oil and Petroleum Products

23.6.2.1 GRADE OR QUALITY

Crude oils have many measurable physical or chemical quality characteristics or properties. Examples of the major qualities are density or API (specific) gravity, sulfur content, and boiling point whereas the minor qualities include total acid number (TAN), gasoline research octane number (RON), PONA (i.e., content of paraffins), kerosine smoke point, diesel cetane, and residuum asphaltenes. In principle, all qualities contribute to the value of crudes, but in practice, certain qualities are far more important than others. Many price contracts include clauses on premium or discount that account for price changes if the quality of crude oils loaded deviates from the contractual grade, which refers to the specification range on whether the refined products meet marketable quality (or simply termed as being “on-spec”). Otherwise, a cargo is considered to be outside of the agreed specification (“off-spec”) and the contract might be invalid. The premium or discount may be based on two factors: (1) important crude oil qualities (i.e., specific gravity, sulfur content, and viscosity) and (2) the date of loading or discharge (e.g., the price may be reduced by an agreed factor for each day’s delay after the agreed date range) [1,15].

23.6.2.2 CURRENCY AND MEASUREMENT UNIT

Crude oils are generally traded internationally in dollars per barrel, but another currency can be used if the trading parties agree. Inland domestic markets generally price crude oils in the local currency and measurement units, in which the latter chiefly refers to whether a volume or weight basis is adopted. Prices are invalid unless accompanied by quality specifications (e.g., crude oil at $40/bbl referred to a certain crude marker) [1].

23.6.2.3 TIMING OF AVAILABILITY OR DELIVERY TIME OF CARGOES

Crude oils may be required at a refinery by a particular date, otherwise stocks, which are always kept close to the operational minimum to reduce costs, may drop too low, causing reduced throughputs or worse, refinery shutdown.

TABLE 23.7—Summary of Significant Events in the History of Crude Oil Price Evolution [14]

Year	Oil Market Events and Features
1859–1870	• High crude prices worth $20.00/bbl or more • High price volatility as kerosine demand sky-rocketed
1870–1970	• Price stability—long-term contracts • Electric light began to replace kerosine lamps • Prices controlled by a few major companies through Achnacarry Agreement of 1928
1930s	• Petrochemical industry developed with thermoplastic resins introduced • Later, crude was cracked to produce ethylene for polyethylene and vinyl chloride monomer for polyvinyl chloride
1940s	• Oil companies enter chemical industry • Low, stable crude prices
1943	Mexico nationalization of crude reserves
1950s, 1960s	80 % of crude supply controlled by “Seven Sisters” of major oil companies: Exxon, Shell, BP, Gulf, Chevron, Texaco, and Mobil
1960	Organization of Petroleum Exporting Countries (OPEC) was founded

Pre-1970s	***Long-term contracts***
	• Supply uncertainty and supply–demand imbalance caused producers to gradually control upstream operations beginning in the 1970s
	• Industry disintegrated to form new trading arrangements between now-distinct purchasers and sellers
	• Previous concession agreement system replaced by long-term multiyear contractual relationships between new NOCs and former concessionaires
	• International market price, previously set by official selling price (OSP)/government selling price (GSP), now set unilaterally by OPEC
	• Private sector corporations:
	  • No longer controlled crude market
	  • Lost privilege of direct access to crude reserves that used to be their sole ownership
	  • But somewhat gained supply security through long-term contracts
	• Oil prices were governed by this system in the next 10 years, but they were gradually modified by spot market development in the 1980s
	• Official prices abandoned in 1988 after undermined by various rebate systems

1970s	***Reign of controlled markets*** • OPEC and major producers dominated • OPEC raised crude price from $2.80/bbl to $10.80/bbl • Decoupling of upstream from downstream operations • Relative stability of supply, price, and differentials • Term contracts used • Refineries designed for a few crudes • Crude selection is based on technical criteria • Long crude runs • All parties made good margins
1973	First supply shock: Yom Kippur War (between Israel and Arab states)— end of era of IOC control
1978	First oil futures contracts
1979	Iranian Revolution—second oil supply shock • Major disruption to oil supply and pricing • Oil prices dipped to $40/bbl

Early 1980s	***Development of free-market-based spot trading system and commoditization under oil crisis***
	• First significant growth in spot markets since second oil shock:
	  • Saudi Arabia agreed to increase production because of crude shortage fears, but purchasers panicked and wanted oil quickly
	  • Drove spot prices above official prices
	  • Term crudes diverted to cause huge increase in a predominant spot trading
	• New supplies and suppliers: surplus (bearish) market in fragmentation meant costs were best optimized by spot purchases
	• Many crude types and mode switches with selection based on economics in term and spot deals
	• Increased price volatility: uncertain prices and differentials resulted in sharp price rise and tight margins
	• Financial risk management products in OTC markets developed

TABLE 23.7—Summary of Significant Events in the History of Crude Oil Price Evolution [14] (Continued)

Year	Oil Market Events and Features
	• Demand decreased because of reduced energy use, alternative energy sources, and new non-OPEC sources (e.g., North Sea and Alaska)—priority of supply security for independent refiners stopped with increased availability • Until 1985, producers continued to offer long-term fixed-price contracts, but terms were increasingly subject to negotiation • No resistance to abandon fixed-price contracts after failure of 1986's netback contract episode • Until today, virtually all crude prices have been determined based on spot markets
1983	NYMEX crude contract trading introduced
1984	Crude price at $30/bbl
Mid-1980s	***Advent of financial paper instrument markets*** • NYMEX energy futures introduced • Traders and speculators became more active • Previous norm of fixed price transactions became too risky • Market needed price mechanisms reflecting rapid changes in market prices
1985	***Netback contract pricing*** introduced by Saudi Aramco but abandoned because resulting supply surplus caused a collapse in product prices and consequently crude prices
1986	• Crude price down to $10/bbl within 6 weeks • Crude oil options introduced (Plourde and Watkins, 1998)
1990	Iraq invaded Kuwait ⇒ price increased to $30/bbl

1990s	***Organization of spot markets and maturity of financial markets***
	• Largely moderate prices under new political order
	• Spot prices established as reference because they reflected the price of marginal oil quantities exchanged on markets that bridged supply–demand gap
	• But large crude varieties prompted need for increased organization:
	  • Marker crudes established
	  • Petroleum exchanges set up to protect parties from risks due to price volatility (in addition to other existing hedging tools)
	  • More sophisticated paper instruments introduced (e.g., swaps and options)

1991	United Nations action started ⇒ price fell to $20/bbl
1993	Price slid to $15/bbl
1994–1997	Price recovered to $19–20/bbl
1997–1999	Asian financial crisis ⇒ price fell to $10/bbl
1999	OPEC cuts production ⇒ price rose to $15/bbl
2000+	Cooperation between purchasers and sellers

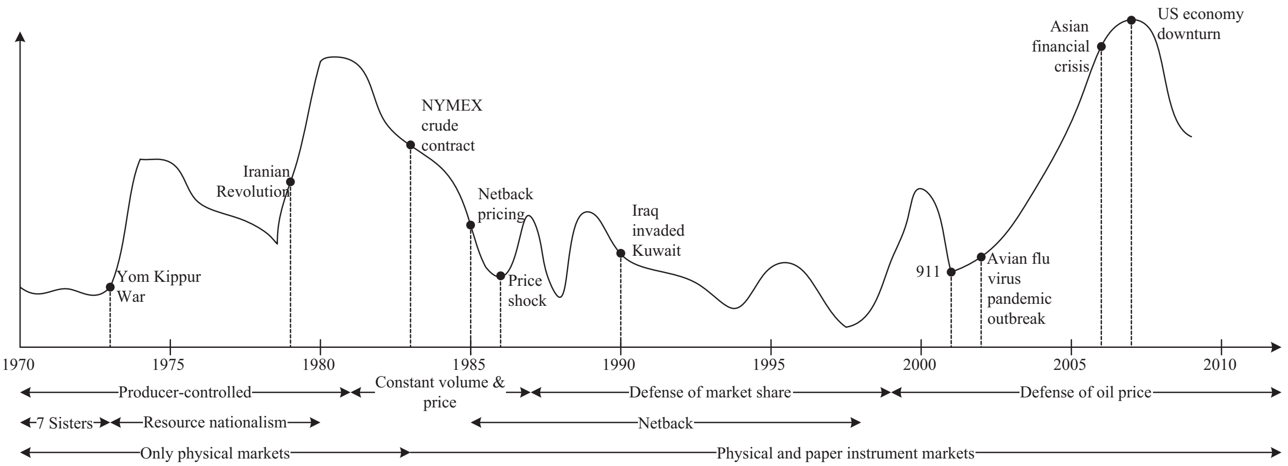


Figure 23.1—Relative rise and fall of crude oil price since 1970. *Source:* Figure modified after [16].

Conversely, products may have to be delivered or lifted from the refinery by a specified date; otherwise storage tanks will be full, thus forcing the refinery to reduce its operations.

At certain times of the year, timing can also have a major effect on pricing because the market is either in backwardation or contango (forwardation). Backwardation refers to the market condition when the commodity future price is below the prompt position. It is the normal market situation, especially with respect to gasoline on NYMEX during the summer season. This is because the driving season in the northern hemisphere starts in March and ends in September, so the demand and, hence, the price for gasoline tails off toward year end. On the other hand, contango ("continue and go") is the market condition when the future price is above the prompt price and becomes progressively more expensive in the future. Such a situation transpires when the rising market is expected and often happens for gas oil with summer approaching because of its highest demand in the heating season.

When gasoline is in backwardation, gas oil may be in contango and vice versa. The classic recent case is illustrated by the crude oil market that was in contango until around July 2008 when it hit a record high price of approximately \$140/bbl. The market was then in backwardation for 6 months when the price kept declining until approximately \$35/bbl. Therefore, when setting oil price, specifications should also include the delivery date range of whether prompt or deferred [1,15].

23.6.2.4 DELIVERY LOCATION

Crude oils are generally sold free on board (FOB; purchaser pays the transport [shipping] costs) at export terminals connected to oil fields. However, some crudes are moved to the pipeline-end to ensure ease of accessibility. Such a provision must be specified when the price is agreed because it affects the purchaser's freight costs and hence, the crude value. However, similar-quality products could be available all over the world, produced by several different refineries. Although many are sold FOB at refineries, many more may be sold cost, insurance, and freight (CIF; seller pays for the transport) at any of the hundreds of ports, pipelines, or terminals [15].

TABLE 23.8—Example of Sources of Price Data on Crude Oil and Petroleum Products [2,17]

Price Reporting Mode and Example of Agencies or Media	Price Reporting Method and General Attributes
Journalistic assessment • McGraw-Hill's Platts (www.platts.com) [18] • Argus Media Ltd. (www.argusmedia.com, www.energyargus.com) [19] • Thomson Reuters (www.reuters.com/finance/commodities/ • energy?mkt=ENERGY) [20] • London Oil Report (LOR) by ICIS-LOR (Independent Commodity Information Services London Oil Reports; North-Sea-based; www.icis.com, www.icispricing.com) • Dow Jones Telerate Energy Service • Bloomberg (www.bloomberg.com) • Oil Daily/Energy Intelligence Group (www.energyintel.com) • Oil Market Intelligence	• Journalists poll market participants using proprietary methodology and develop assessments on appropriate price levels • Thomson Reuters and Dow Jones Telerate Energy Service provide up-to-the-minute prices on screens in customers' offices. Data provided can now be linked to and accessed on personal computers and are directly linked into global networks
Public exchange data	Exchanges trade energy commodities and report actual transactions
• New York Mercantile Exchange (NYMEX) (www.nymex.com, www.cmegroup.com)	Prices on futures and options of petroleum (and metals) for U.S. market
• London's International Petroleum Exchange (IPE)	World's largest energy futures and options exchanges
• Singapore International Mercantile Exchange (SIMEX)	
Formal pricing panel	Organizations involved generally use defined methodology to poll across sections of markets and develop prices using typically rigid formulas or algorithms
• APPI (Asian Petroleum Price Index)	Independent and compiled from assessments by panel of the most active participants in Asia Pacific market; the standard price setting mechanism in Far East
• FEOP (Far East Oil Price; https://feopindex.com) [21]	Average of daily prices of benchmark crudes and physical oil products in Far East based on panelists' assessments; accurate and independent contract pricing mechanism for Asian oil markets
• OPIS (Oil Price Information Service; www.opisnet.com) [22]	Prices for U.S. and Canadian oil business markets, particularly rack prices for heating oil, gasoline, and kerosine as well as contract prices for jet fuel, LPG, residual oil, feedstock, and natural gas; U.S.-based
• RIM (https://www.rim-intelligence.co.jp) [23]	For Asia Pacific and Middle East markets; first independent oil market reporting agency in Japan (1984); based in Tokyo and Singapore

23.6.2.5 TAXES AND DUTIES

Some markets impose duties on the oil imported, and it should thus be taken into account in the pricing. In the United States, oil product prices are generally quoted inclusive of duty, and the value can be as high as 5 % of the total price [1].

23.6.3 Price Information Sources and Reporting Methods for Crude Oils

Because the market operates by mutual agreement between the two trading parties of the seller and purchaser, the price of the deal is a priori known only to the two parties concerned. Thus, because the prices are not reported or governed by an independent official body, price transparency is an issue of major concern in crude oils and petroleum product markets. This is a major disadvantage with using marker crude oils, the price of which serves as a reference for market conditions.

To overcome this issue, there are several independent publishers and media houses providing information on market prices of crude oils and petroleum products. These price-reporting agencies of recognized standard oil and gas industry journalistic price indices and assessments regularly release reports or journals on market prices or price indices. Table 23.8 lists a few examples of reporting service providers of such price index data, in which the prominent ones are Platts and Argus, along with the methods to establish the prices [2].

Platts is the first publication service to regularly quote international oil prices, beginning in the 1930s. Hence, it was the first to be used for pricing formulas based on published prices and reigns supreme in the oil-pricing market still today. The emergence of the crude oil spot market in the 1980s witnessed a few new oil price-reporting industry journals, notably

- *Energy Argus or Petroleum Argus*, popularly referred to simply as "Argus," which was used then for fuel oil pricing by the former Soviet Union;
- *London Oil Report*, now known simply as "LOR," which was used then for feedstock prices; and
- Other agencies such as Reuters and Telerate.

The crude oil future markets of NYMEX and IPE have also been successful and have captured some of Platts' dominance of the price-reporting market. Nevertheless, Platts has retained the ability of not just reporting but also setting the oil market prices, of which such data are widely adopted in pricing formulas and other market-related indices. Other markets that do not yet have formal futures markets, such as jet fuel and fuel oil, can also be influenced by the Platts prices because they are also adopted as a basis for the thriving swaps markets of these products [1]. Table 23.9 discusses the salient features of Platts.

Prices assessed by the pricing agencies are established in the following terms:

- Grades as given by the respective defined qualities;
- Standard loading or delivery locations or markets (typically FOB or CIF); and
- Delivery time, in which the price assessments or "quotes" are published daily.

Prices quoted in the term deals are based on the price assessments that are quoted around or over the agreed periods. Prices of unquoted grades and delivery locations are provided relative to the standard quotes. These prices are estimates made on the basis of the opinions of the different operators contacted by these reporting organizations. Because these data can be manipulated (as is the case with any common opinion poll), only transactions confirmed by seller and purchaser are reported, although this wise precaution does not always obviate the need for concern of possible manipulation [2].

It is noteworthy that agencies publishing daily (or even hourly) price reports continue to be very influential, although pricing mechanisms may not always be based on published prices. That power has been reduced somewhat by the regulated and visible futures exchanges and options contracts, but these are available only for a more limited range of crudes and oil products.

23.6.4 Types of Pricing Agreements

The imperative part of a crude oil deal is the price negotiation; hence, due emphasis to the type of pricing agreement is pertinent. Agreements in deals for purchasing and selling of crude oils and products generally conform to one of the classifications presented in Table 23.10 in accordance with Incoterms (International Commercial Terms) of the International Chamber of Commerce (ICC) [24]. A cargo mainly undergoes an FOB or CIF transaction.

23.6.5 Crude Oil Pricing Mechanisms

The price of crude oils in a transaction is essentially determined through an agreement between the trading parties

TABLE 23.9—Salient Features of Platts As an Example of Price Data Publisher

Feature of Platts	Type of Data Published by Platts
• The almost universal reference for term and spot deals, but open to manipulation • Reporters monitor prices by contacting operators in the zone over the telephone and asking crudes and products price levels for deals made during a particular day • Publishes daily market report assessment of oil prices on the basis of transactions on the previous day on every late evening of the business day in Singapore, London, and New York • Publishes via Internet (including bulletin boards), hard copies, telex, fax, and dedicated landline to screens • Publishes a price bracket for a certain crude (i.e., a low quotation [Platts Low] and a high quotation [Platts High]—average of these two prices, termed as "Platts Mean," is often used as reference price	• Fixed prices and differentials of crude oils (e.g., Platts Crude Oil Marketwire) and petroleum products (e.g., Platts Oilgram European Marketscan) • Daily quotations of price range assessments for spot and forward markets • Information on market developments and relevant events

TABLE 23.10—Common Types of Deals in Crude Oil Trading in Terms of Transport Obligations, Costs, and Risks

Type of pricing deal	Attribute
FOB: free on board	• Price of cargo available at loading port (e.g., Ras Tanura, Saudi Arabia; Yokohama, Japan; Miri, Malaysia) • Ownership of cost and risk transferred when goods pass permanent hose connection of loading tanker • Shipment port is named • Purchaser responsible for carriage, insurance, and freight costs
CIF: cost, insurance, and freight	• Price of cargo delivered to discharge port (e.g., New York; Yokohama; Rotterdam, Netherlands) • Seller (producer) responsible for carriage, insurance, and freight costs • Ownership transferred at tanker's permanent hose connection at loading port
CFR: cost and freight	• Destination port is named • Seller responsible for carriage and freight costs
Outturn	• Seller agrees to deliver certain quantity into purchaser's tankage • Ownership transferred at discharge flange • Payment due on quantity received • Very infrequently adopted, possibly for spot deals (e.g., distressed cargoes)

Source: Table modified after [24].

comprising the purchaser and the seller. The two main pricing approaches are (1) unilateral fixed pricing and (2) market-related floating pricing of absolute and differential crude oil prices, under which there exist several variations of mechanisms practiced or available for adoption as elaborated in Tables 23.11 and 23.12. The price of crudes may be determined by a particular mechanism or a certain combination of them, and it may include a margin taken by the trader acting as the intermediate party. In general, the most common mechanisms today are posted pricing and formula-based pricing [1–3].

23.6.5.1 FLOATING ABSOLUTE PRICING MECHANISM

Transactions at fixed prices become more problematic because of increasingly volatile crude prices and uncertain cargo values when lifting (or offtaking) from inventories, loading, or discharge. Hence, purchasers and sellers are dissuaded from selling cargoes at fixed prices too early before loading. However, at the same time, it is undesirable not to conclude price decisions so as to avoid distressed positions due to price fluctuations that result in an "open" position of being susceptible to be forced to contend with accepting prices other than normal market rates. These have given rise to "floating" pricing mechanisms in concluding deals that better reflect market conditions when a cargo is actually moved. Market conditions are usually represented based on published prices, in which parameters to define prices related to market conditions in a deal are as follows:

- Pricing publication source(s) to determine the reference prices,

TABLE 23.11—Unilateral Fixed Absolute Pricing Mechanism of Crude Oil by Purchaser, Seller, or Regulatory Body [1,25]

Official/Government Selling Pricing (OSP/GSP)	• Introduced in 1973 by producing countries taking over price-setting from the major oil companies • Linked to spot prices via formulas • Still adopted in countries such as Malaysia, but no longer relevant in most other cases
Posted pricing	• Introduced during an era of concession agreements, mainly to calculate royalties because minimal intercompany trade existed • Typically set by producer (seller), often based on formula • Becomes OSP/GSP if set by NOC • Countries with regulated mogas price (e.g., Malaysia) have same posted prices at all pump stations throughout a country—companies would fix prices of crudes and products ex-refinery • U.S. law requires every refinery to post price at which it will purchase crude oil at refinery gate—these prices fluctuate daily based on market and between refiners who place different values for each crude depending on circumstances (which mainly involve plant operations) • A seller may have a cargo to be sold at average of all posted prices plus quality differential, but a purchaser may prefer to exclude posted prices of two refiners considered not representative of market; therefore, the final price is agreed upon based on a more limited number of available posted prices
Wholesale pricing	• Price in Europe at which road tanker can purchase fuel when loading from refinery or depot • Known as "rack price" in the United States because road tanker will be driven to a "rack" • Quoted in local currency by many pricing organizations; has good coverage in United States • Price is specific to cargo quality and location; therefore, a country may have many different wholesale prices for a particular oil quality

TABLE 23.12—Market-Related Floating Pricing Mechanism of Crude Oil [1,10,25,26]

Fixed differential to published pricing	• Transaction using published prices of only one day (e.g., BL date): • e.g., concluded based on mean of the means of Platts and Argus high and low quotations for CIF fuel oil NWE as quoted on BL date plus fixed differential with premium of $1/t • Parties are open to two possibilities: (1) one off-price increases or decreases, or (2) scope for manipulating published (i.e., payable) price • To minimize these, use a distribution of published prices, e.g., mean of published prices on BL date and 2 working days before and ahead of BL date (i.e., mean of five reported prices from each publication) • Typical practice is to use mean of 11 published prices (i.e., on BL date and ±5 working days) • Transactions using published prices based on mean of the means use quotes from • Different agencies (e.g., 50:50 split of Platts and LOR for a certain marker crude) • Different agencies but on oil products • Other crudes (especially those commonly-traded) • Different deals on oil products (e.g., CIF gas oil cargoes North-West Europe [NEW]) • Combinations of above (e.g., based on other crudes and oil products) • Over half of internationally traded crudes are quoted at differential to Brent marker crude because it is • Most widely traded in international oil markets, thus sufficiently transparent to be a valid benchmark • Of generally consistent quality that does not vary significantly over time • Considered a reliable supply sourced from a politically stable region. • Any change in the differential to Brent for a certain crude will reflect relative market interest in that crude compared with Brent
Formula pricing	• Introduced by Saudi Aramco (Saudi Arabian NOC and world's largest oil company) after their unsuccessful netback pricing system • Uses a mathematical formula to price a crude oil cargo over a fixed number of specified published prices (including IPE futures) quoted as differential to spot market • Considers varying prices into regional markets • Component values in formulas are negotiated between trading parties • Relates to commonly traded crudes • e.g., netback formula: values theoretical product yields from crude at a specific end-use location with subtractions to cover profit margins and costs (operating, transport, and others), hence "netbacks" crude price to point of origin • Mainly used by OPEC generally only for difficult-to-market crudes
Fixed differential to futures pricing	• Parties must agree on the following as pricing formula basis when concluding deals: • Fixed differential to market futures prices • Method to determine absolute futures prices—parties normally agree on last traded price displayed on futures screen or settlement price of given futures contract at close of business on BL's date • Date (time) at which agreed pricing formula is valued • *Trigger pricing*: • A deal in which seller usually grants purchaser with right to elect timing to fix ("trigger") agreed differential price of cargo (or part of cargo in smaller lots) • Recent popularity has declined because of recognized opportunity for either party to manipulate marker price ahead of pulling the trigger, but still used under certain circumstances
Formula-based pricing for floating differential to published or futures pricing	• Extension of trigger pricing involving formula agreed between purchaser and seller to calculate differential to published or futures prices rather than fixed differential • e.g., price a cargo at Platts published differential of relevant grade to Brent on BL date (or use IPE futures prices for Brent)
Exchange of futures for potential (EFP)	• Now popular other extension of trigger pricing, as is its swaps equivalent known as EFS (exchange of futures for swaps) • A physical crude cargo is sold to purchaser; in return, purchaser transfers ownership of some futures contracts to seller for a value equivalent (or as close as possible) to traded physical volume • Trading parties either use or create existing futures positions, rather than published futures prices, to match exposure on physical market • Cost to purchaser and seller can be different because each party can place associated futures positions at different times • Parties must agree on the following when concluding deals: • Differential physical price to futures contracts price, • Futures contracts value at agreed time of ownership transfer, and • Date for valuation of physical price and futures contracts.

(Continued)

TABLE 23.12—Market-Related Floating Pricing Mechanism of Crude Oil [1,10,25,26] (Continued)

	• Advantage: allows two parties—one with long futures contracts (long oil) and another with short futures contracts (short oil)—to strike deals in which both share same views on where market is heading

Basket pricing	• Adopts a basket of price quotes to avoid overdependence on prices of crude markers or oil products vulnerable to manipulations
	• e.g., Dated Brent cargoes with fixed loading date could be squeezed if a trader buys all available physical Brent cargoes and then raises the price artificially—to avoid this, crudes are priced based on average of dated Brent, Forties, and Ekofisk
	• Mainly used in transactions involving producers rather than spot markets, e.g.:
	  • OPEC basket (OPEC's own reference price)
	  • U.S. importers of West African crudes sometimes use diverse pricing baskets to ensure that geographical supply dislocations in an area (due to geopolitical instability) will not affect prices in another
	• Extension includes agreement on percentage for applying each published price, e.g., to price vacuum gas oil feedstock as percentages of gasoline plus gas oil quotations on BL, with total percentages not necessarily 100 %
	• Feedstock and chemical components are often priced this way because these more specialized, less-traded (hence less transparent) products are not quoted in absolute terms by published prices

Formal panel pricing	Crudes in Far East markets are commonly priced in relation to widely adopted pricing panels, notably APPI prices that have the following attributes:
	• Panel members are key market participants comprising active producers, refiners, and traders
	• Used to calculate official Indonesian crude prices by its NOC, PERTAMINA, and subsequently used to price term sales and assess upstream tax owed by producers
	• Members supply prices weekly for local crudes (from Indonesia, Malaysia, China, and Australia) and key imported grades (e.g., Dubai, Oman, and Murban)
	• Prices submitted to an independent agent (e.g., the international accounting firm KPMG) are averaged after excluding highest and lowest prices for publication on every Thursday
	• Two major inadequacies:
	  1. Less useful, especially during volatile market conditions because published weekly compared with daily reports of Platts and Argus
	  2. Restricted composition of panel membership
	• Generally lower than spot prices; hence, spot transactions are often concluded at APPI prices plus premium
	• Similar to refiners, producers are also interested to keep APPI prices low because upstream taxes are based on them
	• Suggested for adoption in Europe but with low response because Europe continues to depend heavily on Platts

Contract pricing	• Also called "term" pricing because negotiated in term contracts • Any factor is applicable, particularly formulas linked to spot markets • Typically involves several large-volume cargoes for 3 months to 1 year • Not monitored by price reporters
Spot pricing (or cash pricing)	• Quoted daily by standard journals, particularly the key industry reference Platts • Involves prompt loading and typical delivery window of 2–25 days

- Market (e.g., barges FOB Amsterdam–Rotterdam–Antwerpen),
- Grades (e.g., diesel 10 ppm),
- Date(s) of assessment related to calendar or specific event (e.g., loading date), and
- Discount or premium compared to the reference prices.

In the last 20 years, this method has emerged as the primary pricing mechanism with the introduction of paper instruments. It has become increasingly sophisticated and complex, especially in forward markets with pricing mechanisms increasingly separated from physical oil.

23.6.5.2 FIXED AND FLOATING PRICING DIFFERENTIALS MECHANISM

Many trading arrangements adopt differentials or price variations to certain published prices. Agencies such as Platts publish differentials on the basis of market conditions for crudes and oil products. Floating differentials or "floats" are linked to agreed quoted prices or the average of a set of published quotations until the prices become fixed based on the terms and timing agreed between involved parties, usually around the time vessels are loaded or discharged. Fixed differentials do not depend on market conditions (e.g., agreed fixed magnitude of 10 cents more than Platts prices) whereas floating differentials vary according to market conditions as based on certain formulas, which could involve spot or futures prices. Term supplies could still be agreed upon for extended periods, but cargo prices would vary based on the market at loading or discharge time. The floats are typically the average of prices for an agreed period (e.g., on or around the actual loading date as given in BL in an FOB sale or on the discharge date or delivery day or month average given in the Notice of Readiness [NOR] in a CIF sale). Hence, a wide variety of formulas are available as trading parties attempt to protect themselves against price fluctuations after concluding agreements, as further detailed in Tables 23.11 and 23.12, with some examples of pricing mechanisms in the East markets presented in Table 23.13.

On the basis of the historical review presented, the trading approaches of purchasing and selling currently used in the oil business can be categorized into two major ranges of arrangements for crude oil and petroleum products. As compared in Table 23.1, these commercial transactions are term contract sales (or supplies) and spot contracts. However, in most situations today, the absolute crude oil price is established by spot prices based on marker crude oils.

23.6.6 Concluding Remarks on Crude Oil Pricing

Fixed-price deals work well when prices are reasonably constant. However, price volatility due to supply disruptions and political situations has prompted trading parties to recognize that fixed prices may be very different from market prices at lifting time, hence the development of the more flexible floating pricing mechanisms, which rules out situations of a substantially lower fixed selling price agreed upon earlier at delivery time and a substantially lower spot market price than an agreed upon earlier fixed buying price. As paper trading has developed and market liquidity has grown, oil has increasingly been treated as a standardized commodity, implying that discussions between parties need only focus on the price or pricing mechanism and the timing. Independent pricing services have also greatly increased market transparency, making it somewhat easier to gauge the oil market price. However, much of the traded oil is not of standardized lots but varies chiefly in quality, quantity, timing, and location. Such cargoes must be accurately valued relative to the standardized grades quoted by the pricing services before the floating formula based on published prices can be used effectively. At the same time, there is movement to intensify the use of IPE Brent futures prices that many companies now increasingly regard as more representative of actual market prices. Despite the trend toward floating pricing, end users may still need fixed pricing to ascertain their feedstock costs over a certain period and this has led to the emergence of swaps. In the final analysis, the ultimate cargo price in a transaction still boils down to the agreement between the trading parties [1,2].

23.7 PETROLEUM PRODUCT TRADING, PRICING, AND VALUATION

Pricing of refined petroleum products is more varied that that of crude oil and thus may be relatively less exact. Its market volume is often smaller than that for crude oils. Many oil product markets are often determined from a single spot price quotation.

For countries with an unregulated market, product prices depend generally on the regional or local supply-demand balance. Thus, most countries' domestic prices are determined by regional product prices and local governmental policy. However, in practice, the prices are based on published prices (typically Platts) of the nearest world market as quoted by region. Because products must be shipped to and from the country and from and to the notional market for which the price quotations are valid, the associated freight cost is also significant. Product prices frequently follow crude oil market movement, which helps to keep crude and product prices within a reasonable range of each other as fluctuations occur [2].

23.7.1 Pricing of Petroleum Products

A refinery is constantly faced with the need to estimate the cost of materials to buy or the value of goods and services to sell to evaluate and compare available refining options. These goods and services sometimes have an established price resulting from market forces outside of the refinery's control. A refinery often has to cost or value goods comprising feedstock, intermediate streams, and products with nonstandard quality for which no suitable price reference is available. In such cases, a refinery needs to use suitable costing and valuation techniques to systematically consider the major factors, as listed in Table 23.14, that influence product values to estimate the value and ultimately the price of products on the basis of accepted standards [1].

TABLE 23.13—Examples of Pricing Mechanisms in the East Markets (Unless Otherwise Stated)

Crude Oil Type	Price Publisher	Example of Formula Used in the East (unless otherwise stated)[1]	Period of Prices Quoted
Arabian Light (ALC)	Platts	• Into Europe: Dated Brent – \$1.80/bbl • Into United States: WTI – \$2.00/bbl • Into East: (Oman + Dubai)/2 + (OSP premium) (*Note:* OSP premium is typically \$0.30/bbl)	Average of daily prices quoted over 1 month (i.e., monthly average)
Iranian Light (ILC)	Platts	$\frac{1}{2}(\text{Oman} + \text{Dubai}) + (\text{OSP premium})$	Monthly average
Malaysian crudes	APPI	Tapis + (OSP premium)	Monthly average
Bach Ho (Vietnamese crude)	Platts, APPI	$\frac{50\,\%\ \text{Minas Platts}}{50\,\%\ \text{Minas APPI}} + (\text{market premium})$	3 weeks around BL
Australian crudes	APPI	Tapis + (market premium)	3 weeks around BL
Products	Platts	MOPS + (market premium)	5 days after BL
Jet fuel	Platts	MOPS + (market premium)	Previous month average

Note: The crude oil type indicated represents the price of a particular crude oil according to the corresponding price publisher.

TABLE 23.14—Factors Determining Pricing of Petroleum Product

Factor	Example
Market prices, forces, and structure	Spot crude prices based on publications; supply-demand over time; price differentials (arbitrage); perceptions; seasonality; prompt market conditions; storage, transportation, and refining
Supply-demand balance	Export–import parity (see Table 23.15 for more explanation)
Other economic factors	• Supply: crude reserves, stock levels, and inventories; OPEC and non-OPEC crude production; imports-exports; infrastructure and supply flexibility; shipping availability and cost; strategic petroleum reserves • Demand: weather, climate (season), refinery margins and operating levels, refinery turnarounds, product stock levels, product prices, interfuel economics

Crude oil quality	• Lighter crude has higher refinery gate value
	• Sources of quality-related costs:
	  • Need for purchasing expensive components
	  • Treating costs
	  • Unit conversion limitation
	  • Blending component restrictions
	  • Blending margins and quality giveaway

Alternative supplies of other products (besides crude) to meet the same objective	• Alternatives for chemical feedstock (e.g., for ethylene cracker feed: natural gas, LPG, naphtha, or gas oil) • Alternatives for power generation (e.g., natural gas or coal)
Alternative purposes that product can be used for	• Naphtha: as reformer feed or chemical feedstock • LPG: as automotive fuel, chemical feedstock, or refinery fuel • Kerosine: as jet fuel, gas oil component, or fuel oil diluent
Cost of all necessary processing steps to bring product to recognized standard specifications	Grade differential based on quality premium (e.g., crude heaviness sulfur content, and RON)
Storage	Type of facility and size (volume)
Product characteristics	Key specification issues, price drivers
Subjective considerations	Preferred brands, trade names, fashion, or images
Political factors	Geopolitical risks, terrorism activities, sanctions, civil unrest, OPEC policies, labor strikes
Other factors	Trading activities, market speculations, news and rumors

TABLE 23.15—Effects of Export-Import Parity on Product Pricing

	Market Situation	
	In Deficit	***In Surplus***
Recourse action	Market needs to import part of requirements (because structurally short)	Refiner needs to export part of product make (because structurally long)
Refinery gate price (RGP) = breakeven price	• CIF = maximum price for domestic spot sales (because imports have to be transported to utilizing market) • Achieves import parity	• FOB = minimum price for domestic spot sales • Achieves export parity
Refiner's position	Strong	Weak
Disadvantage	Importer might not be able to sell at the CIF price because competing seller would offer a lower price	Buyers in the domestic market can force down RGP because the refiner will prefer any increment above FOB price instead of exporting
Remark	It is desirable to be self-sufficient in meeting market demand; otherwise, exposed to high freight cost (except term contract with fixed price)	

23.7.2 Price Information Sources and Reporting Methods for Petroleum Products

The published oil product prices represent the estimated value at a certain time for a cargo of a standard product of known characteristics. The sources and reporting methods for product prices are similar to that of crude oil except for the qualities considered. In the instance of gas oil, the main qualities include tonnage, relative density, sulfur content, and cetane index. Table 23.16 lists the benchmark product grades with roles similar to that of the marker crude oils. These price quotations are far from representative of the various products actually traded, which is accounted for in

TABLE 23.16—Benchmark Product Grades
• NWE gas oil • New York harbor gasoline and heating oil • Singapore fuel oil • ICE/NYMEX futures

a cargo's agreed upon selling price in terms of its differential from an agreed upon quotation. The differential or adjustment factor accounts for the quality, tonnage, transport method, and other aspects relevant to a commercial transaction. For some products, there are three price quotations depending on whether shipment is by cargo or barge and whether the price is of FOB or CIF [2].

23.8 COSTS AND ECONOMICS IN PETROLEUM REFINING INDUSTRY

The two essential types of costs are operating costs and capital costs. The breakdown of these two cost components largely depends on the intended use, and all costs and values must be derived based on market prices and operating costs. Operating costs can be categorized as fixed or variable, and most components are somewhat between the two categories. For example, many fixed costs have some form of relationships to the throughput, which potentially varies (e.g., labor), whereas many variable costs have some fixed components (e.g., power). Even so, costs can be practically treated as purely fixed or purely variable without degrading the estimated values. Table 23.17 further discusses their major features. For accounting purposes, direct and indirect costs are mainly recorded as averages by cost elements and cost centers whereas for economic evaluations the potential for cost variabilities is the main concern. In addition, transfer price is the price at which products are "sold" by the separate functions of manufacturing to marketing at the refinery gate to assess each sector's profitability—it is also important for a joint-venture-owned refinery [27].

23.8.1 Operating Costs of Manufacturing

23.8.1.1 RAW MATERIAL SUPPLY COST OF CRUDE OIL DELIVERED

Raw material supply cost refers to the total cost incurred by a refinery to get the desired products into the product storage tanks. It is the total "in-tank" cost associated with the purchase of crudes and feedstock that includes blending additives but excludes fuel purchases. The transportation

TABLE 23.17—Major Features of Refinery Capital and Operating Cost

Cost Type	**Feature**	
Capital costs	• For purchasing of major process units and equipment • Major concern is on profitability of potential investment, either for ranking of alternatives or comparison to a yardstick	
Operating costs	Cover all costs related to production, distribution, and marketing of goods	
	Fixed:	• Constant with time • Do not depend on production or activity level • A portion can be related to process units (e.g., maintenance and direct labor); others are miscellaneous overheads
	Variable:	• Highly dependent on the production level • Largely defined by process chemistry and technology • Can be calculated and shown at the equipment level, operating unit level, or refinery level • Typical items are fuel, purchased utilities, and additives

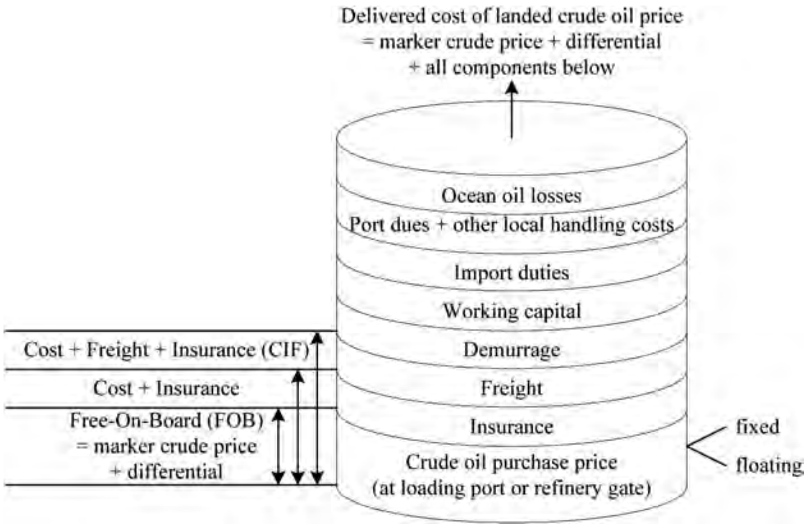


Figure 23.2—Components of the supply (delivered) cost of landed crude oil price.

involved is mostly through shipping, in which a cargo may be purchased on the basis of FOB or CIF. Supply cost is by far the largest refinery cost item, representing almost 90 % of total refining costs, with Figure 23.2 explaining its typical components and Table 23.18 its primary features.

23.8.1.2 OTHER COMPONENTS OF MANUFACTURING OPERATING COSTS

There is no single universal definition or classification of whether a cost component is variable, fixed, direct, or overhead costs. The status of a cost component likely depends on the specific problem in terms of the range of variation, time frame, and other factors. Table 23.19 provides some general guidelines on the cost components [28].

23.8.2 Capital Costs of Manufacturing

The cost of establishing new refineries or adding major conversion technologies varies mainly according to the associated refining capacities or sizes. Table 23.22 provides the capital costs for individual process units consistent with the crude distillation unit capacities of 50, 100, and 200 kbbl/day [29]. Although the scaling coefficient of 0.65 actually varies according to unit complexity, it is generally valid for small capacity changes. Accordingly, costs for intermediate capacities may be estimated as follows:

$$\text{intermediate capacity cost (\$'000)} = \text{base cost (\$/bpd)} \times \text{base capacity (bpd)} \times \left(\frac{\text{new capacity}}{\text{base capacity}}\right)^{0.65} \quad (23.1)$$

$$\text{intermediate capacity cost (\$/bpd)} = \frac{\text{intermediate capacity cost (\$'000)}}{\text{new capacity}} \quad (23.2)$$

These data may also provide a sense of magnitude on the cost of upgrading existing refineries by adding new process units (e.g., fluid catalytic cracking [FCC] unit or hydrocracker).

Note that the figures in Table 23.22 have an accuracy of approximately ±50 %. These figures are only the equipment cost and not the total installed cost; therefore, they are the same regardless of the location where the equipment is manufactured. This is especially because procurement is a global business in which the decision to procure equipment mainly depends on which equipment manufacturer could offer the best deal rather than the location where the equipment is manufactured. However, the total installed cost at a particular site would be different because of a myriad of factors, which include location. Note also that the cost reported is the same whether it is reported in weight basis (e.g., \$/t) or in volume basis (e.g., \$/bbl). The figures are also independent of the currency because the equipment cost remains the same.

23.8.3 Refinery Profit Margins and Costs

The term “margin” as it is used in our context simply means “difference,” and refinery profit margins refer to the difference between product values or prices and crude oil cost. That difference is more significant and meaningful to a refiner than the absolute price level of crudes and refined products. Refinery profit margins depend on which

TABLE 23.18—Primary Features of Components of Supply (Delivered) Cost of Landed Crude Oil Price

Component of Crude Oil Supply Cost	Attribute

Freight	• Vary in large magnitude reflecting market situation
	• Typically expressed in per ton of cargo
	• Negotiable (in principle) for each cargo based on industry standard references:
	  • Worldscale (of Worldscale Association): annually updated list of freight rates for standard voyages between any two ports in the world
	  • AFRA (Average Freight Rate Assessment; of London’s Tanker Brokers Association): monthly market assessment of the last month for each ship class (classified by size)
	• Basis is tanker nominal freight scale
	• Standardization refers to ship type and route (if applicable) for a round trip with cargo on one leg only (i.e., single journey)
	• Rates quoted in terms of 100 points of Worldscale (indicate percentage of applicable standard rate)
	• Special premium can be charged for exceptional situations (e.g., sailing into war zones)
	• In addition to agreed freight, the charter party (i.e., transport contractor) always includes a clause to compensate the ship owner for demurrage costs if the ship is made to spend more than the agreed upon time for a loading-unloading operation

Demurrage costs	Compensation to ship owner if ship is made to spend more than the agreed upon time for a loading-unloading operation (always included by charter party)—can involve significant amount
Working capital	• Crudes are largely acquired via FOB deals with number of credit days starting to run from BL date • Can result in positive or negative value on the basis of required transport time
Port dues and other local handling costs	Includes costs of inspection, heating, trading, pipelines, terminals, etc.
Ocean oil losses	• Quantity measured at loading port serves as payment basis in most cases • Ocean losses refers to difference in quantity actually received (resides in tanks) that is less due to various reasons (e.g., evaporation, left as tank bottoms, or incorrectly measured water when loading)

TABLE 23.19—Other Components of Manufacturing Operating Costs

Cost Component	Attribute
Fuels and purchased utilities	• Mostly variable, although part of refinery fuel consumption is for general purposes and as such is part of overheads • Fuel consumption of certain individual plants comprises a fixed part (consumed as soon as plant is onstream regardless of intake or throughput) and a variable part
Process materials	• Mainly variable, e.g., additives and catalysts • May be fixed, e.g., solvent inventories for extraction unit
Labor	• Essentially fixed unless involves major changes in operations (e.g., new plants, shutdown of existing unit, staff retrenchment) • Table 23.20 lists its major components • Depends on refinery and its location • Partly direct (e.g., operating personnel including maintenance), partly overheads (e.g., administration) • Include field operators through refinery manager • Include overtime, benefits, and other related costs • Cost per person varies based on local costs for a skill level • Number of employees at a facility varies widely by refinery configuration and related local factors • Advantage of lower rate is often offset by lower productivity • Maintenance management is included but direct maintenance labor is considered as maintenance cost
Maintenance	• Table 23.21 lists its major categories • Fixed (at least for short term) but varies by process units • Units with dirty, severe processes and solids handling are far higher than mild processes • Typically estimated as fraction of unit's replacement cost • Units lacking sustaining capital tend to experience rising maintenance costs over time • Possible to reduce through careful management
Royalties	• Depend on license agreement • Typically include annual prepaid intake, which is either annual fixed cost or once-off lump sum
Taxes, insurance, and miscellaneous costs	• Fixed and depend on individual company and country of operations • Taxes generally include property tax but not income or value-added taxes • Proportion of refinery replacement cost: tax 0.1–0.7 %; insurance 0.2–0.5 %
Miscellaneous overheads	• Technical support functions: technology, engineering, inspection, laboratory, security, fire-fighting • General support functions: finance, environmental, information technology equipment, communications, human resource, medical services, site management, public relations • Office expenses and service fees • Personnel expenses: training, housing, recreation • 0.5–1.5 % of refinery replacement cost

TABLE 23.20—Components of Labor Costs

• Refinery management	• Project engineering
• Operations supervision	• Maintenance management
• Operations planning	• Technical service
• Environmental	• Information systems
• Financial	• Process engineering
• Human resources	• Inspection
• Health, safety, and security	• Laboratory

products are made and, by extension, typically benefit from falling crude oil prices.

Refinery margins can be defined in multiple ways as delineated in Table 23.23, in which each has a useful purpose and can be calculated with appropriate refinery and market information. To assist the explanation, we consider the money flowing in and out of the refining business strictly in terms of costs with no explicit regards for a refinery as a processing plant.

Standard refinery margins are reported in publications such as Platts and Petroleum Intelligence Weekly (PIW) [30]. These are based on standard yields assuming a certain configuration (e.g., hydroskimming or complex refinery, with its precise meaning depending on the region considered) and operating mode (e.g., "maximum gas oil," which is typical of the European winter season or "maximum diesel," which is attractive for the current market situation of Malaysia [at the point of writing].

23.8.4 Effects of Production Rate on Refinery Margins and Product Valuation

Tiering of product value occurs whenever an operating constraint is encountered and correspondingly results in tiered refinery margin, implying that every barrel of oil processed does not contribute equally to the refining margin. It can be described by a step function representing discontinuity in the cost or value of a feed or product, as shown in Figure 23.3. The effects of tiered refinery margin include situations in which the most profitable market segment is fully satisfied and a plant upgrading is fully utilized.

We consider the processing of the first barrel of crude oil in a crude distillation unit as illustrated in Figure 23.4. Assume the throughput-related operating cost to be fixed. For instance, consider that the CDU processing hits a

TABLE 23.21—Categories of Maintenance Costs

Categories of Maintenance Costs	Attribute
Routine operating	• Undertaken without interrupting operations • Limited to minor items
Major turnaround	• Undertaken every few years • Requires closing process units for 2–8 weeks • Opportunities to inspect or repair internals of major vessels
Sustaining capital investment costs	• Capital expenditures for improvements (capital replacements) • Typically ~2 % per year on long-term basis • Failure to invest in this will lead to long-term degradation of process units • Includes obligatory and profit-driven projects • Excludes refinery major expansion or revamp projects • Actual construction is typically timed with unit turnaround

TABLE 23.22—Capital Costs for Individual Process Units for Crude Distillation Unit Capacities of 50, 100, and 200 kbbl/day [29]

	Capacity (kbbl/day)	Cost ($'000/ bbl per day)	Capacity (kbbl/day)	Cost ($'000/ bbl per day)	Capacity (kbbl/day)	Cost ($'000/ bbl per day)
Atmospheric distillation unit	50	925	100	825	200	650
Vacuum distillation unit	25	1,150	50	725	100	575
Catalytic condensation unit	0.3	20,000	1.6	11,000	2.3	9,750
Naphtha hydrotreater	13	1,250	26	1,000	47.5	750
Kerosine hydrotreater	5	4,750	8	3,500	18	1,750
Diesel hydrotreater	18	1,750	38	1,250	55	1,000
Gas oil hydrotreater	1.5	6,000	3	4,750	6	3,500
Catalytic reformer	12	3,500	24	3,000	46	2,500
FCC	17	4,500	34	3,250	68	3,000
Hydrocracker	17	12,500	34	10,000	68	8,000
Coker (includes delayed coker)	5	10,750	9	8,750	18	6,750
Alkylation unit (hydrofluoric-acid-based)	0.7	25,750	4	18,500	10.6	8,000
Visbreaker	2.2	5,000	4.5	4,250	9	3,500
Hydrogen production unit (in t/day)	0.06	1,250,000	0.13	950,000	0.25	757,500
Sulfur recovery unit	0.08	657,500	0.33	400,000	0.64	317,500

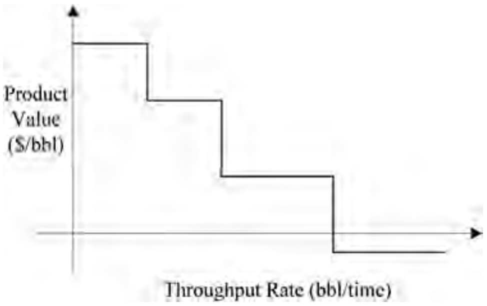


Figure 23.3—Tiering of product value based on the processing margin for incremental throughput. Note that the horizontal axis represents rate (typically throughput rate [in bbl/ time, e.g., kbbl/day]). Product value on the vertical axis is given by gross product worth (GPW) less feedstock (i.e., crude oil) cost and less operating cost.

thermodynamic constraint of insufficient heating duty in the furnace. Then it hits a second constraint on the rundown pump that causes the yield of the middle distillate to fall to diesel—this will immediately cause the refinery margin to be eroded because of the lower price of kerosine compared with diesel. If there is insufficient furnace duty to lift the products, then refinery margin for every next incremental barrel of crude processing will be further reduced. Note that with more constraints, the product value will not increase—it stays fixed or equal to the previous value or it reduces. As depicted in Figure 23.5, the maximum product value corresponds to the maximum processing rate, as in the maximum crude oil processing rate in the case of a CDU. This is the optimal production rate for an incremental barrel of processing because operating at a higher rate will erode the refinery margin.

TABLE 23.23—Calculations of Refinery Margins

Definition of Refinery Margin	Attribute

Product yields	• Depend on refinery configuration
	• Highly sophisticated linear programming (LP) model computer programs are used as decision tools to determine the optimal refinery operation mainly on the basis of crude assay and product yields and prices
	  • LP incorporates mathematical representations of each step in refining processes
	  • Refineries have many alternative ways to operate from which the operator must choose only one that is optimal economically and operationally
	  • Product yield is one of the many decision outputs from an LP model by considering parameters of all operating conditions

+ Proceeds or gross product revenue (GPW)	• Weighted sum of products from crudes • Products are sold to customers at spot price and transfer price by considering export–import parity and other factors • At any rate, refinery receives a "netback" with the total for the considered period forming the GPW
− Supply cost of crude oil delivered	Total "in-tank" cost associated with purchase of crudes and feedstock
= Hydrocarbon margin	• Refineries use part of their own hydrocarbon intake as possible energy source except for purchased electricity • In mass terms, less products are sold than feeds purchased • Crude cost should be on delivered basis, but may be FOB in certain cases • Includes fuel cost • The margin often quoted in the press • Very rough guide to refining industry strength
− Other Variable Operating Costs	• Includes purchased utilities, additives, catalysts, chemicals, and royalties in addition to other internal energy costs • Vary with crude processing rate, e.g., fuel
= Gross Refinery Margin (GRM) (or Variable Refinery Margin)	• Includes all variable costs • Must be positive on incremental crude processing • Used for crude price differentials in spot market for analysis of incentive to process incremental barrel of crudes
− Fixed Operating Costs	• Excludes financing, interest payments, and stock effects
= Net Refinery Margin (NRM)	• Includes all operating costs but excludes capital (financial) costs and stock effects) • "Current cost of supply" margin • No depreciation and working capital • For monitoring industry profitability trends • Used by producers to monitor actual customer profit levels and baseload economics for negotiations • Must be positive on average in long term to stay in business

**Note:* In certain publications and companies, the term "gross refinery margin" does not subtract variable costs, most likely because a good sense of what constitutes that cost component (of variable costs) is not available.

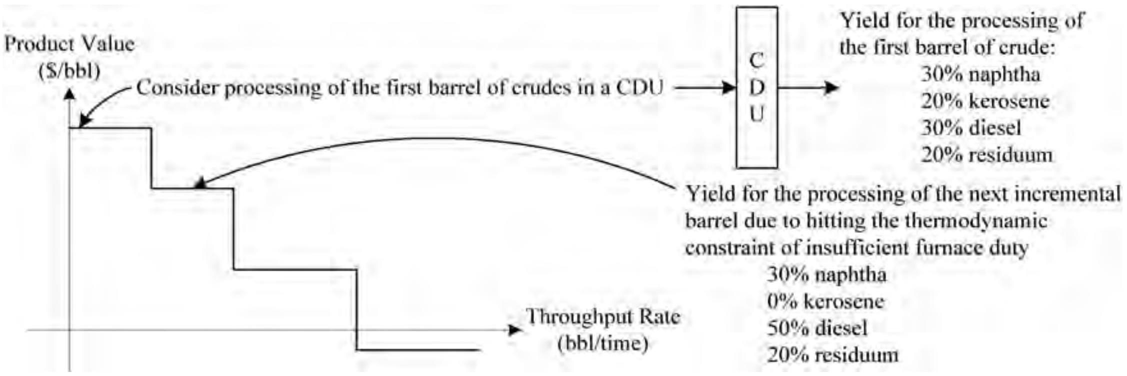


Figure 23.4—Tiering of product value in the case of CDU processing.

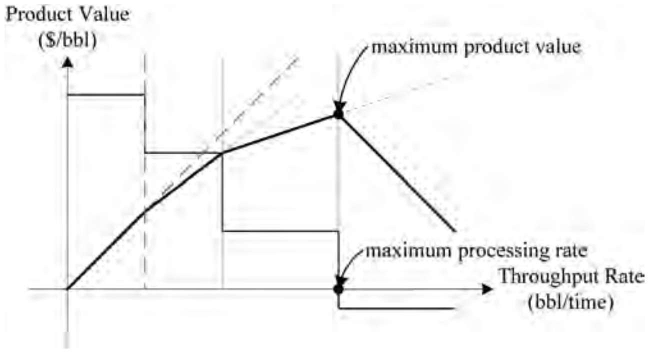


Figure 23.5—Product value changes with time (typically in $/day).

23.9 CONCLUDING REMARKS

It is evident through this chapter that the methods and practices of crude oil and petroleum product trading, costing, and valuation have evolved extensively from their beginnings of the physical markets to the highly sophisticated financial markets that they are today as the world's biggest and perhaps most strategic commodity market. With the impending new global climate-related policies and agreements after the Kyoto Protocol in 2012, the refining business is clearly set for further challenges with respect to the ever important interplay of costs, pricing, and valuation.

ACKNOWLEDGMENTS

The main author is grateful to the Enterprise Optimization Unit of the Oil Business Division of PETRONAS (Malaysia's national oil company) for providing opportunities for discussions and clarifications on numerous issues presented in this work in an effort to ensure the relevance of its contents to real-world situations as much as possible.

REFERENCES

[1] Long, D., Ed., *Oil Trading Manual: A Comprehensive Guide to the Oil Markets*, Cambridge, United Kingdom, Woodhead Publishing, 2001.

[2] Favennec, J.-P., Ed., Baker, R., trans., *Refinery Operation and Management*. Vol. 5 of *Petroleum Refining* Series, Paris, Editions Technip, 2001.

[3] Shell International Petroleum Company Limited, *The Petroleum Handbook*, 6th ed., Amsterdam, The Netherlands, Elsevier, 1983.

[4] Eydeland, A., and Wolyniec, K., *Energy and Power Risk Management: New Developments in Modeling, Pricing, and Hedging*, New York, Wiley, 2002.

[5] Chen, K.C., Sears, R., and Tzang, D.-N., "Oil Prices and Energy Futures," *J. Futures Markets*, Vol. 7, 1987, pp. 501–518.

[6] Hull, J.C., *Options, Futures, and Other Derivatives with Deriva-Gem CD*, 7th ed., London, Prentice Hall, 2008.

[7] Kaminski, V., *Managing Energy Price Risk: The New Challenges and Solutions*, 3rd ed., London, Risk Books, 2004.

[8] Battley, N., Ed., *The World's Futures & Options Markets*, Chichester, UK, Wiley, 2000.

[9] Leppard, S., *Energy Risk Management: A Non-Technical Introduction to Energy Derivatives*, London, Risk Books, 2005.

[10] Weiner, R. J., "Default, Market Microstructure, and Changing Trade Patterns in Forward Markets: A Case Study of North-Sea Oil," *J. Banking Finance*, Vol. 18, 1994, pp. 955–977.

[11] Fattouh, B., "The Dynamics of Crude Oil Price Differentials," *Energy Econ*., Vol. 32, 2010, pp. 334–342.

[12] Burucoa, X., and Favennec, J.-P., "International Oil Markets," In J.-P. Favennec, Ed., Baker, trans., *Refinery Operation and Management*. Vol. 5 of *Petroleum Refining* Series. Paris, Editions Technip, 2001, pp. 77–115.

[13] Drollas, L.P., "Oil Price Stability: A Charming Delusion," Presented at *Platts' 2nd Annual New Challenges for Oil*, Geneva, Switzerland, May 29, 2009, http://www.cges.co.uk/pub/LD%20PlattsGeneva%20May09.pdf (accessed January 17, 2010).

[14] Plourde, A., and Watkins, G.C., "Crude Oil Prices between 1985 and 1994: How Volatile in Relation to Other Commodities?" *Res. Energy Econ*., Vol. 20, 1998, pp. 245–262.

[15] Weiner, R. J., "Speculation in International Crises: Report from the Gulf," *J. Int. Bus. Stud*., Vol. 36, 2005, pp. 576–587.

[16] BP, *BP Statistical Review of World Energy June 2009*, London, BP, 2009, http://www.bp.com/statisticalreview.pdf (accessed February 4, 2010).

[17] "Energy Market Data Solutions: GlobalView. MarketView Database," http://www.gvsi.com (accessed July 17, 2010).

[18] "Platts Crude Oil Marketwire," http://www.platts.com/Products.aspx?xmlFile=crudeoilmarketwire.xml (accessed December 1, 2010).

[19] Petroleum Argus, http://www.argusmedia.com/pages/StaticPage.aspx?staticurl=snips/bir/WPA_Resource.shtml&tname=Home&pname=Petroleum (accessed December 1, 2010).

[20] "Commodities: Energy. Energy: Commodities," www.reuters.com/finance/commodities/energy?mkt=ENERGY (accessed December 1, 2010).

[21] OTA Limited, "Far East Oil Price (FEOP)," https://feopindex.com (accessed January 4, 2010).

[22] OPIS Energy Group, "Oil Price Information Service (OPIS)," http://www.opisnet.com (accessed January 4, 2010).

[23] RIM Intelligence Co., "RIM," https://www.rim-intelligence.co.jp/cgi-bin/e/index.cgi (accessed January 4, 2010).

[24] Incoterms®, 2010, ICC rules for the use of domestic and international trade names, International Chamber of Commerce (ICC), 2010.

[25] Hamer, C., "Oil Pricing Arrangements." In Long, D., Ed., *Oil Trading Manual: A Comprehensive Guide to the Oil Markets*, Cambridge, UK, Woodhead Publishing, 2001.

[26] Bohi, D.R., and Toman, M.A., "Futures Trading and Oil Market Conditions," *J. Futures Markets*, Vol. 7, 1987, pp. 203–221.

[27] Johnston, D., and Johnston, D., *Introduction to Oil Company Financial Analysis*, Tulsa, OK, PennWell, 2005.

[28] Wright, C. J., and Gallun, R.A., *Fundamentals of Oil & Gas Accounting*, 5th ed., Tulsa, OK, PennWell, 2008.

[29] PETRONAS, personal communication, 2010.

[30] Energy Intelligence Group, "Petroleum Intelligence Weekly (PIW)," http://www.energyintel.com/publicationhomepage.asp?publication_id=4 (accessed September 6, 2010).

24

A Review of Refinery Markets and Cost Estimation

Mark J. Kaiser[1] and James H. Gary[2]

24.1 INTRODUCTION

Crude oil in its natural state has no value to consumers and must be transformed into products that can be used in the marketplace. The first refineries used tanks to heat the crude oil and vaporize its volatile components. The hot vapor would rise, cool, and condense in a batch operation. The process was repeated at different temperatures to separate the various fractions. The technology was simple, and refineries were easy to set up; before long, refining capacity exceeded crude supply. The need for improved product separation led to the use of fractionating columns, which allowed the different boiling point cuts to be separated out in a continuous process. John D. Rockefeller sought to consolidate the U.S. refining business, and in 1870 he established the Standard Oil Company with his partners [1]. By 1879, Standard Oil controlled 90 % of the U.S. refining capacity [2].

The number of automobiles and the demand for gasoline greatly increased after the advent of mass production. However, distillation processes could only produce a certain amount of gasoline depending on the composition of the crude oil; therefore, scientists and engineers searched for new ways to increase the supply by breaking down, rearranging, and combining hydrocarbon molecules to increase the yield and performance of gasoline. In Table 24.1, a brief history of the major technical achievements in refining is presented.

The introduction of catalytic cracking and polymerization processes in the mid- to late-1930s met the demand for higher octane gasoline. Eugene Houdry discovered that if cracking was done in the presence of clay minerals, not only did the large hydrocarbon molecules break apart, but the products were also converted to branched paraffins, naphthenes, and aromatics with desirable properties [3]. Visbreaking, another form of thermal cracking, was developed in the late 1930s to produce a more desirable and valuable product slate. In the 1940s, alkylation processes were developed to create high-quality aviation fuel for the war effort; these processes were later used to produce gasoline blending stocks [4].

Isomerization converted straight-chain hydrocarbon molecules to branched-chained hydrocarbons to improve the burning characteristics of gasoline. In catalytic reforming, the presence of certain catalysts, such as finely divided platinum placed into a support of aluminum oxide, was discovered to reform and dehydrogenate straight-chain hydrocarbons with low octane into aromatics and their branched isomers with higher octane numbers. In the mid-1950s, a process called hydrotreating was developed to remove contaminants that would damage the catalyst used in catalytic reforming. Improved catalysts and processes such as hydrocracking were developed in the 1960s to further increase gasoline yields and improve antiknock characteristics.

24.2 REFINERY PROCESSES AND OPERATIONS

Refining begins with the distillation of crude into separate hydrocarbon groups by boiling range; these groups are called “fractions” or “cuts.” All crude oils undergo separation processes through distillation; therefore, it is common to express the capacity of a refinery in terms of its distillation capacity. Two measures are commonly used: barrels per stream day (BPSD) and barrels per calendar day (BPCD). A barrel per stream day is the maximum number of barrels of input that a distillation facility can process when running at full capacity under optimal crude and product slate conditions with no allowance for downtime. A barrel per calendar day is the amount of input that a distillation facility can process under usual operating conditions, making allowances for the types and grades of products to be manufactured, environmental constraints, and scheduled downtime due to maintenance, repairs, and shutdown.[3]

After crude oil is separated into its fractions, each stream is further converted by changing the size and structure of the molecules through cracking, reforming, and other conversion processes. The converted products are then subjected to various treatment and separation processes to remove undesirable constituents and improve product quality.

Petroleum refining processes and operations are generally classified into five types [5]:

1. Distillation is the separation of crude oil in atmospheric and vacuum distillation columns into groups of hydrocarbon compounds on the basis of molecular size and boiling-point ranges.
2. Conversion processes change the size or structure of hydrocarbon molecules by
   - *Decomposition*: Breaking down large molecules into smaller molecules with lower boiling points through cracking and related processes.
   - *Unification:* Building small molecules into larger molecules through alkylation, polymerization, and related processes.
   - *Reforming:* Rearranging molecules into different geometric structures in isomerization, catalytic reforming, and related processes.

---

[1] Center for Energy Studies, Louisiana State University, Baton Rouge, LA, USA

[2] Dept. of Chemical Engineering, Colorado School of Mines, Golden, CO, USA

[3] Capacity expressed in BPSD is usually a few percent higher than BPCD capacity.

TABLE 24.1—Brief History of Refining Technologies

Year	Process Name	Purpose	Byproducts, etc.
1862	Atmospheric distillation	Produce kerosine	Naphtha, tar, etc.
1870	Vacuum distillation	Lubricants (original) Cracking feedstocks (1930s)	Asphalt, residual coker feedstocks
1913	Thermal cracking	Increase gasoline	Residual, bunker fuel
1916	Sweetening	Reduce sulfur and odor	None
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulfur	Sulfur
1932	Coking	Produce gasoline basestocks	Coke
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Solvent dewaxing	Improve pour point	Waxes
1935	Catalytic polymerization	Improve gasoline yield and octane number	Petrochemical feedstocks
1937	Catalytic cracking	Higher octane gasoline	Petrochemical feedstocks
1939	Visbreaking	Reduce viscosity	Increased distillate, tar
1940	Alkylation	Increase gasoline yield and octane	High octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield and octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
1954	Hydrodesulfurization	Remove sulfur	Sulfur
1956	Inhibitor sweetening	Remove mercaptans	Disulfides
1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality and reduce sulfur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking	Increase gasoline yield from residual	Heavy residuals

Source: Adapted from [5].

3. Treatment processes prepare hydrocarbon streams for additional processing and prepare finished products using chemical or physical separation. Processes include desalting, hydrodesulfurization, solvent refining, sweetening, solvent extraction, and dewaxing.
4. Blending is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.
5. Other refining operations include light-ends recovery, sour-water stripping, solid waste and wastewater treatment, process-water treatment and cooling, storage and handling, product movement, hydrogen production, acid and tailgas treatment, and sulfur recovery.

24.3 PRODUCT DEMAND AND SUPPLY

Over the past 2 decades, the demand for petroleum products in the U.S. has risen steadily, in part because of a growing population, falling fuels prices, Americans' preference for heavier and more powerful vehicles, and an increase in passenger and goods travels (Figure 24.1). In 2008, demand for refined products in the United States was 22 million bbl/day [6], equivalent to a daily consumption rate of approximately 20 lb of petroleum per person. The transportation sector consumes the majority of petroleum at approximately 15 million bbl/day, whereas the industrial, residential and commercial, and electric power sectors consumed 4 million, 1 million, and 0.5 million bbl/day, respectively. The composition of the particular products consumed in each sector is shown in Figures 24.2–24.5. The residential sector consumes mostly distillate fuel oil for heating purposes, followed by LPG. The electric power industry only consumes the "bottom of the barrel" resid, which would otherwise be wasted, although in some parts of the world (the Middle East), oil plays a larger role as fuel stock for electric power.

U.S. demand for crude oil and petroleum products exceeds domestic supply (Figure 24.6), and the United States imports various intermediate and final petroleum products in addition to crude oil. Approximately 60 % of the U.S. petroleum requirements are currently imported. The United States is still one of the world's largest producers of crude oil, but it holds only 3 % of the world's proven reserves [7].

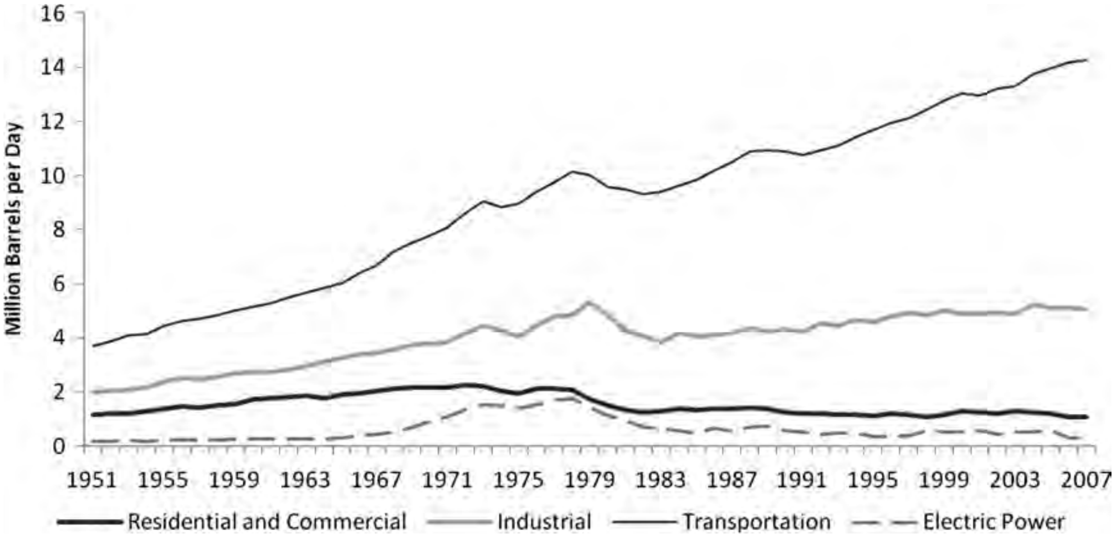


Figure 24.1—U.S. petroleum consumption by sector. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

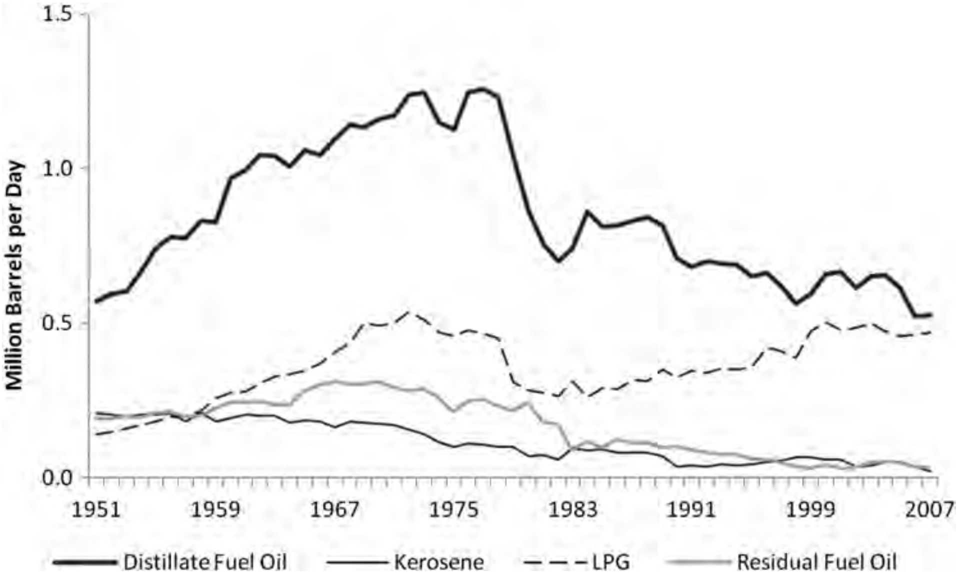


Figure 24.2—U.S. petroleum consumption—residential and commercial sectors. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

Raw crude and intermediate materials are processed at refineries into gasoline, distillate fuel oil (diesel fuel, home heating oil, industrial fuel), jet fuels (kerosine and naphtha types), residual fuel oil (bunker fuel, boiler fuel), liquefied petroleum gases (propane, ethane, butane), coke, and kerosine. Input-output graphs are depicted in Figures 24.7 and 24.8. Approximately 90 % of crude oil in the United States is converted to fuel products. Nonfuel products such as asphalt, road oil, lubricants, solvents, waxes and nonfuel coke, and petrochemicals and petrochemical feedstocks[4] comprise the remaining crude conversions.

Refinery production in the United States is dominated by gasoline, followed by distillate kerosine and jet fuel (Table 24.2). Gasoline yield typically fluctuates between 44 and 47 % and depends on the crude input stream and refinery configuration, with distillate and residual fuels contributing 32–35 % of refinery production. Approximately half of gasoline production is conventional, with 25 % satisfying various state and local requirements and 25 % produced according to federal reformulated gasoline specifications. Approximately 60 % of diesel fuel produced is ultra-low-sulfur fuel (15 ppm maximum) for the on-road (highway) market, and 40 % is higher-sulfur fuel for the offroad market (e.g., construction, farming, locomotives, shipping, and mining). U.S. Environmental Protection Agency (EPA) specifications require that all diesel fuels except railroad and marine fuels meet the 15-ppm sulfur specification by 2011.

---

[4] Includes naphtha, ethane, propane, butane, ethylene, propylene, butylene, benzene, toluene, and xylene.

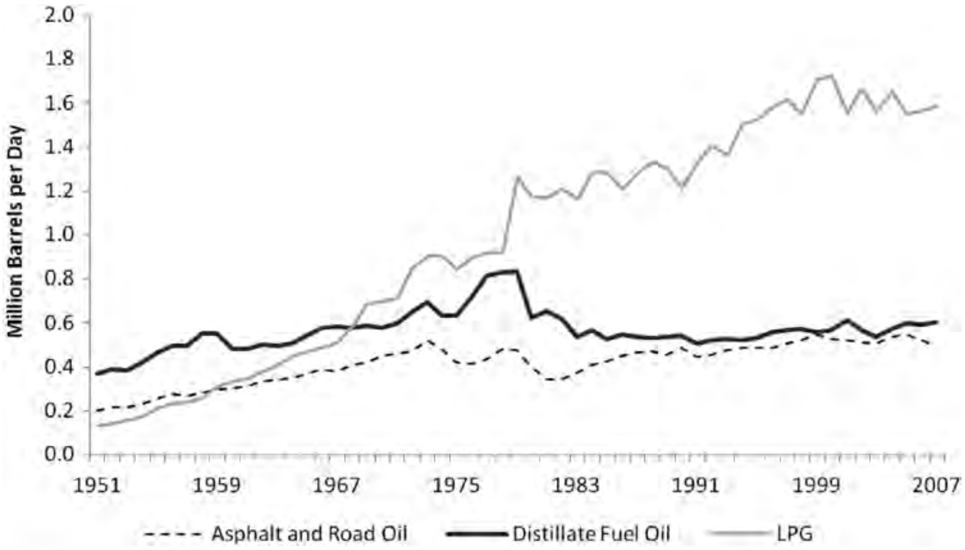


Figure 24.3—U.S. petroleum product consumption—industrial sector. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

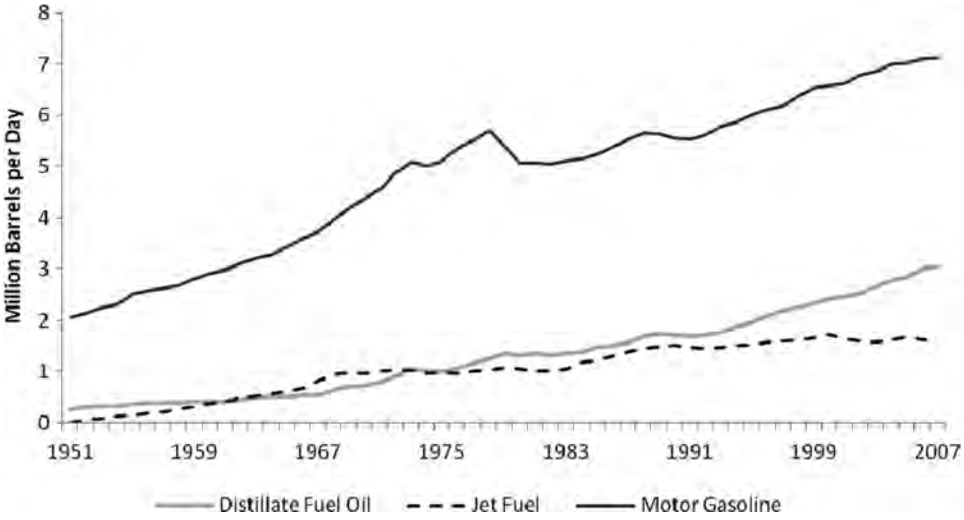


Figure 24.4—U.S. petroleum product consumption—transportation sector. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

24.3.1 U.S. Statistics

24.3.1.1 CAPACITY

The U.S. refining industry in 2009 consisted of 149 operable[5] refineries with 17.6 million BPCD crude charge capacity. Figure 24.9 shows that the range of capacity is wide, with the largest refinery having a capacity of over 550,000 bbl/day. The trend in U.S. refinery capacity over the past half century is depicted in Figure 24.10. Changes in refining capacity are due to plants being idled or shutdown, expansion through bottleneck removal and more intensive use ("capacity creep"), and grassroots construction.

In the late 1970s, the growth in product demand and subsidies under the U.S. Crude Oil Entitlement Program brought forth an expansion of refinery capacity, and by 1981, 324 refineries were operating at 19.4 million BPCD capacity. The Crude Oil Entitlement Program favored production from small, unsophisticated refineries, and the construction of simple hydro-skimming plants with less than 30,000 BPCD capacity accelerated [9]. By 1981, the U.S. government removed price and allocation controls on the oil industry, and many small refineries and inefficient plants could not compete and began to shut down. From 1981 to 2004, 171 refineries were shut down or closed, most being small, inland facilities associated with local crude oil production or specialty products such as asphalt, with less than 100,000 BPCD and without access to water transportation (Figure 24.11). Refineries associated with local crude production will eventually close when their source of

---

[5] Operable refineries are defined as those refineries that are in one of three states at the beginning of a given year: in operation; not in operation and not under active repair, but capable of being placed into operation within 30 days; or not in operation but under active repair that could be completed within 90 days [8].

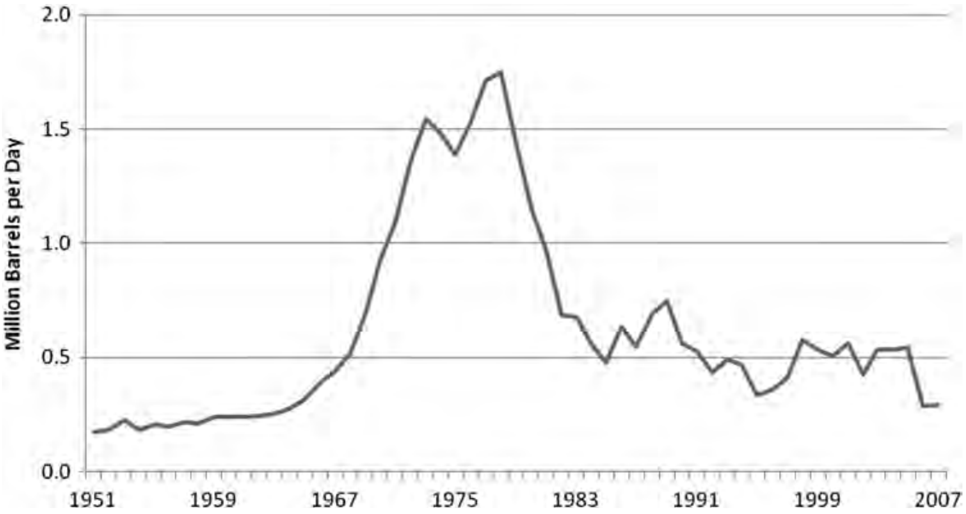


Figure 24.5—U.S. petroleum consumption—electric power sector. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

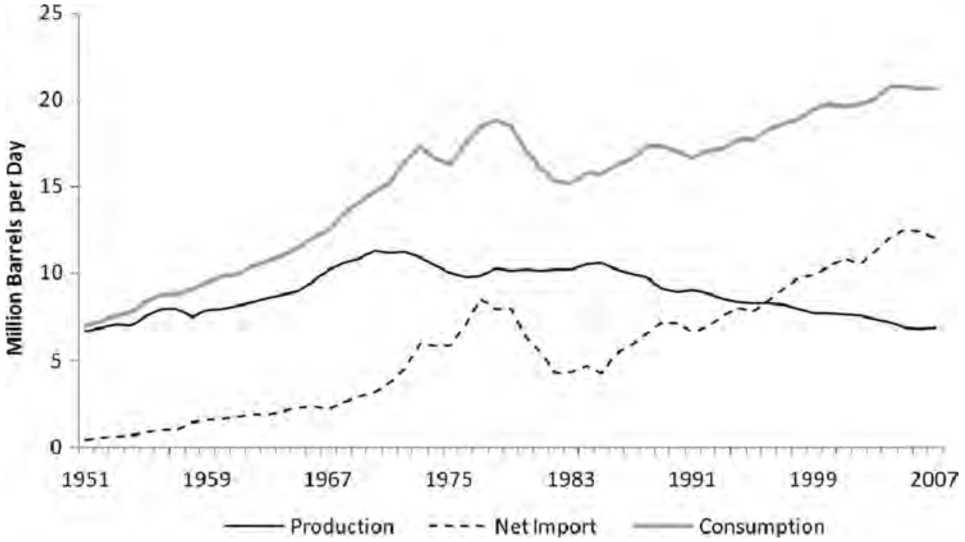


Figure 24.6—U.S. production, consumption, and net imports of crude oil. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

crude dries up. Economic rationalization, the lack of scale economies, domestic supply constraints, environmental regulations, and technological developments have all contributed to plant shutdowns [10,11].

24.3.1.2 CAPACITY CREEP

As small refineries close and existing facilities add to their capacity, the average capacity in the United States continues to increase (Figure 24.12). Over the past decade, the capacity of the refining industry has increased incrementally, at an average rate of approximately 1.7 % per year (130,000 BPD/year). Approximately 0.2 % annual capacity has been lost to refinery shutdowns. Expansion is often a more economic option than constructing a grassroots facility because of scale economies and the avoidance of fixed costs associated with a new facility. In terms of regulatory requirements, expansion is also likely to be less costly, less time-consuming, and less subject to challenge by local groups [10].

24.3.1.3 COMPLEXITY

In the late 1970s and early 1980s, the United States experienced a dramatic reduction in fuel oil demand, and plants were reconfigured using more complex processing units. As a result, the average Nelson complexity of U.S. refineries is the highest in the world at approximately 10.2 (Figure 24.13). In recent years, refineries continue to upgrade their plants to handle heavier crudes and bitumen from oil sands production.

24.3.1.4 UTILIZATION

The U.S. refining industry's ability to meet short-term increases in demand can be measured by the rate at which operable capacity is utilized. Utilization is defined as the gross inputs to crude oil distillation divided by operable capacity. Utilization fluctuates as refinery operations adjust to changes in demand (Figure 24.14). The amount of gross inputs to refineries has risen steadily throughout the past

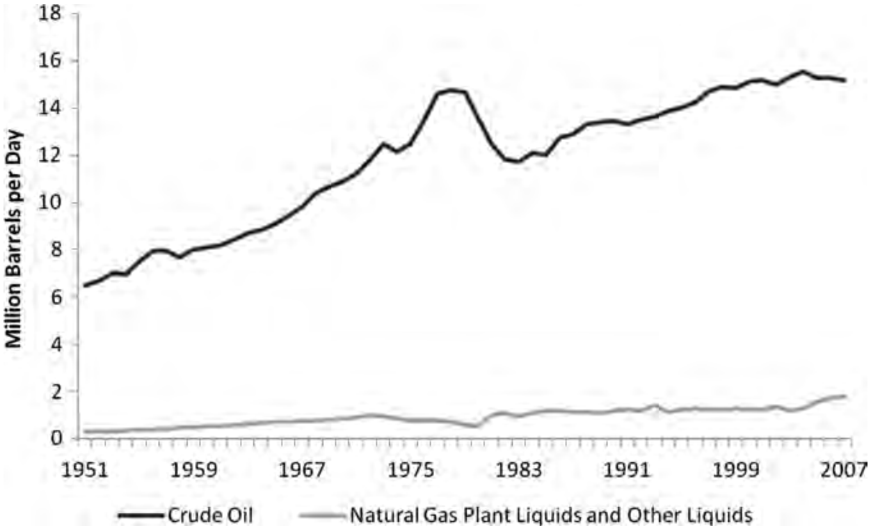


Figure 24.7—U.S. refinery input. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

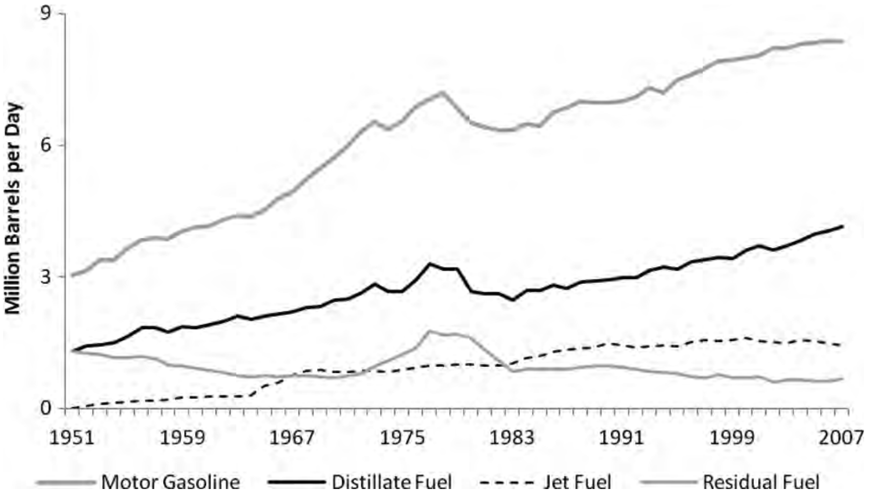


Figure 24.8—U.S. refinery output. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

TABLE 24.2—Percentage Yields of Refined Petroleum Products from Crude Oil in the United States, 1964–2008 (%)

	1964	**1974**	**1984**	**1994**	**2004**	**2008**
Gasoline	44.1	45.9	46.7	45.7	46.9	44.2
Distillate fuel oil	22.8	21.8	21.5	22.3	23.7	27.8
Resid fuel oil	8.2	8.7	7.1	5.7	4.2	4.0
Jet fuel	5.6	6.8	9.1	10.1	9.5	9.6
Coke	2.6	2.8	3.5	4.3	5.1	5.3
Asphalt	3.4	3.7	3.1	3.1	3.2	2.7
Liquefied gases	3.3	2.6	1.9	4.2	4.2	4.1
Total	90.1	92.3	92.9	95.4	96.8	97.7

Source: U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Monthly*, Washington, DC, 2009.

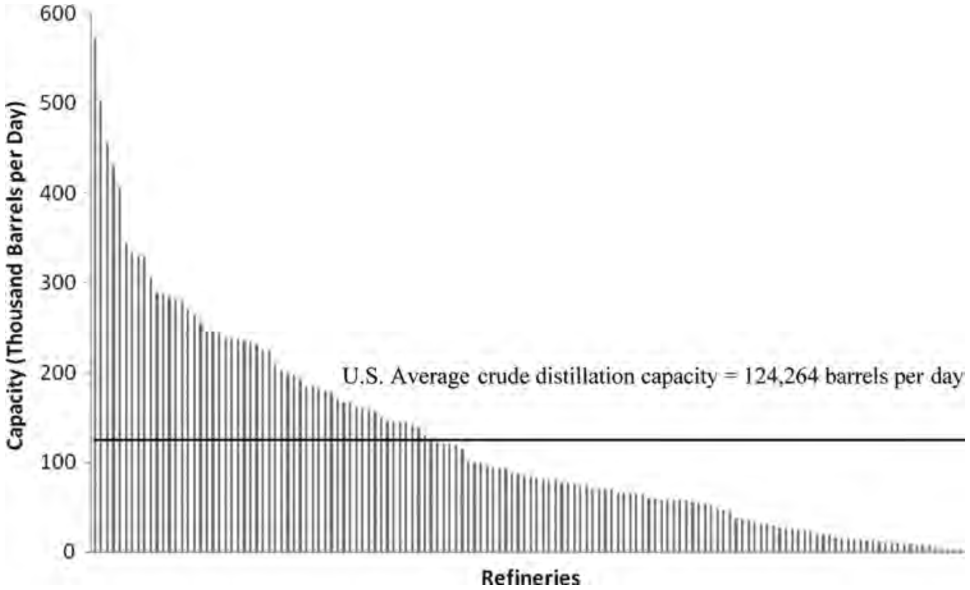


Figure 24.9—U.S. refinery crude distillation profile. *Source:* U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008, Vol. 1*, Washington, DC, 2009.

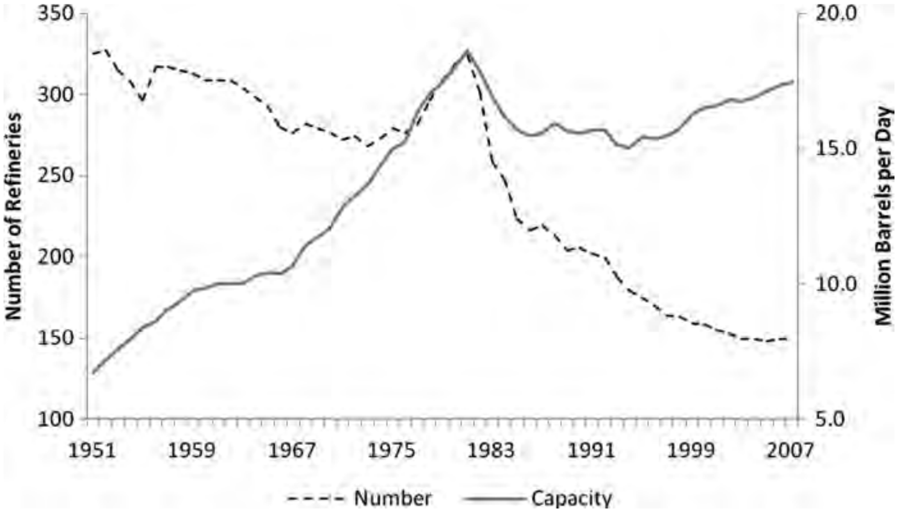


Figure 24.10—Number of operable refineries and total refining capacity in the United States. *Source:* U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008, Vol. 1*, Washington, DC, 2009.

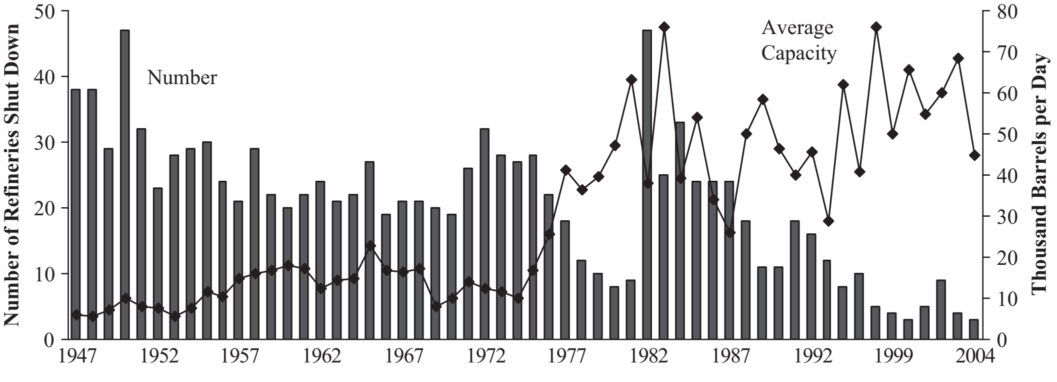


Figure 24.11—Number of refineries shut down and average refinery capacity in the United States. *Source:* U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2004, Vol. 1*, Washington, DC, 2005.

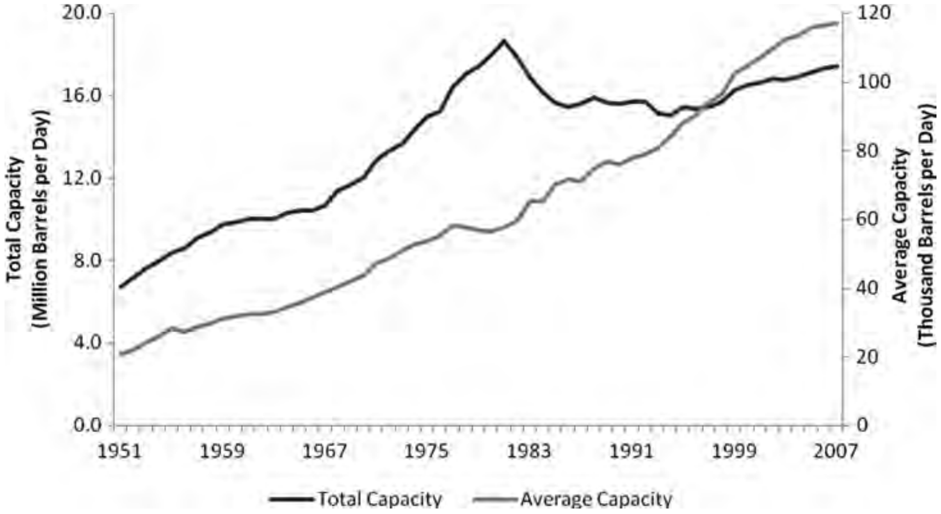


Figure 24.12—Average and total refinery capacity in the United States. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

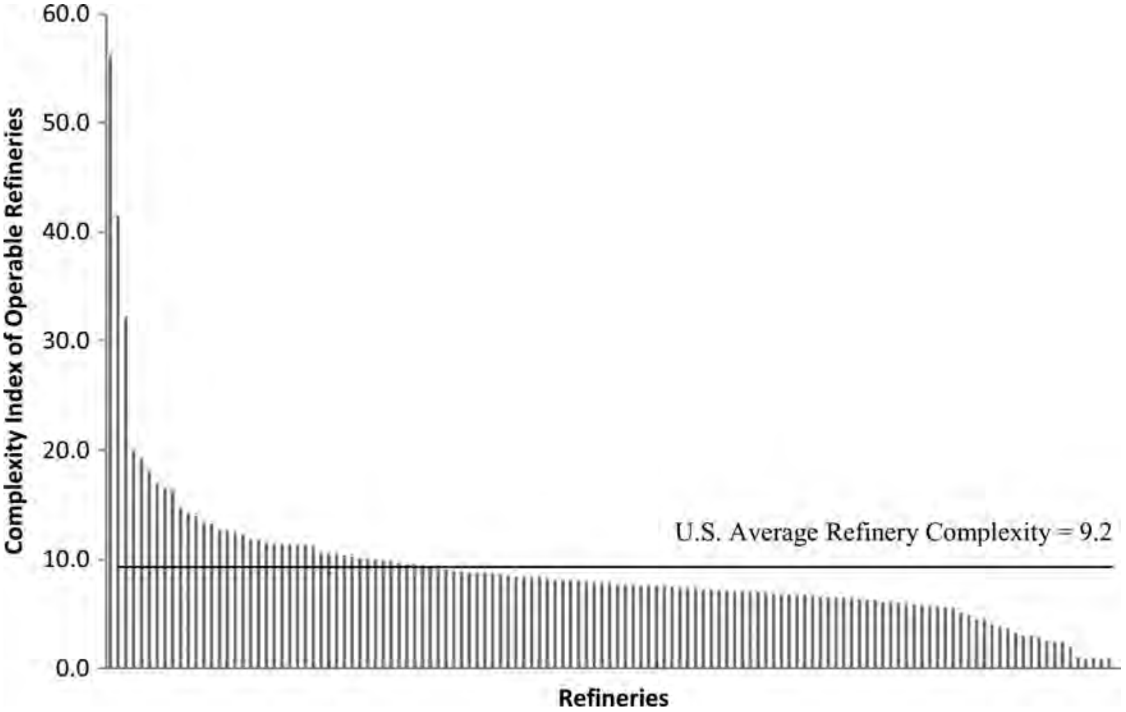


Figure 24.13—U.S. refinery complexity profile. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

two decades in response to rising demand for petroleum products. The trend in recent years toward high utilization has been due to a decrease in the number of operating refineries and by operations changes, including reducing refinery downtime and the number of unplanned outages, executing maintenance and revamps more efficiently, and extending run times through improved catalyst performance [11].

24.3.1.5 INDUSTRY STRUCTURE

The structure of the refining industry has undergone significant change over the past decade. Once led by a half-dozen vertically integrated majors, the industry is now characterized by a handful of supermajors and an array of mid-size and small independents focused on refining and marketing within specific regions and product lines. Integrated oil companies are involved in all segments of the energy supply chain, from exploration and production (“upstream”) to refining and marketing (“downstream”). Companies that operate in one or more but not all segments are called partially integrated or independents. Independent refiners and marketers are typically only involved in downstream activities. The traditional industry model of refining, which is based on ownership by vertically integrated oil companies and profitability viewed within the context of a linked supply chain, has been replaced by refineries operated in a stand-alone profit center mode.

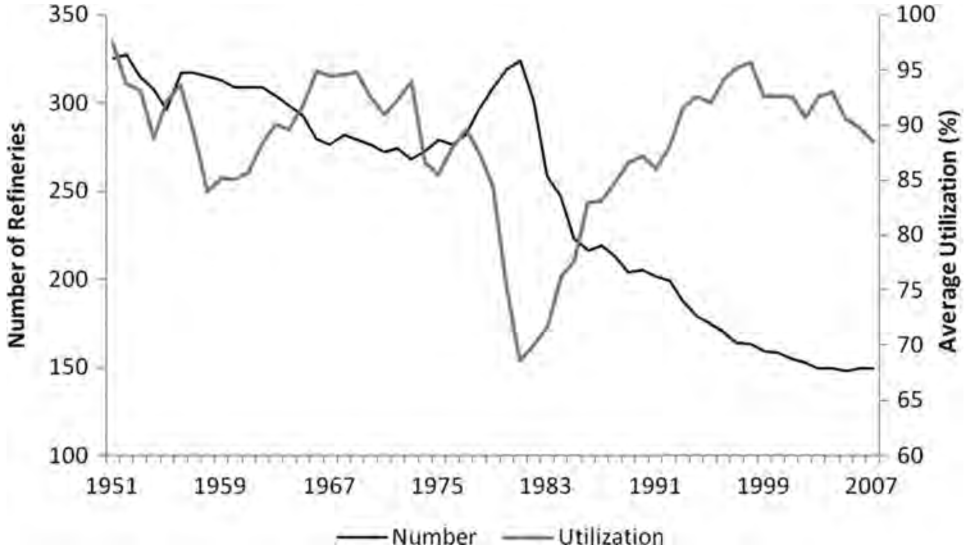


Figure 24.14—Average utilization and number of operable refineries in the United States. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

Before 1980, nearly all U.S. refineries were held by integrated oil companies; today, ownership structure is more diverse and increasingly concentrated (Table 24.3, Figure 24.15). In 2008, the top three U.S. refiners processed 36 % of total crude oil, the top 10 refiners processed 77 %, and the top 20 refiners processed 92 %. Independents owned approximately 64 % of U.S. refining capacity in 2008 versus 51 % in 1990. Foreign ownership has risen from 19 %

TABLE 24.3—Top 20 U.S. Refiners, 1994 vs. 2008

Company	1994 Capacity (MBPCD)	Company	2008 Capacity (MBPCD)
Chevron	1373	Valero Energy	2001
Exxon	990	Exxon Mobil	1868
Amoco	984	Conoco Phillips	1787
Mobil Oil	903	BP	1364
Shell	739	Chevron	1033
BP	666	Marathon	1016
Star Enterprise	600	Sunoco	903
Amerada Hess	575	KOCH Industries	779
Marathon	570	PDV America	760
Sun	470	Motiva Enterprises	756
Conoco	429	Tesoro	664
Arco	416	WRB Refining	452
Ashland	347	Shell	442
Koch Refining	345	Deer Park Refining	330
Texaco	330	Access Industry	271
Citgo Petroleum	305	Total	232
Phillips	305	Alon Israel Oil	232
Lyondell Citgo Refining	265	Western Refining	224
Phibro Energy	255	Chalmette Refining	193
Unocal	235	Frontier Oil Refining	177

Source: API *Basic Petroleum Data Book* XXV(1), Washington, DC, February 2008. U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008*, Washington, DC, 2009.

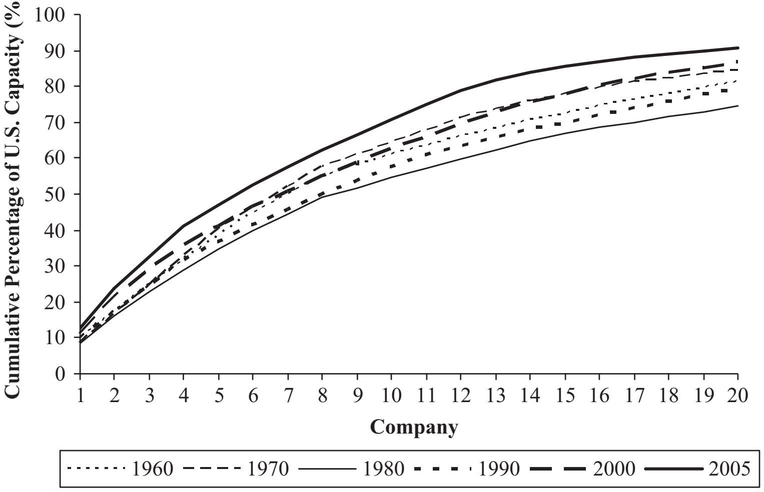


Figure 24.15—Refinery concentration in the United States. *Source:* API *Basic Petroleum Data Book* XXV(1), Washington, DC, February 2005; *Oil & Gas Journal World Refinery Capacity Report*, December 19, 2005.

of total capacity in 1990 to approximately 25 % in 2005. Royal Dutch Shell, BP, Total, Saudi Aramco, and Petroleos de Venezuela SA are major foreign owners of U.S. refining capacity.

Most distillation capacity is currently concentrated in large, integrated companies with multiple refining facilities. Fifty-four firms, ranging in size from 880 BPCD to a combined refinery capacity of 1.8 million BPCD, comprise the industry (Table 24.4). Approximately two thirds of firms are small operations producing less than 100,000 BPCD and representing approximately 5 % of the total output of petroleum products. Large refiners often manage large and small refineries (Table 24.5), whereas small operators mainly specialize in asphalt, lubricants, and other niche products. Valero and Conoco Phillips operate the most refineries.

Integrated firms such as Exxon Mobil, BP, and Chevron maintain a global portfolio of upstream and downstream petroleum assets. Independent companies such as Valero and Sunoco focus primarily on domestic refining, although they may also be involved in marketing and other operations. Independents grew to prominence in the mid-1990s as the majors restructured their downstream petroleum operations and sold their refining assets to new entrants [11]. Joint ventures and partnerships such as Motiva Enterprises also exist. Koch is a privately owned independent. In 2011–2012, ConocoPhillips and Marathon split off their refining divisions into separate corporations.

TABLE 24.4—Number of Refiners' Atmospheric Distillation Capacity (2008)

Number	Capacity (BPCD)	Total Capacity (BPCD)
28	>100,000	16,725,277
10	30,001–100,000	692,420
8	10,001–30,000	126,750
8	<10,000	49,400
54		17,593,847

Source: U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual, 2008*, Vol. 1, Washington, DC, 2009.

TABLE 24.5—Top 10 U.S. Refining Companies (2008)

Company	Capacity (1000 BPCD)	Number of Refineries	Average Size (BPCD)	Largest Plant (BPCD)	Smallest Plant (BPCD)
Valero Energy	2001	14	143	287,000	6,300
Exxon Mobil	1868	6	311	572,500	60,000
Conoco Phillips	1787	11	162	247,000	58,000
BP	1364	5	273	455,790	12,780
Chevron	1033	6	172	330,000	45,000
Marathon	1016	7	145	256,000	74,000
Sunoco	903	5	181	335,000	85,000
KOCH Industries	779	3	260	288,468	210,000
PDV America	760	3	253	429,500	163,000
Motiva Enterprises	756	3	252	285,000	235,000

Source: U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Monthly*, Washington, DC, March 2008.

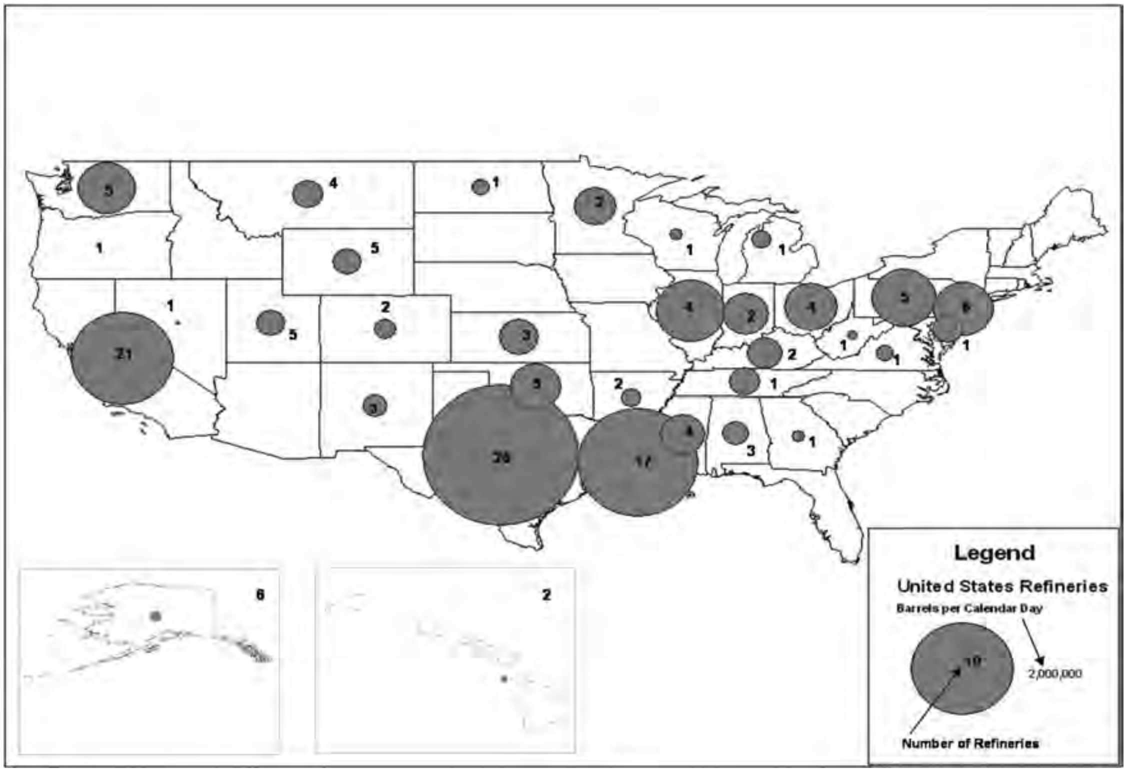


Figure 24.16—Number of refineries and crude distillation capacity in the United States (2008).

24.3.1.6 REGIONAL SPECIALIZATION

Refining capacity in the United States is concentrated in the Gulf Coast and West Coast region as well as along the corridor from Illinois to New Jersey (Figure 24.16). Table 24.6 depicts the top 10 refining states and total distillation capacity. Refineries were historically located near the sources of oil, and over time they developed in regions with easy access to water and shipping routes to minimize transport and logistical cost [12].

The Gulf Coast (PAD District III) is the nation's leading supplier of refined products, accounting for nearly half of the total capacity in the country (Table 24.7). Refineries in PADD III are large, integrated, and complex facilities, leading the nation with a regional complexity of 9.9, followed closely by PADD V with a regional complexity of 9.5 (Table 24.7). The Gulf Coast imports significant quantities of crude oil as refinery feedstock (Figure 24.17) and ships refined products to the East Coast and to the Midwest

TABLE 24.6—Top 10 Petroleum Refining States (2008)

State	Number of Operating Refineries	Distillation Capacity (MBPCD)
Texas	26	4752
Louisiana	19	2976
California	21	2042
Illinois	4	916
Pennsylvania	5	773
New Jersey	6	655
Washington	5	628
Ohio	6	520
Oklahoma	4	515
Indiana	2	433
Subtotal 10	98	14,210
U.S. total	150	17,594

Source: U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008, Vol. 1*, Washington, DC, 2009.

TABLE 24.7—Number and Capacity of Operable Petroleum Refineries by PAD District (2008)

PADD[a]	Number	Distillation Capacity (BPCD)	Refining Capacity (%)	Average Capacity (BPCD)	Average Complexity
I	15	1,721,850	9.8	114,790	8.0
II	27	3,658,050	20.8	135,483	8.2
III	56	8,415,829	47.8	150,283	9.9
IV	16	603,300	3.4	37,706	7.4
V	36	3,194,818	18.2	88,745	9.5
U.S. total	150	17,593,847	100.0	117,292	9.2

[a] Petroleum Administration for Defense Districts (PADD) were delineated during World War II to facilitate oil allocation. The PAD district states are as follows:
I: CT, ME, MA, NH, RI, VT, DE, DC, MD, NJ, NY, PA, FL, GA, NC, SC, VA, WV
II: IL, IN, IA, KS, KY, MI, MN, MO, NE, ND, SD, OH, OK, TN, WI
III: AL, AR, LA, MS, NM, TX
IV: CO, ID, MT, UT, WY
V: AK, AZ, CA, HI, NV, OR, WA
Source: U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008, Vol. 1*, Washington, DC, 2009.

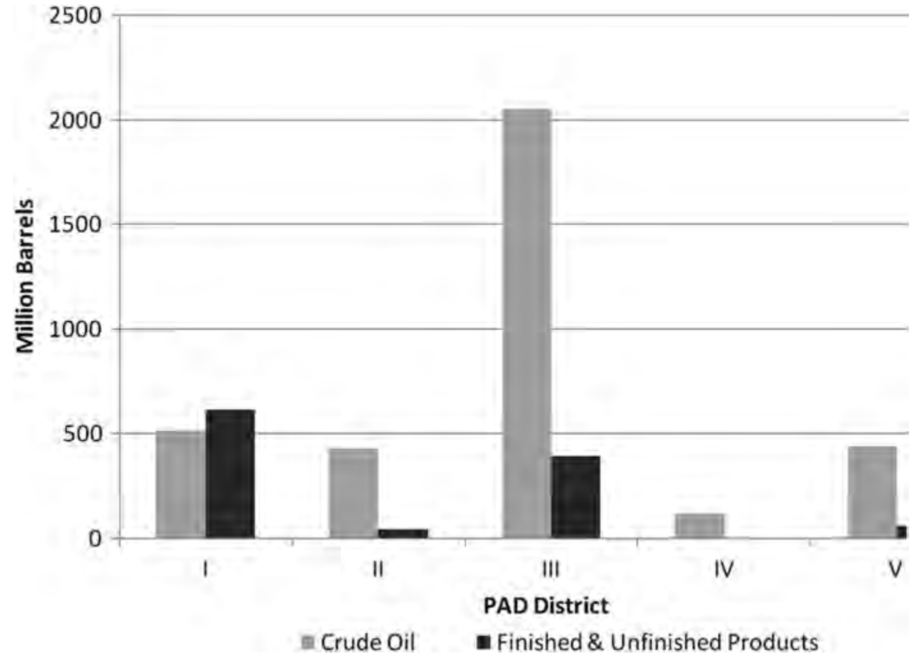


Figure 24.17—Imports of crude oil and petroleum products by PAD district in 2008. *Source:* U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008, Vol. 1*, Washington, DC, 2009.

(Table 24.8). The East Coast is the largest consuming area in the United States and imports over half of all of the refined products that enter the United States because of its limited refining capability. The Pacific Northwest and Rocky Mountain region have small to mid-size facilities and only limited pipeline access from Gulf Coast and California refineries. Southern California, Nevada, and parts of Arizona have significant distribution infrastructure constraints and stringent local environmental regulations.

The Midwest and East Coast account for approximately 90 % of the inter-regional flow of petroleum products, with the Gulf Coast by far the largest supplier, accounting for more than 80 % of the flow. In contrast, the Rockies and West Coast regions are isolated because of the physical terrain and great distances involved, but also partially because of the stringent quality restrictions on gasoline and diesel requirements.

TABLE 24.8—Movements of Petroleum Products by Pipeline, Tanker, and Barge between PAD District, 2008 (Million Barrels)

PADD	(To):	I	II	III	IV	V
(From):						
I		–	114.6	3.6	–	0.0
II		26.5	–	103.0	25.5	0.0
III		1053.2	373.5	0.0	10.7	61.6
IV		–	22.8	68.1	–	11.6
V		0.1	0.0	1.3	0.0	–

Source: U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008, Vol. 1*, Washington, DC, 2009.

24.3.2 World Statistics

24.3.2.1 PRODUCT DEMAND

Demand for gasoline, middle distillates, and heating oil varies with each region of the world. Asia's demand for gasoline in the last decade has increased over 50 %, with U.S. demand growing by approximately 15 % (Figure 24.18). European gasoline demand has actually dropped because of high taxation rates and conversion of their transportation fleet to diesel fuel. For distillates, the demand pattern is consistent worldwide with continued and sustained growth [13]. The primary use of diesel fuels is for transportation requirements.

24.3.2.2 CAPACITY

There were currently 655 refineries worldwide in 2009 with a total capacity of 85.6 million BPCD (Table 24.9). The world's largest refining region is Asia (22.5 million BPCD), followed by North America (20.9 million BPCD). The top refining countries in the world are the United States, followed by China, Russia, and Japan (Figures 24.19 and 24.20). Global refinery capacity relative to oil demand is depicted in Figure 24.21. The ratio of refinery capacity to demand declined from 113 % in 1990 to 103 % in 2004 despite continued growth in global capacity because demand accelerated at a faster rate.

The world's largest refining companies include Exxon Mobil, Royal Dutch Shell, and Sinopec (Table 24.10). Several national oil companies, including Petroleos de Venezuela SA (PDVSA), China National Petroleum Corporation (CNPC), Saudi Aramco, Petroleos Brasieiro (Petrobras), Petroleos Mexicanos (PEMEX), and National Iranian Oil Company (NIOC), are also major players. PDVSA's Paraguana refinery was the largest installation in the world in 2009 with an installed capacity of 940,000

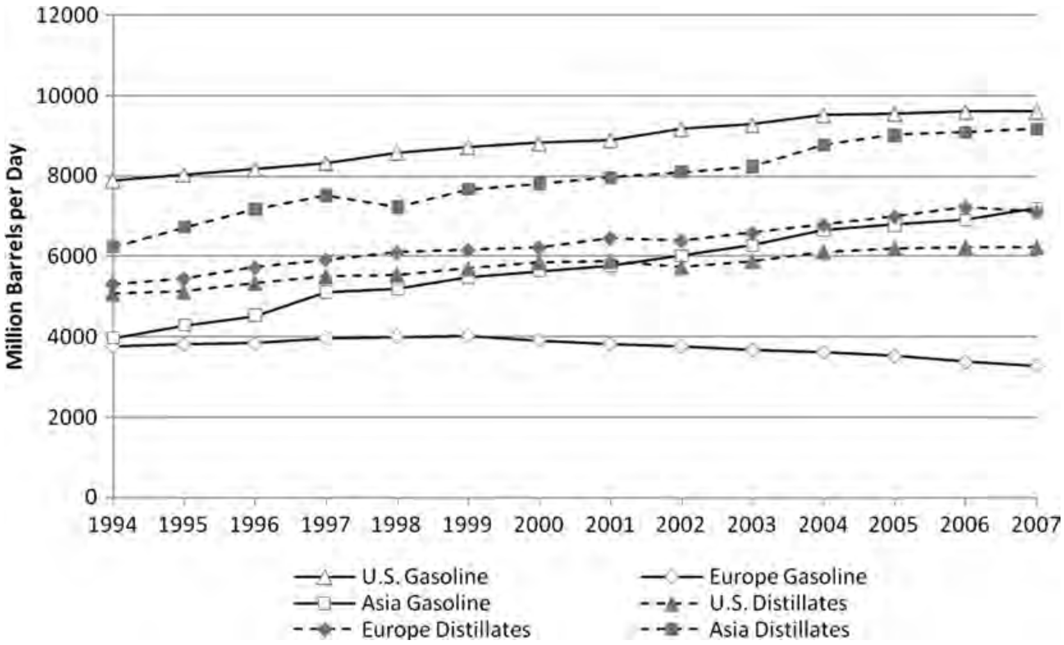


Figure 24.18—Global product demand trends by region. *Source:* BP, *Statistical Review of World Energy 2008*.

TABLE 24.9—Refining Operations on a Regional Basis—Thousand Barrels per Calendar Day (2008)

Region	No. of Refineries	Crude Distillation	Vacuum Distillation	Catalytic Cracking	Catalytic Reforming	Catalytic Hydrocracking	Catalytic Hydrotreating	Coke
Africa	45	3278	508	206	458	62	831	1841
Asia	157	22,483	4389	2800	2141	1018	9387	20,110
Eastern Europe	89	10,344	3903	877	1474	330	4274	12,570
Middle East	42	7036	1984	364	653	602	2044	3300
North America	154	20,949	9141	6669	4176	1828	16,081	128,763
South America	66	6603	2846	1310	402	132	1904	24,640
Western Europe	102	14,911	5786	2192	2183	1173	9880	11,534
Total	655	85,604	28,556	14,417	11,488	5145	44,400	202,758

All capacities are expressed in 1000 BPCD except coke, which is expressed in tons per day.
Source: Oil and Gas Journal World Refinery Capacity Report, December 22, 2008.

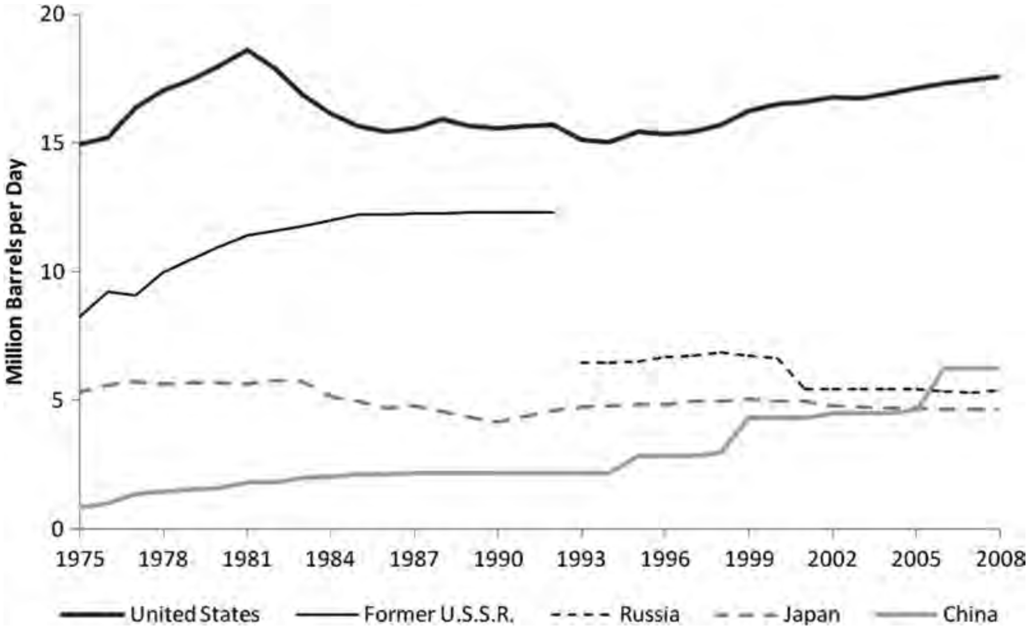


Figure 24.19—Top refining countries in the world. *Source:* U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008, Vol. 1*, Washington, DC, 2009.

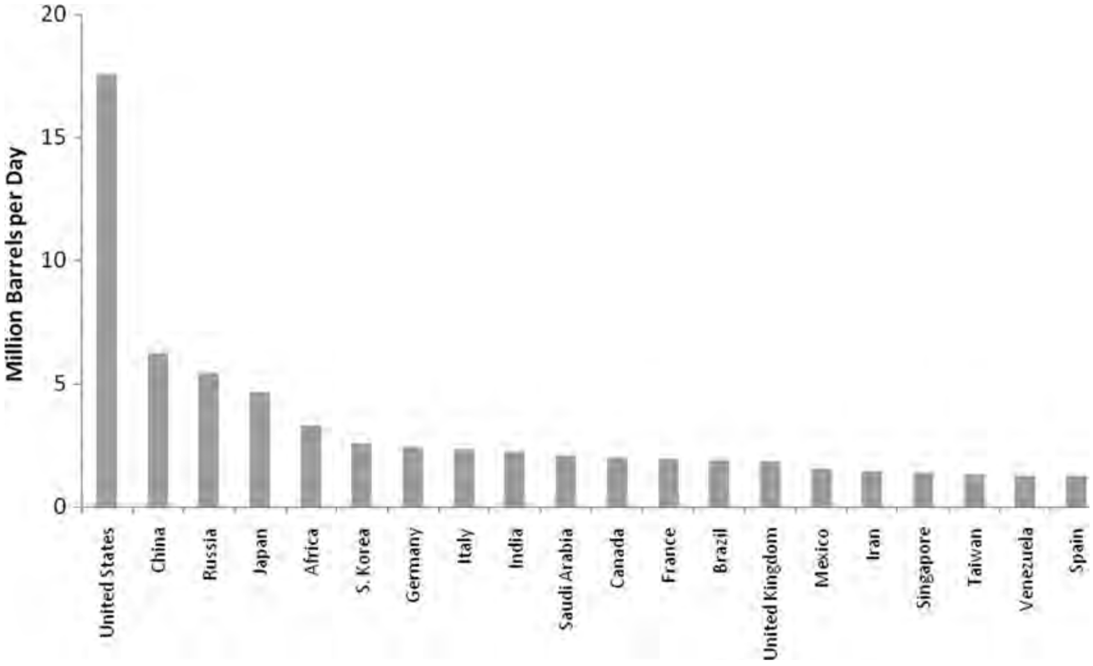


Figure 24.20—Top refining countries in 2008. *Source:* U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Annual 2008, Vol. 1*, Washington, DC, 2009.

BPCD, followed by South Korea's SK Corporation with 817,000 BPCD capacity.

24.3.2.3 CONFIGURATION, COMPLEXITY, AND YIELD

Refining configuration varies widely on a regional basis, depending on the demand for gasoline, diesel, and fuel oil (Table 24.11). Catalytic hydrotreating is the most widely applied process technology, followed by catalytic cracking and catalytic reforming (Table 24.9). Western Europe has more diesel and jet fuel demand and lower gasoline and heating gas oil requirements because of the prevalence of diesel engines and the use of natural gas for domestic heating. Therefore, Western European refiners have more hydrotreating and hydrocracking capacity and less catalytic cracking capacity. The conversion capacity of refineries as a percentage of distillation capacity is often used as a measure of refining complexity [14]. North America has the most complex refinery configurations, followed by Asia (Figure 24.22). Catalytic cracking capacity may reach 20 % of crude capacity where there is a high demand for gasoline

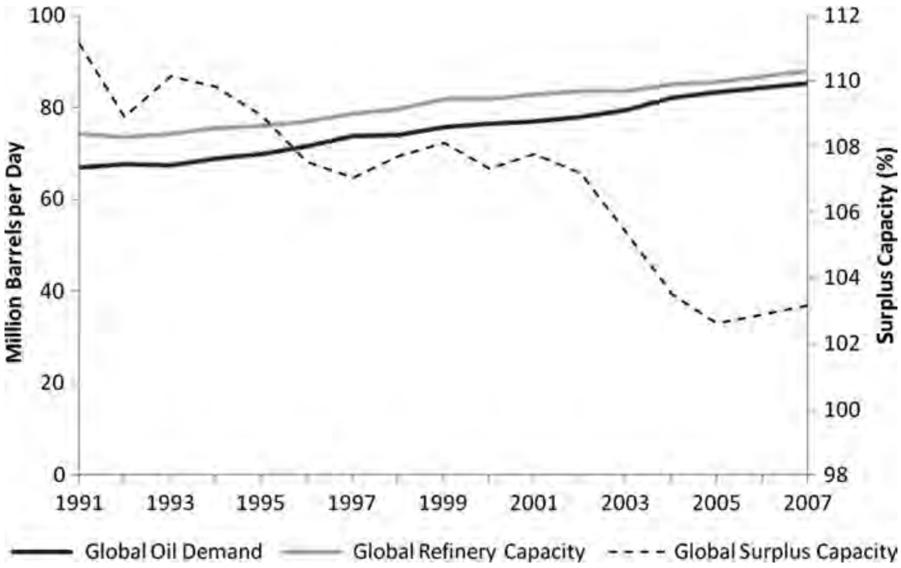


Figure 24.21—World refinery capacity trends. *Source:* BP, *Statistical Review of World Energy 2008*.

TABLE 24.10—World's Largest Refiners (2008)

Rank (January 1, 2009)	Rank (January 1, 2008)	Company	Crude Capacity (1000 BPCD)
1	1	Exxon Mobil	5690
2	2	Royal Dutch Shell	5172
3	3	Sinopec	3871
4	4	BP	3611
5	6	Conoco Phillips	2830
6	7	Petroleos de Venezuela	2792
7	5	Total	2738
8	8	Valero Energy	2659
9	9	China National Petroleum	2440
10	10	Saudi Aramco	2417
11	12	Petroleo Brasileiro	2066
12	11	Chevron	1953
13	13	Petroleos Mexicanos	1851
14	14	National Iranian Oil	1451
15	17	Nippon Oil	1182

Source: Oil and Gas Journal World Refinery Capacity Report, December 22, 2008.

as in North America and Asia (Table 24.12). Hydrocracking is required in regions with high diesel and jet fuel demand and is used to convert heavy fuel oils to high-quality transportation fuels (North America, Western Europe). Coking is used where there is low demand and value for heavy fuel oil.

24.3.2.4 INVESTMENT PATTERNS

Changes in global refinery capacity over the past five years are shown in Table 24.13. Investment in crude processing capacity has been limited. The primary growth in process expansions has been to reduce sulfur levels, which is shown by increases in hydrotreating and hydrocracking capacity as well as in sulfur production capacity. Sulfur reductions were mandated by government regulation, and refineries had to decide whether to invest to manufacture saleable product or shut down operations. Capacity to process heavier and cheaper crude oils through coking has also been a major focus point. Investment to process heavy crude oils allows refiners to potentially improve their products by reducing the cost of their raw materials.

TABLE 24.11—World Refinery Output by Area for Major Petroleum Products as Percentage of Total, 2005 (%)

Region	Gasoline	Distillate	Residual	Other
United States	46.7	22.2	3.5	27.5
Canada	35.6	29.8	7.1	27.5
Mexico	30.7	22.5	24.8	22.0
South America	23.1	28.9	18.6	29.4
Western Europe	22.5	35.4	13.3	28.8
Middle East	14.6	27.7	23.4	34.3
Africa	16.8	26.9	23.7	32.6
Asia	18.1	31.0	13.4	37.5
Former Soviet Union	18.3	28.1	27.2	26.4
World	25.9	29.0	13.9	31.2

Source: API *Basic Petroleum Data Book* XXV(1), Washington, DC, February 2009. U.S. Department of Energy, Energy Information Administration, *Petroleum Supply Monthly*, Washington, DC, March 2009.

24.4 INDUSTRY CHARACTERISTICS

24.4.1 Each Refinery and Crude Oil Is Unique

A refinery is an installation that manufactures finished petroleum products from crude oil, unfinished oils, natural gas liquids, and other hydrocarbons using heat, pressure, catalysts, and chemicals. Early refineries were simple, batch distillation units that processed hundreds of barrels of crude oil per day from one or a small collection of fields. The refineries of today are complex, highly integrated facilities that may contain as many as a dozen or more process units capable of handling numerous crude oils from around the world with capacity up to a million barrels a day or more.

Every crude oil produced in the world has a unique chemical composition that will determine the optimal manner in which to process the crude and the final product slate. Crude oil contains distillates of different molecular composition and shape, burning qualities, and impurities such as metals, asphaltenes, nitrogen, and sulfur. The types, size, number, and flow sequences for each refinery vary depending on crude oil input quality, output product slate and quality, and environmental, safety, and economic conditions.

24.4.2 Input Streams Play an Important Role in Refinery Configuration

Each crude oil produced in the world has a unique chemical composition that varies according to the manner of its formation. Currently, more than 150 crude grades are traded [15], and many of these are streams blended from two or more fields. The gravity, sulfur content, and total acid number (TAN) are the most important properties of crude oil.

Gravity is a measure of the density of the crude oil and is described in terms of degrees API. The higher the API number, the lighter the crude. Crude oils with low carbon, high hydrogen, and high API number are usually rich in paraffins and tend to yield greater proportions of gasoline and light petroleum products. Worldwide, the average gravity for crude oil is about 31° API and ranges from a high of 45° for light crude to a low of 8–15° for heavy crude and oil sands (bitumen).

Sulfur is an undesirable impurity because of pollution and corrosion concerns [16]. Sulfur content is measured in terms of weight percentage. Crude oils that contain appreciable quantities of hydrogen sulfide or other reactive sulfur compounds are called "sour" whereas crudes low in sulfur are labeled "sweet." The split between sweet and sour crude was historically approximately 0.5 %; today, the crossover is generally in the range of 0.5–1.5 %.

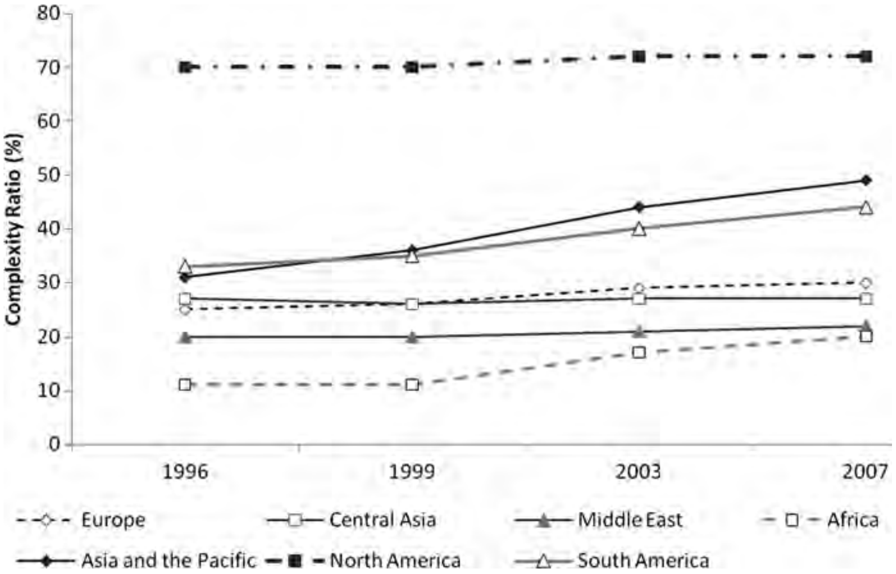


Figure 24.22—Conversion capacity as a percentage of distillation capacity (complexity ratio) by region. *Source:* ENI, *World Oil and Gas Review 2008*.

TABLE 24.12—World Refining Configuration as a Percentage of Crude Distillation, 2008 (%)

Region	Catalytic Cracking	Catalytic Reforming	Catalytic Hydrocracking	Catalytic Hydrotreating
Africa	1.4	4.0	1.2	1.9
Asia	19.4	18.6	19.8	21.1
Eastern Europe	6.1	12.8	6.4	9.6
Middle East	2.5	5.7	11.7	4.6
North America	46.3	36.3	35.5	36.2
South America	9.1	3.5	2.6	4.3
Western Europe	15.2	19.0	22.8	22.3

Source: Oil & Gas Journal World Refinery Capacity Report, December 22, 2008.

TABLE 24.13—World Refining Investment Patterns, 2000–2008

	Million BPCD		Growth Rate
Process	**2000**	**2008**	**(%)**
Atmospheric distillation	81.3	85.6	5.3
Coking	3.7	4.4	18.9
Coking, t/day	176.7	202.8	14.8
Cracking	13.7	14.4	5.1
Hydrocracking	4.3	5.1	18.6
Hydrotreating	36.6	44.4	21.3
Sulfur, t/day	56.1	79.8	42.2

Source: Oil & Gas Journal World Refinery Capacity Report, December 22, 2008 and [13].

The TAN of crude oils is a measure of potential corrosivity and quantifies the number of milligrams of potassium hydroxide (KOH) needed to neutralize 1 g of crude oil. A crude with TAN greater than 1 mg KOH/g is usually considered corrosive and labeled a high TAN crude, but corrosion problems can occur with TANs as low as 0.3 [17].

The gravity, sulfur content, and TAN of crude oil have important economic and technical effects on refining operations. Heavy, sour crude requires more sophisticated processes to produce lighter, more valuable products, and are thus more expensive to manufacture. To attract buyers, heavy crude producers offer heavy oil at a significant discount to light crude. The size of the discount varies according to demand and supply conditions and other factors. Light, sweet crudes are generally more valuable because they yield more of the lighter, higher-priced products than heavy crude and are cheaper to process. Acidity has also become increasingly important as the production of high acid crudes, particularly from West Africa, has steadily increased. Very few refineries are able to refine high TAN crude oil; therefore, these are sold at a substantial discount to market crudes [18]. Refineries typically blend high TAN crudes with other streams before refining.

24.4.3 Refinery Configuration Evolves over Time

Refineries are built at a specific point in time using specific technologies that evolve with changes in market demand, feedstock, product specification, and environmental regulation. Refineries will typically possess both very old and modern process units. There are many ways to classify and group refineries, but most schemes refer to the complexity of the process technology, which describes its capacity to convert heavy products (e.g., fuel oil and resid) to lighter products such as gasoline, diesel, and jet kerosine. Upgrading capacity comes in several different types of units—from the common catalytic cracking facilities to the more sophisticated and expensive hydrocracking and coking units.

24.4.4 Standard Technologies Are Used

About a dozen or so process technologies are used in the refining industry, from coking, to thermal processes, catalytic cracking, catalytic reforming, catalytic hydrocracking, catalytic hydrotreating, alkylation, polymerization, aromatics extraction, isomerization, oxygenates, and hydrogen production [19,20]. For each process, one or more subcategories can be defined based on technology specifications, operating conditions, or feedstock.

24.4.5 Refinery Complexity

The simplest refinery, frequently referred to as a "topping" or "hydroskimming" refinery, consists of atmospheric distillation and typically one or more pretreatment facilities, catalytic reforming, and hydrodesulfurization. "Simple" refineries have limited capacity to change the composition of the crude oil input. A "complex" (cracking) refinery or "very complex" (coking) refinery is characterized by significant upgrading capacity and a high level of integration (Figure 24.23). Simple refineries have the lowest margins and are often operated by small, niche players. Complex refineries are able to change the composition of the crude oil input, taking low-value, heavy oils and converting them to high-value, light products, supplying the marginal barrel and realizing profits from base margins [21,22].

Cracking refineries typically comprise vacuum distillation units; naphtha, distillate, kerosine, and vacuum gas oil hydrodesulfurization; catalytic reforming; fluid catalytic cracking; alkylation; and light naphtha isomerization. Deep conversion refineries use a coking process to eliminate the vacuum residue, converting virtually the entire barrel of crude to valuable light products. Coking refineries enjoy the highest upgrading margins and are highly flexible. Unlike cracking refineries, the economics of coking refineries are driven largely by the light-heavy differential (i.e., the difference in price between light sweet crude oils and heavy sour crude oils). Complex refineries tend to make large margins when processing heavy sour crudes and smaller margins when processing light crudes.

24.4.6 Refineries Are Capital-Intensive, Long-Lived Assets

Refining projects are capital-intensive, long-lived, and highly specific assets that require large initial investments before production can begin. The decision to invest in capacity is complex and depends primarily on expectations of return on investment. The capital-intensive nature means that investments are exposed to substantial financial risks, such as changes in interest rates and investment cycles, and will need to compete with other investment opportunities.

Refineries are designed and engineered by a combination of internal company resources and third-party firms. Feasibility studies may take several months, followed by construction times that last anywhere from six months to two years or more. Grassroots construction projects in the United States may take five years or more to secure all of the necessary permits.

Large-scale capital-intensive projects typically require that owners and contractors form an alliance. Engineering, procurement, installation, and construction contracts are typically handled on a lump sum, turnkey basis. The contractor enlists subcontractors for work involving special units, pipelines, export facilities, and construction [23].

24.4.7 Refined Products Are Commodities Sold in Segmented Markets

The main products of refining are commodities. Commodities are products that are undifferentiated from a competitor and sold on the basis of price, defined in competitive markets through the intersection of supply and demand curves [24]. Product slate is determined by demand, inputs and process units available, and the result of intermediaries entering into the production of other products.

Refined product markets differ from crude markets in several respects because of the scale of operations, quality considerations, price differentials, and market size [24,25]. Refined product markets are more regional than crude oil markets, and no refiner or marketer is able to operate a completely balanced system. The function of the physical market is to redistribute the individual surpluses and deficits that arise at each location. There are regular flows of products from one region to another, and price levels are set accordingly.

24.4.8 Product Prices Are Volatile

In competitive markets, refined product prices are determined by regional supply, demand, and inventory conditions at a given time. The most fundamental economic relationship governing commodities is that the quantity demanded is a function of price. Demand for commodities is generally inelastic in the short term, and inventories, when they exist in sufficient volumes, allow supply and demand to achieve an equilibrium of sorts that acts to smooth out spot prices and reduce volatility [24,25]. Supply is defined by production and inventory. Balancing supply and demand occurs at the regional and world level, with prices in efficient markets reflecting the combined influence of all market information, including expectations of future supply and demand, seasonal factors, and inventory levels.

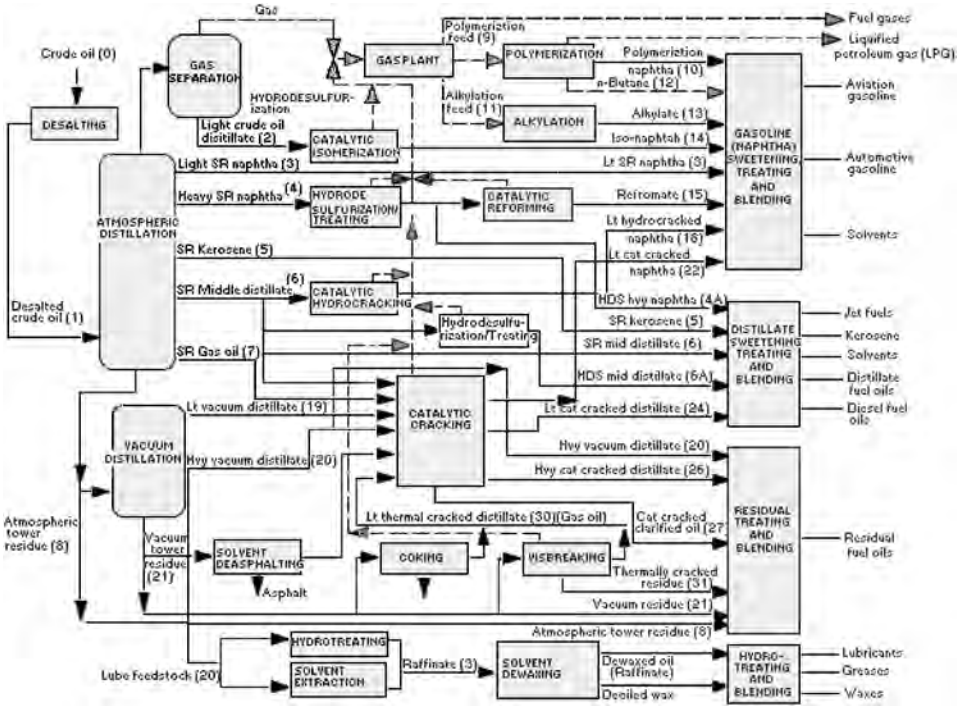


Figure 24.23—Typical flow diagram for a complex refinery. *Source:* [5].

24.4.9 Product Prices Are Correlated to Crude Oil Prices

Crude oil prices are more volatile than other commodities, reflecting the influence of political and economic events, supply and demand conditions, perceptions about resource availability, and many other factors [26]. The price of oil is determined on a world market, and its availability can change dramatically within a very short period of time. The price of oil also strongly influences the prices of refined products and primary fuels (natural gas, liquefied natural gas, coal) depending on market conditions.

Crude oil prices are a fundamental determinant of gasoline prices. Crude oil and refinery petroleum products, especially gasoline and the middle distillates, generally follow similar paths (Figure 24.24). Refined products prices have historically reacted to changes in the acquisition cost of crude oil in both directions, with falling crude prices leading to declines in refined product prices and vice versa [27]. The price differential between gasoline and fuel oil and other products represents the supply-demand requirements for the fuel and the premium for production [28].

24.4.10 Refineries Are Price Takers

Most refineries use a mixture of crude oils from various domestic and foreign sources that change based on the relative cost and availability. Refiners competitively determine the relative prices paid for various crude oil to reflect quality and location differentials, but they do not establish absolute prices. Large crude oil producers that supply crude to U.S. refineries (Saudi Arabia, Mexico, Canada, Norway, Venezuela) use models for U.S. refinery centers and develop pricing strategies to minimize refiner pricing power and attempts to game the system.

24.4.11 Gravity Down, Sulfur Up

World crude production by gravity and sulfur over the past decade is shown in Figures 24.25 and 24.26. The average gravity for crude oil is currently approximately 31° API and the average sulfur content is approximately 1.25 %. World crude oil production by quality class is depicted in Figure 24.27. Medium and sour production has been the most prolific, reflecting the nature and location of geologic discoveries. On a regional basis, the changes in crude quality can be pronounced (Figure 24.28). The well-known relationship between sulfur and gravity is shown in Figure 24.29 for world crudes.

Heavy, high-sulfur crude is more difficult and expensive to process and yields heavier products that require additional processing. Capacity in the United States that has been added over the past decade has primarily been in the form of downstream processing, particularly "bottom of the barrel" processing, to clean up the heavy crude and satisfy environmental regulations. For example, the average U.S. Gulf Coast (USGC) refinery configuration has shifted toward coking refineries that process heavy sour crude oil (Figure 24.30). The number of cracking refineries in the USGC has fallen by more than half over the past 20 years, but the number of coking refineries has increased by more than one third. USGC coking refineries currently make up approximately 90 % of the total crude capacity in the region [29].

24.4.12 Refining Optimization Involves Multiple Tradeoffs

In most refineries, there are usually several ways to accomplish the same task. Various operating variables—temperature, pressure, residence time, feed quality, cut-points, recycle-gas ratio, space velocity, and catalysts—are used to balance feedstock, product, and quality. The limits of these variables are specific to the plant design and nature of the input and output requirements. For a specific feedstock and catalyst package, the degree of processing and conversion increases with the severity of the operation.

The subsystems that make up a refinery are continually optimized, expanded, or idled to enhance operations. Because refining is an integrated, continuous operation, optimization requires a sophisticated treatment that links the operating variables, product specifications, input and output prices, and environmental and economic constraints. Total site integration is used to optimize the interaction of the refinery units with the existing utility infrastructure. Optimizing a refinery is a matter of balance because every benefit has a cost, every incremental gain has an offsetting loss, and every attempt to remove one unwanted product creates a new waste stream.

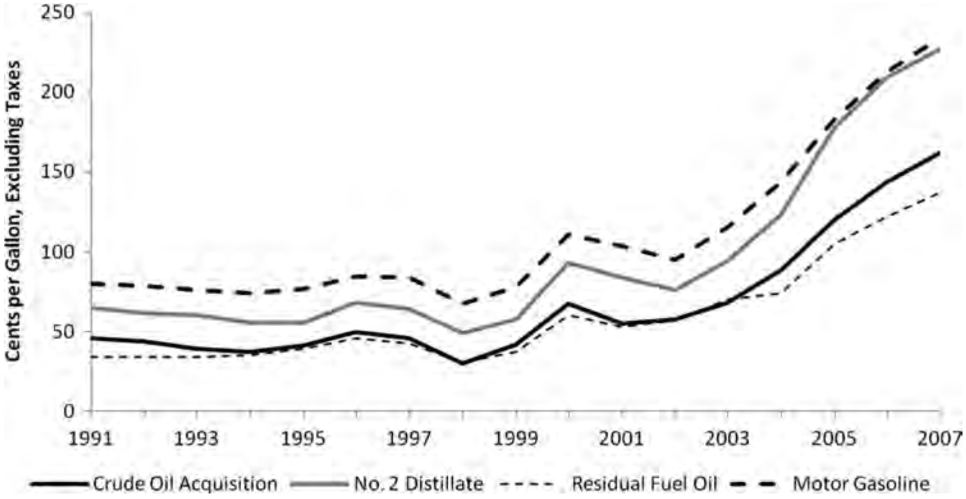


Figure 24.24—U.S. crude oil refiner acquisition costs and refiner sales prices for selected petroleum products. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

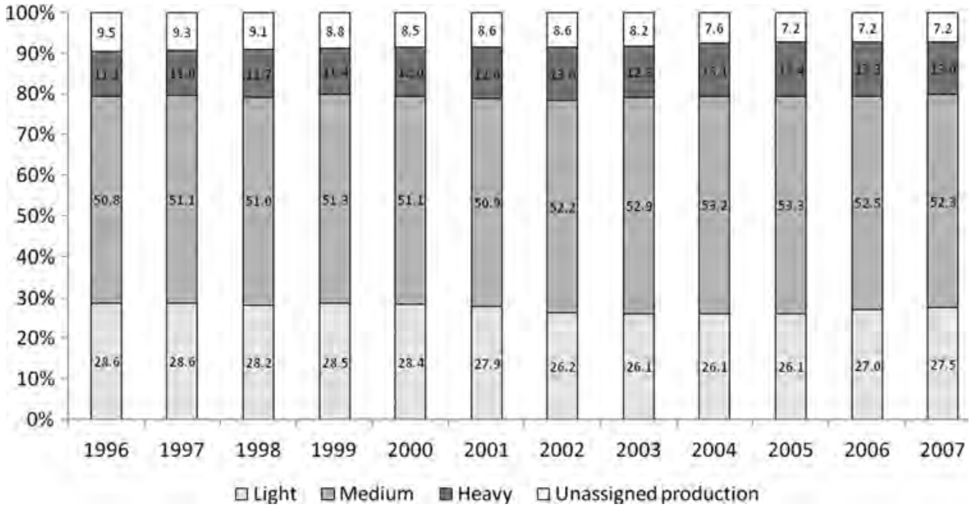


Figure 24.25—World crude production by gravity. *Source:* ENI, *World Oil and Gas Review 2008*.

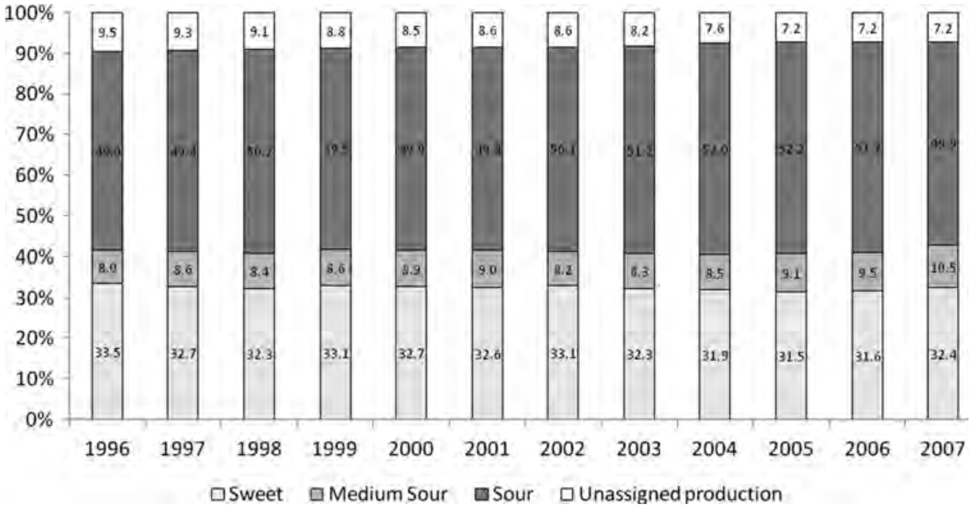


Figure 24.26—World crude production by sulfur content. *Source:* ENI, *World Oil and Gas Review 2008*.

24.4.13 Petroleum Refining Is Energy-Intensive

Petroleum refining is the most energy-intensive manufacturing industry in the United States. In 2002, the U.S. refining industry consumed 6.391 quads (quadrillion Btu, or 10^{15} Btu) of energy, accounting for approximately 28 % of the energy consumption in U.S. manufacturing [30]. Process units consume or produce, or both, various utilities, such as steam, electric power, boiler feed, fuel gas, gas oil, cooling water, nitrogen, water, and plant air [31,32]. Electric power may be produced or purchased, but fuel requirements can usually be met internally. Each unit has its own specific requirements depending on the design configuration and the need to integrate with existing facilities.

Processes that have the greatest throughput dominate energy consumption. Atmospheric and vacuum distillation account for 35–40 % of the total process energy consumed in the refinery (Figure 24.31), not because they are necessarily the most energy-intensive, but because every barrel of crude is subjected to an initial separation by distillation [32]. Likewise, because many refinery streams must be hydrotreated before entering downstream refining units and to achieve the desired product quality, another 20 % of energy consumption in a refinery is spent in hydrotreating.

24.4.14 Refining Operations and Products Affect the Environment

The oil and gas industry is one of the most heavily regulated industries in the United States, with regulations on the manner in which petroleum is produced, imported, stored, transported, and consumed [33]. Refining operations are affected by environmental and political legislation. The manufacturing processes used to refine petroleum generate various air emissions and other residuals, some of which are hazardous or toxic chemicals, or both [34–36]. The environmental impacts of refining and the use of refined products have resulted in several environmental laws and regulations. Some of the most significant statutes focus on altering the product formulation to reduce air emissions generated by their use.

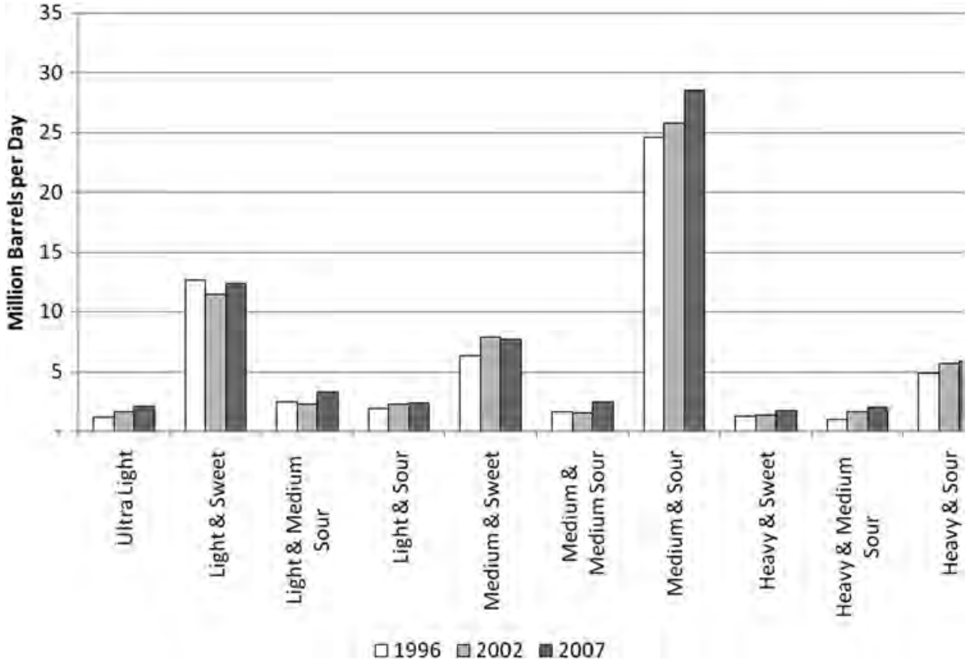


Figure 24.27—World crude production by quality. *Source:* ENI, *World Oil and Gas Review 2008*.

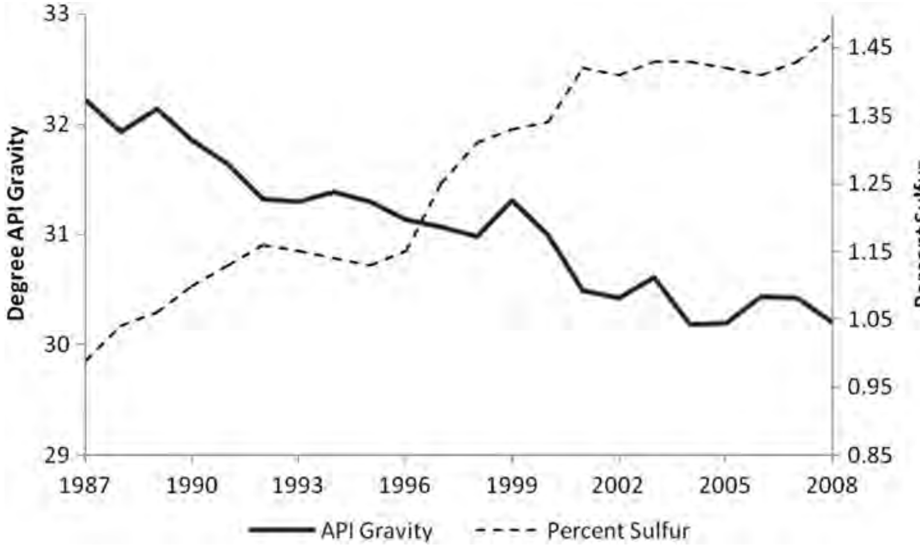


Figure 24.28—U.S. refinery crude input quality. *Source:* U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2007*, Washington, DC, June 2009.

24.5 REFINERY ECONOMICS

24.5.1 Performance Is a Function of Many Factors

The economic performance of a refinery is a function of many variables, including the plant configuration, the acquisition price of crude oil, product prices, strategic decisions, operating cost, and environmental requirements; therefore, simple economic models rarely provide sufficient guidance as an aid in decision-making. Crude oil and product prices change relative to each other subject to the supply and demand forces in the market. The refinery has some control over the cost of production, but price structures exhibit a much more complex relationship. Refiners attempt to maximize earnings from fluctuations in the market price of the crude oil and product slate. The potential for economic gain arises when there is a large price spread between light and heavy crude and light and heavy products.[6]

24.5.2 Financial Reporting System

One of the best sources of historic data on the financial and operating developments in the U.S. petroleum sector is the Energy Information Administration's (EIA) *Performance Profiles of Major Energy Producers*. The EIA collects

---

[6] In this case, a refiner will buy heavy crude to minimize input costs and sell a light product mixture to maximum product revenues.

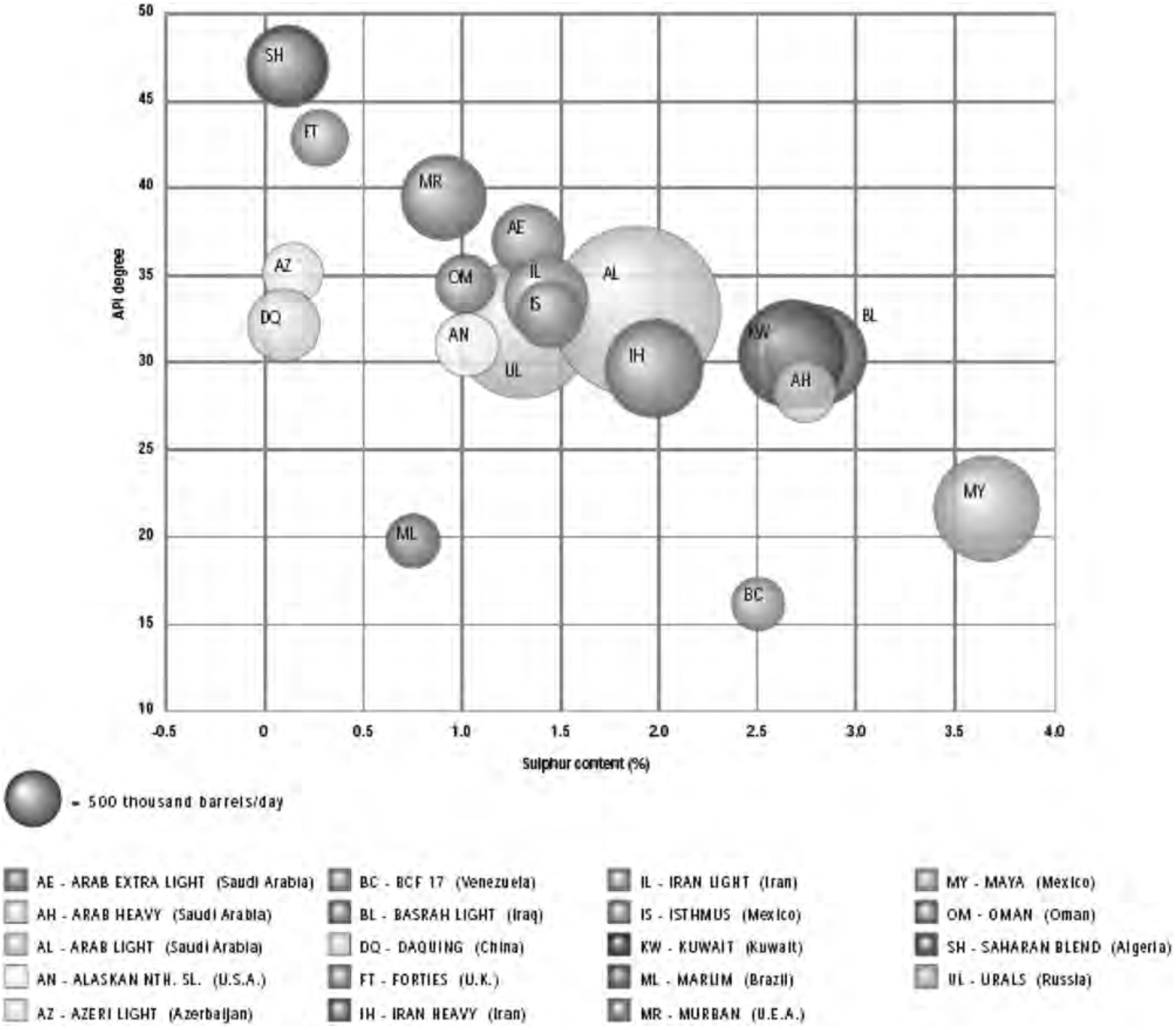


Figure 24.29—Gravity and sulfur content relationship of the main crude oil supplies. *Source:* ENI, *World Oil and Gas Review 2008*.

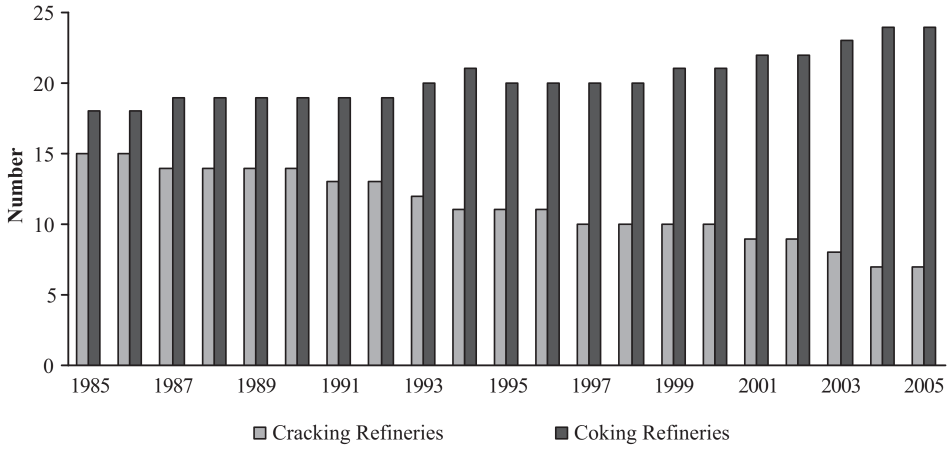


Figure 24.30—Classification of USGC refineries. *Source:* [29].

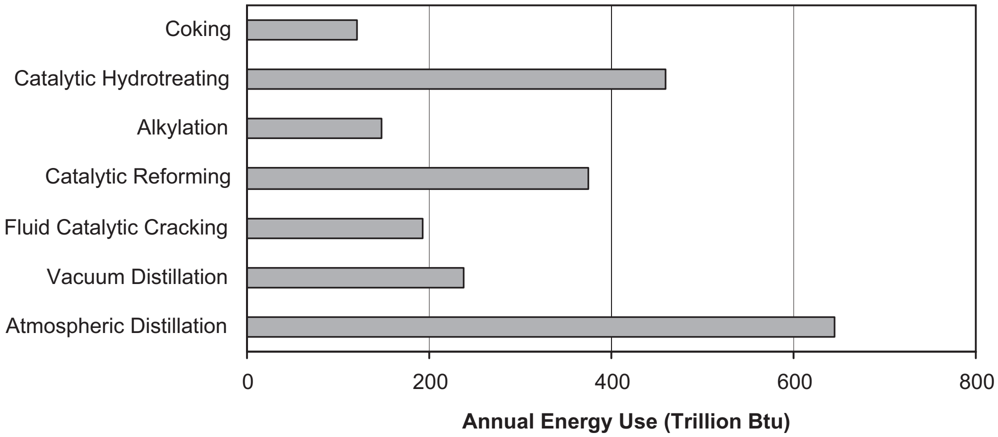


Figure 24.31—Relative energy use of major refinery processes, 2002. *Source:* U.S. Department of Energy, Office of Industrial Technologies, *Manufacturing Energy Consumption Survey*, Washington, DC, August 2004.

financial and operating data through a Financial Reporting System (FRS) Form EIA-28 from a sample of U.S. major[7] energy companies that are considered representative of the U.S. energy industry.

The composition of the FRS group of companies changes over time, but the annual changes are usually incremental; therefore, year-to-year comparisons are considered meaningful. Information is collected for the corporate entity as well as by the lines of business within the company—petroleum, downstream natural gas, electric power, nonenergy, and other energy. The petroleum line of business is further segmented into exploration and production, refining and marketing, crude and petroleum product pipelines (for domestic petroleum), and international marine transport (for foreign petroleum).

In 2007, 29 major energy companies reported data through FRS, representing operating revenues of $1.13 trillion, equal to approximately 15 % of the $7.4 trillion in revenues of the Fortune 500 corporations [37]. Approximately 94 % of the FRS companies' operating revenues were derived from petroleum operations, and they accounted for 46 % of total U.S. crude oil and natural gas liquid production, 43 % of U.S. natural gas production, and 84 % of U.S. refining capacity. Of the 29 major companies in the survey, 21 own refineries in the United States. In 2011, the EIA discontinued publication of the *Performance Profiles* report, although FRS data continues to be collected.

24.5.3 Boom and Bust Industry

The refining industry has historically been a high-volume, low-margin industry characterized by low return on investments (ROIs) and volatile profits. In Figure 24.32, profitability is measured by ROI, defined as the net income contributed by refining/marketing as a percentage of net fixed assets (net property, plant, and equipment plus investments and advances) in U.S. refining and marketing. The profitability of refining peaked in 1988 at 15 %, averaged 2 % from 1992 to 1995, peaked again in 2001 at 15 %, and then plunged to –1.7 % in 2002, the worst in the history of the FRS survey. In 2004, domestic and foreign ROI exceeded 18 %, and in 2007, ROI peaked at 26 %. High utilization capacity, fewer competitors, and increasing product demand usually make for a high-profit margin scenario, but it has only been in the last few years when this combination of conditions has resulted in high profits.

24.5.4 Refining Margins

Industry performance is also frequently assessed through the gross and net refining margins. The gross margin of a refinery is computed as the total revenues from product sales minus the cost of crude oil. Net margin is defined as the gross margin minus petroleum product marketing costs, internal energy costs, and other operating costs. The domestic refining/marketing gross margin exceeded $12/bbl in 2007, the highest since 1985 (Figure 24.33). Operating costs have mostly declined over time resulting in a net refined product margin of $4.50/bbl in 2007. Muse, Stancil, & Co. average refining margins for the United States, Northwest Europe, and Southeast Asia are shown in Table 24.14.

24.5.5 Investment Decision-Making

Capital expenditures in refining are used to enhance, upgrade, modify, and debottleneck existing configurations; to keep the refinery site and the products it produces in compliance with environmental standards; and for merger and acquisition activity.[8]

The decision to invest is complex and depends on expectations of ROI and several other factors. For the refining sector to attract funding, it must offer terms and rates of return that compare favorably with those offered in other sectors, taking into account the different risk profiles. The FRS companies normally spend between $5 billion and $15 billion on capital expenditures, with refining/marketing

---

[7] To be included within the annual survey, a "major" energy-producing company must control at least: (1) 1 % of U.S. crude oil or natural gas liquids reserves or production, (2) 1 % of U.S. natural gas reserves or production, or (3) 1 % of U.S. crude oil distillation capacity or product sales.

[8] All segments of the petroleum industry experienced mergers during the 1990s, with over 2600 transactions reported by John S. Herold, Inc., from 1991 to 2000 [37]. The upstream segment of the business accounted for most (85 %) of these mergers, with 13 % occurring in the refining and marketing segment. Approximately half of the downstream activity was asset mergers.

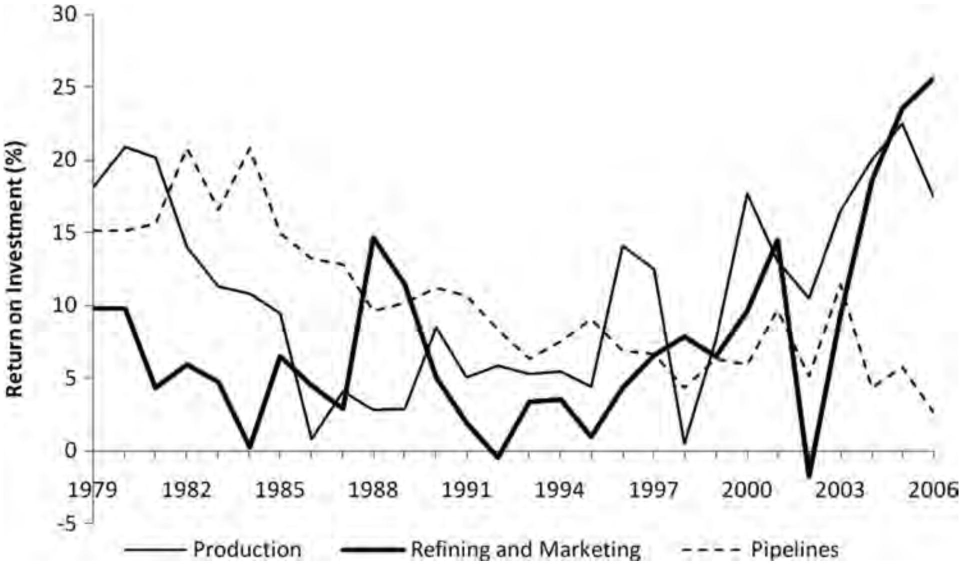


Figure 24.32—U.S. petroleum profitability for FRS companies. *Source:* U.S. Department of Energy, Energy Information Administration, *Performance Profiles of U.S. Major Producers*, Washington, DC, June 2009.

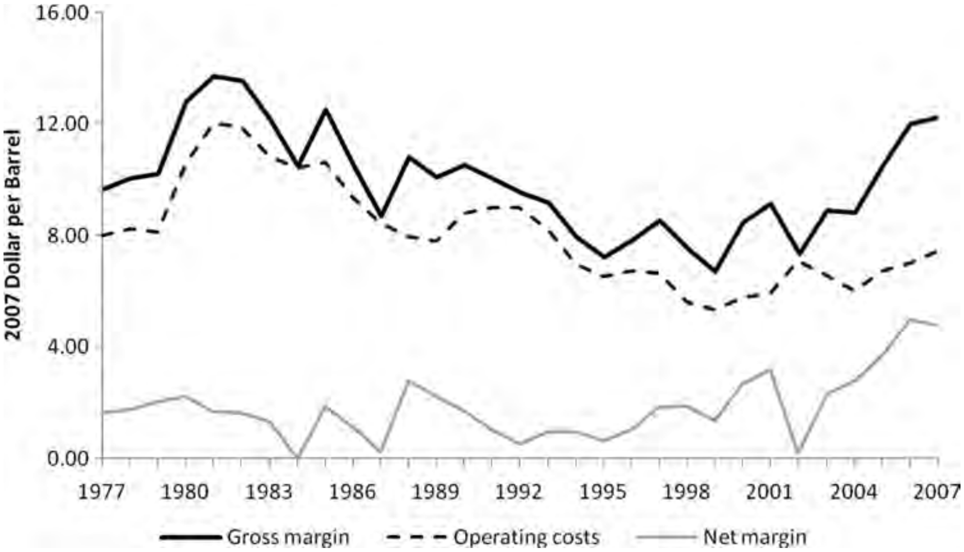


Figure 24.33—U.S. refined product margins and costs per barrel of petroleum product sold for FRS companies. *Source:* U.S. Department of Energy, Energy Information Administration, *Performance Profiles of U.S. Major Producers*, Washington, DC, June 2009.

TABLE 24.14—Muse, Stancil, & Co. Average Net Operating Refining Margins

	U.S. Gulf Coast	U.S. East Coast	U.S. Midwest	U.S. West Coast	Northwest Europe	Southeast Asia
2009 avg.	3.96	1.51	5.90	12.70	3.31	0.89
2008 avg.	9.09	3.04	11.53	13.42	6.35	3.07
2007 avg.	12.60	6.65	18.66	20.89	5.75	2.25
2006 avg.	12.54	6.38	14.97	23.69	5.88	0.90
2005 avg.	12.53	6.98	12.31	20.55	5.51	1.52

Source: Muse, Stancil, & Co. Average Net Operating Refining Margins is published in the June issue of *Oil & Gas Journal*.

contributing approximately 20 % of the total [38]. Capital and environmental expenditures for FRS companies are shown in Figure 24.34 [39]. Environmental investments incur expenses, but they do not produce revenues directly and do not result in lower cost or increased output; therefore, they are expected to reduce ROI.

24.5.6 Cost Estimation

24.5.6.1 DATA SOURCES

Various data sources are available to estimate the construction cost of refinery units and include government organizations, private and public companies, commercial databases, trade and academic publications, and press releases for licensors and companies.

Planned capacity expansions for refineries are reported annually in the October issue of the *Oil and Gas Journal* and *Hydrocarbon Processing*. The data coverage is similar in both surveys and provides information on the capacity that is expected to be added at a given location by project type (increment of capacity added; total capacity after construction; revamping, modernization, or debottlenecking; expansion); licensor, engineering company, and constructor; estimated completion date; estimated cost; and project status (abandoned, engineering, feed, completed, maintenance, planning, under construction). The data are subject to availability, and because project descriptions are not provided, they are of limited use for cost estimation. *Hydrocarbon Processing* also publishes the *Refining Handbook* that includes basic economic data for process units [40]. The quality of the information is somewhat better than the survey data but is subject to the same constraints and restrictions.

The best public sources of information for cost data are technical articles found in *Oil and Gas Journal*, *Hydrocarbon Processing*, and *Petroleum Technology Quarterly*; material presented at professional conferences such as the National Petrochemicals and Refining Association; and industry studies. Robert Meyer's *Handbook of Petroleum Refining Processes* [20] is an excellent source of process and sample economic data for a wide compendium of technologies. Kaiser and Gary [41] and Gary et al. [19] provide cost estimates circa mid-2000. Maples [42], Raseev [43], Sadeghbeigi [44], and Gary and Handwerck [45] provide cost estimates for mid-1990 and earlier configurations and technologies.

Commercial databases from Baker & O'Brien (www.bakerobrien.com), Purvin and Gertz (www.purvingertz.com), Solomon Associates (www.SolomonOnline.com), Stancil Company (www.stancil.co), Turner and Mason (www.turnermason.com), and Independent Project Analysis (www.ipa.com) are used widely throughout the industry for benchmarking and industry studies. The cost information from commercial sources is the best, often being collected from detailed project analyses and related assignments over an extended period of time. However, each agency considers its database and modeling software proprietary; therefore, the quality, reliability, and consistency of commercial sources are difficult to compare.

24.6 PROCESS TECHNOLOGIES

The primary technologies used in refining are summarized in Table 24.15. For each process, one or more subcategories are defined based on technology attributes, operating conditions, or feedstock.

24.6.1 Function Specification

The capital cost for refining units are frequently specified as a function of capacity and scaled using the power-law relation:

$$\frac{C(U_i, Q_1)}{C(U_i, Q_2)} = \left(\frac{Q_1}{Q_2}\right)^x, \qquad (24.1)$$

where $C(U_i, Q_i)$ denotes the cost of process unit U_i of capacity Q_i. The value of x varies with each unit and technology and frequently ranges between 0.5 and 0.7 [46,47]. If cost data are available for units of comparable design and technology, regression analysis can be used to estimate the coefficient value.

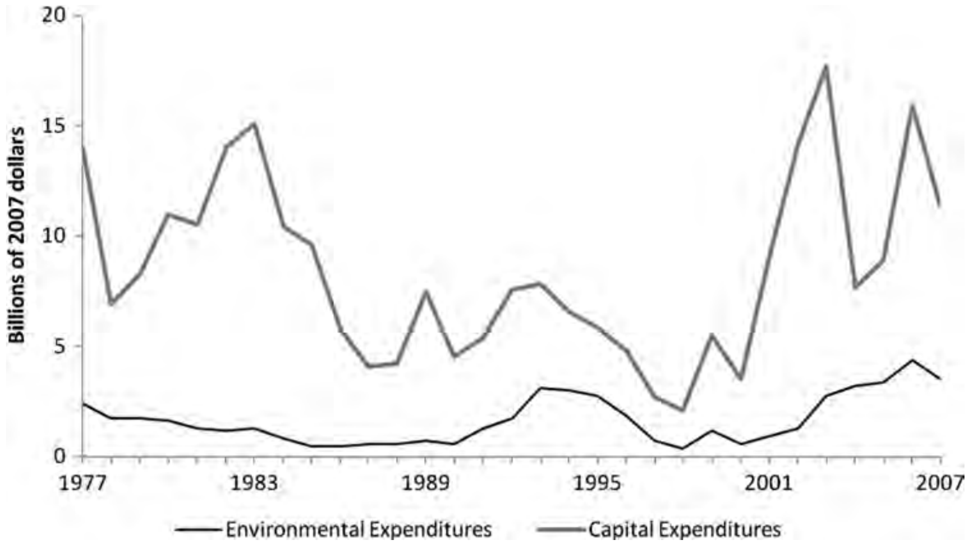


Figure 24.34—U.S. refining capital expenditures for FRS companies. *Source:* U.S. Department of Energy, Energy Information Administration, *Energy Finance*, Washington, DC, February 2009.

TABLE 24.15—Refining Production Process Technologies

Process Operation	Technology
Coking	Fluid coking, delayed coking, other
Thermal process	Thermal cracking, visbreaking
Catalytic cracking	Fluid, other
Catalytic reforming	Semiregenerative, cycle, continuous regeneration, other
Catalytic hydrocracking	Distillate, upgrading residual, upgrading lube oil, other
Catalytic hydrotreating	Pretreatment of cat reformer feeds, other naphtha desulfurization, naphtha aromatics saturation, kerosine/jet desulfurization, diesel desulfurization, distillate aromatics saturation, other distillates, pretreatment of cat cracker feeds, other heavy gas oil hydrotreating, resid hydrotreating, lube oil polishing, posthydrotreating of fluid catalytic cracking naphtha, other
Alkylation	Sulfuric acid, hydrofluoric acid
Polymerization/dimerization	Polymerization, dimerization
Aromatics	Benzene, toluene, xylene, hydrodealkylation, cyclohexane, cumene
Isomerization	C_4 feed, C_5 feed, C_5 and C_6 feed
Oxygenates	MTBE, ETBE, TAME
Hydrogen production Hydrogen recovery	Steam methane reforming, steam naphtha reforming, partial oxidation Pressure swing adsorption, cryogenic, membrane, other

Source: Oil & Gas Journal World Refinery Capacity Report, December 19, 2005.

24.6.2 Utility Requirements

The utility requirements for each refinery are specific to the process and operations and are usually presented on a per barrel unit feed or product basis corresponding to the "average" characteristics associated with the midpoint of a cost curve. Wide variability in utility values can be expected depending on the capacity of the unit and other process-specific factors.

24.6.3 Normalization

The cost data of units of roughly comparable design and technology are normalized with respect to construction requirements, process specifications, location, and time of installation.

24.6.3.1 DEPENDENT VARIABLE

The normal basis in computing construction cost is the liquid-volume fraction of the crude that is fed to each process, but for several units (e.g., alkylation, polymerization, aromatics manufacture), barrels of product rather than feed are frequently applied. In other units (e.g., isomerization, hydrotreating, catalytic reforming, hydrogen production), it may be necessary to cross-correlate the cost with other factors, whereas in gas processing and sulfur manufacture, the liquid-volume basis needs to be replaced with cubic feet (of gas) and long tons (of sulfur). For hydrogen production thousand cubic feet per day (MCFPD) is used.

24.6.3.2 PROJECT TYPE

Projects are classified according to new capacity, expansion of existing capacity, or a revamp or modernization of existing facilities. Grassroots construction is limited to equipment inside of the battery limits (ISBL) of each process and includes materials and labor; design, engineering, and contractor's fees; overheads; and expense allowance.

24.6.3.3 OFFSITE EXPENSES

Offsite expenses include the cost and site preparation of land, power generation, electrical substations, offsite tankage, or marine terminals. Offsite costs vary widely with the location and existing infrastructure at the site and depend on the process unit. ISBL costs do not include offsite expenses.

24.6.3.4 LOCATION

It is common practice to state cost estimates relative to the USGC because this location historically has very favorable construction costs relative to other domestic and international markets. Design requirements, climate, regulations, codes, taxes, and availability and productivity of labor all influence and affect the cost of construction and to some extent the operating cost of a facility.

24.6.3.5 TIME

The purchase cost of processing equipment in refining is generally obtained from charts, equations, or quotes from vendors at a particular time. Factors such as regulatory requirements, feedstock quality, and the cost of materials may increase costs and inflate refinery investment over time whereas other factors may act to lower cost, such as improvements of a technological and process nature such as improved catalyst, control and instrumentation, and materials technology. Time captures long-term dynamics such as improvements in technology and operational efficiency as well as local effects such as the cost of steel, permit requirements, and pollution control.

24.6.3.6 NELSON-FARRAR COST INDICES

An estimate of the purchase cost at time t_2, $C(t_2)$, is obtained by multiplying the original (quoted) cost at time t_1, $C(t_1)$, by a ratio of cost indices:

$$C(t_2) = C(t_1)\left(\frac{I(t_2)}{I(t_1)}\right). \tag{24.2}$$

The Nelson-Farrar (NF) construction cost index normalizes cost during the time required to construct a process unit. The NF cost index is not suitable for determining the cost for refineries or process units that are more than five years old. The NF cost index also does not account for productivity attained in design, construction, or management skills. The NF construction cost index is published each month in the *Oil and Gas Journal* (Table 24.16).

The NF operating cost indices are used to compare operating costs over time (Table 24.17). Unlike the construction index, the operating cost indices are normalized for the productivity of labor, changes in the amounts and kinds of fuel used, productivity in the design and construction of refineries, and the amounts and kinds of chemicals and catalysts used [48,49].

24.7 REFINERY COMPLEXITY

24.7.1 Data Source

The *Oil and Gas Journal* publishes a refining survey in December of each year and lists the capacity ratings of all refineries in the world by company and location in terms of charge and production capacities. The EIA also publishes data on U.S. refineries that are similar in format to the *Oil and Gas Journal* [50].

Distillation, thermal processes, catalytic cracking, catalytic reforming, and catalytic hydrocracking are described in terms of charge capacity, which describes the input (feed) capacity of the facilities. Production capacity represents the maximum amount of product that can be produced and is presented for alkylation, polymerization/dimerization, aromatics, isomerization, lubricants, oxygenates, hydrogen, coke, sulfur, and asphalt facilities.

TABLE 24.16—Nelson-Farrar Refinery Construction Cost Index (1970–2009)

X	197X	198X	199X	200X
0	365	823	1226	1543
1	406	904	1253	1580
2	439	977	1277	1642
3	468	1026	1311	1710
4	523	1061	1350	1834
5	576	1074	1392	1919
6	616	1090	1419	2008
7	653	1122	1449	2107
8	701	1165	1478	2251
9	757	1196	1497	2218

Source: Oil & Gas Journal, 1946 = 100. The Nelson-Farrar Refinery Construction Cost Index is published each month in *Oil & Gas Journal*.

24.7.2 Unit Complexity

Wilbur Nelson introduced the concept of complexity factor to quantify the relative cost of components that make up a refinery [51–53]. Nelson assigned a complexity factor of one to atmospheric distillation units and expressed the cost of all other units in terms of their cost relative[9] to distillation.

The complexity factor of process unit U_i of capacity Q_i with a construction cost of $C(U_i, Q_i)$ is thus defined as

$$\gamma(U_i) = \frac{C(U_i, Q_i)/Q_i}{C(U_o, Q_o)/Q_o}, \tag{24.3}$$

where:

$\gamma(U_i)$ = the complexity index of unit U_i and

U_o = the atmospheric distillation unit.

Various methodological issues limit the use of complexity factors in cost estimation. For example, complexity factors do not account for the effect of capacity on cost because the complexity factor is capacity invariant, and trends in complexity factors change slowly (or not at all) over time (Table 24.18) and may not accurately reflect relative cost. A more serious issue arises from the nature of the trends observed, which suggests that the complexity values are not empirically based, but rather, appear fixed in nature. Nonetheless, the Nelson complexity factor is widely used and continues to serve a useful function.

24.7.3 Refinery Complexity

Refinery complexity indicates how complex a refinery is in relation to a refinery that performs only crude distillation. Refinery complexity is an often-cited industry statistic and is a useful tool in comparative analysis, frequently being used as a correlative or descriptive variable in marketing and valuation studies (e.g., [54]).

The complexity index of refinery R is determined by the complexity of each individual unit weighted by its percentage of distillation capacity:

$$\gamma(R) = \sum_i \frac{Q_i}{Q_o}\gamma(U_i), \tag{24.4}$$

where:

$\gamma(R)$ = the complexity index of refinery R,

$\gamma(U_i)$ = the complexity index of unit U_i, and

Q_i = the capacity of unit U_i, and

Q_o = the capacity of the atmospheric distillation.

A simple refinery is typically defined by $\gamma(R) < 5$; a complex refinery by $5 \le \gamma(R) \le 15$; and a very complex refinery by $\gamma(R) > 15$.

24.7.4 Example

Exxon Mobil's charge and production capacity of its Louisiana facilities in 2008 are shown in Tables 24.19 and 24.20. The complexity index of the Baton Rouge facility is computed as 11.5 (Table 24.21) which identifies it as a complex refinery.

---

[9] For example, if a crude distillation unit of 100,000 BPD capacity costs \$10 million to build, then the unit cost per daily barrel of throughput would be \$100 BPD. If a 20,000 BPD catalytic reforming unit costs \$10 million to construct, then the unit cost is \$500 BPD of throughput and the "complexity" of the catalytic reforming unit would be 500/100 = 5.

TABLE 24.17—Nelson-Farrar Refinery Operating Cost Indices (2003–2011)

	2003	2004	2005	2006	2007	2008	2009	2010	2011
Fuel and power cost	935	972	1360	1569	1531	1951	979	1185	1204
Labor cost	201	192	202	204	216	238	265	282	277
Wage rate	972	984	1007	1015	1043	1092	1177	1279	1304
Productivity of labor	485	513	501	498	483	461	455	455	471
Investment related	643	687	716	744	777	831	850	850	856
Chemicals and catalyst	238	268	311	365	386	473	406	450	537
Refineries	465	487	542	579	597	674	583	628	652
Processes	613	638	787	871	873	1045	706	797	815

Source: Oil & Gas Journal, 1956 = 100. The Nelson-Farrar Refinery Operating Cost Index is published in each month of *Oil & Gas Journal*.

TABLE 24.18—Trends in Complexity Factors

Process Operation	1946	1961–1972	1976	1989
Atmospheric distillation	1	1	1	1
Vacuum distillation	2	2	2	2
Vacuum flash	1	1	1	1
Thermal process				
Thermal cracking	4.5	3	3	3
Visbreaking	2	2	2	2
Coking	5	5	5.5	5.5
Calcining		63	108	108
Catalytic cracking				
60 % conversion	4	5	5	5
80 % conversion		6	6	6
Catalytic reforming	5	4	5	5
Catalytic hydrocracking		6	6	6
Catalytic hydrorefining		4	3	3
Catalytic hydrotreating		2	2	1.7
Alkylation	9	9	11	11
Aromatics, benzene, toluene, and xylene		40–70	20	20
Isomerization		3	3	3
Polymerization	9	9	9	9
Lubes				60
Asphalt	2		3.5	1.5
Hydrogen (MCFPD)				
Manufacturing		1.2	1.2	1
Recovery		0.7	0.7	1
Oxygenates				10
Sulfur (t/day)				
Manufacturing		85	85	85
Manufacturing from dilute gas		250–300	220–600	220–600

Source: [48,51].

TABLE 24.19—Charge Capacity of Exxon Mobil's Louisiana Facilities—BPCD (2008)

Location	Crude	Vacuum Distillation	Delayed Coking	Thermal Operations	Catalytic Cracking	Catalytic Reforming	Catalytic Hydrocracking	Catalytic Hydrotreating
Baton Rouge	503,000	231,500	115,000	–	230,000	75,500	26,500	451,500
Chalmette	192,500	112,000	38,000	–	68,000	47,000	18,500	172,500
Total	695,500	343,500	153,000	–	298,000	122,500	45,000	624,000

Source: Oil & Gas Journal 2008 Worldwide Refining Survey, December 22, 2008.

TABLE 24.20—Production Capacity of Exxon Mobil's Louisiana Facilities—BPCD (2008)

Location	Alkylation	Poly/Dim	Aromatics	Isomerization	Lubes	Oxygenates	Hydrogen (MMcfd)	Coke (t/day)	Sulfur (t/day)	Asphalt (t/day)
Baton Rouge	38,500	9500	–	–	16,000	–	12	5,430	690	–
Chalmette	12,500	–	10,000	10,000	–	–	–	2,050	920	–
Total	51,000	9500	10,000	10,000	16,000	–	12	7480	1610	–

Source: Oil & Gas Journal 2008 Worldwide Refining Survey, December 22, 2008.

TABLE 24.21—Complexity Index of Exxon Mobil's Baton Rouge Facility (2008)

Process Operation	Capacity (BPSD)	Percent of Distillation Capacity	Complexity Factor	Complexity Index
Atmospheric distillation	503,000	100	1	1.0
Vacuum distillation	231,500	46.0	2	0.9
Coking	115,000	22.9	5.5	1.3
Catalytic cracking	230,000	45.7	6	2.7
Catalytic reforming	75,500	15.0	5	0.8
Catalytic hydrocracking	26,500	5.3	6	0.3
Catalytic hydrotreating	451,500	89.8	1.7	1.5
Alkylation	38,500	7.7	11	0.8
Polymerization	9,500	1.9	9	0.2
Lubes	16,000	3.2	60	1.9
Hydrogen (MCFD)	12,000	2.4	1	0.0
Complexity index				11.5

Source: Oil & Gas Journal 2008 Worldwide Refining Survey, December 22, 2008 and [48,51].

24.8 PROCESS COST FUNCTIONS

Construction cost functions for the main process units that comprise a refinery are summarized. The cost estimates pertain exclusively to grassroots construction, limited to equipment ISBL, and include materials and labor; design, engineering, and contractor's fees; overheads; and expense allowance. Cost functions for the U.S. Gulf Coast in 2005 are described as Cost = α Capacity$^{\beta}$ in Table 24.22.

24.8.1 *Distillation*

The first step in every refining process is the separation of crude oil into fractions by distillation. The crude oil is desalted and heated in a furnace to temperatures of approximately 600–700°F before being charged to a distillation tower. The components of crude oil separate according to their boiling point range into butanes and lighter wet gas, unstabilized light naphtha, heavy naphtha, kerosine, atmospheric gas, and topped (reduced) crude. Topped crude is sent to a vacuum distillation tower and separated into vacuum gas oil and vacuum-reduced crude bottoms. Cost functions for desalting, atmospheric distillation, and vacuum distillation are summarized in Table 24.22. In Figure 24.35, the cost curve on a log-log plot is depicted.

24.8.2 *Coking and Thermal Processes*

In thermal cracking, heat and pressure are used to break down, rearrange, and combine hydrocarbon molecules. Delayed coking, visbreaking, fluid coking, and flexicoking

TABLE 24.22—Process Cost Functions: *Cost* = α *Capacity*$^{\beta}$ ($ million)

Process Unit	α	β	**Capacity Unit**
Desalter	0.44	0.555	MBPSD
Atmospheric distillation	8.20	0.510	MBPSD
Vacuum distillation	8.34	0.493	MBPSD
Delayed coking			
10 bbl feed/t coke 30 bbl feed/t coke	17.56 24.42	0.657 0.644	MBPSD MBPSD
Visbreaking	5.80	0.741	MBPSD
Fluid catalytic cracking			
Distillate feed	24.67	0.461	MBPSD
Resid feed	32.98	0.510	MBPSD
Catalytic hydrocracking			
1000 scf/bbl H_2	15.65	0.719	MBPSD
3000 scf/bbl H_2	26.18	0.714	MBPSD
Catalytic hydrotreating			
Naphtha desulfurization	4.96	0.524	MBPSD
Distillate desulfurization	8.62	0.576	MBPSD
Resid desulfurization	8.61	0.834	MBPSD
Catalytic reforming			
Semiregenerative	7.96	0.572	MBPSD
Continuous	12.19	0.547	MBPSD
Isomerization			
Butane	9.57	0.514	MBPSD
Pentane/hexane; once through	3.11	0.565	MBPSD
Pentane/hexane; recycle	6.17	0.599	MBPSD
Alkylation	12.19	0.606	MBPSD
Hydrogen production			
Steam methane reforming	3.35	0.599	MMCFPD
Partial oxidation	5.44	0.601	MMCFPD
Gas processing			
1 gal/Mscf	1.91	0.627	MMCFPD
10 gal/Mscf	4.38	0.593	MMCFPD
20 gal/Mscf	5.83	0.610	MMCFPD
Amine-gas treating	0.064	0.746	GPM
Sulfur recovery	2.84	0.412	Long ton per day
Sulfur removal			
S-zorb, gasoline	4.77	0.602	MBPSD
S-zorb, diesel	4.62	0.553	MBPSD
Dewaxing	5.82	0.598	MBPSD
Ether production	8.96	0.472	MBPSD

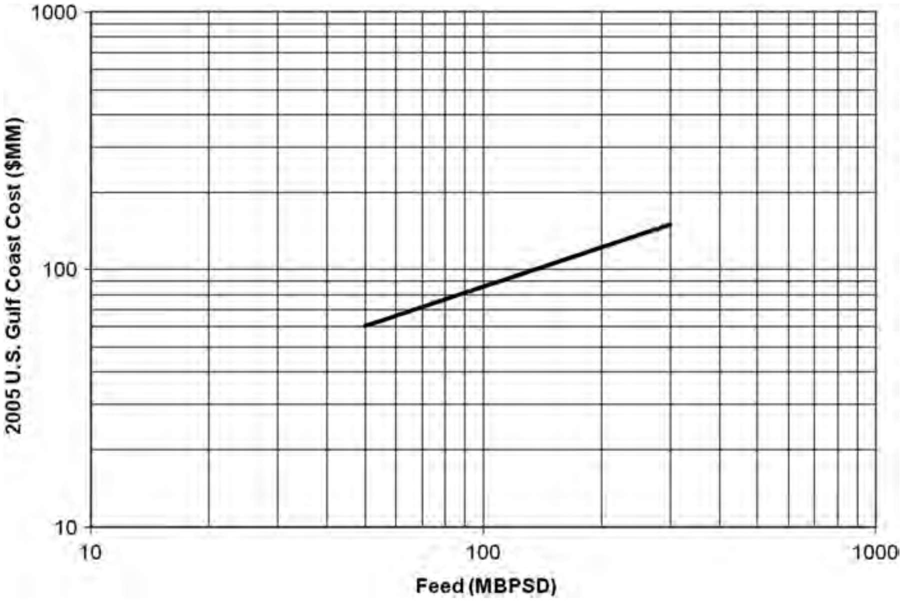


Figure 24.35—Atmospheric crude distillation investment cost—2005 USGC.

are common thermal cracking units. The reduced crude bottoms from the vacuum tower are thermally cracked in a delayed coker to produce wet gas, coker gasoline, coker gas oil, and coke. The light oils can be processed in other refinery units to meet product specifications, and the coke is used either as a fuel or in other applications such as the manufacturing of steel or aluminum. Without a coker, heavy resid would be sold for heavy fuel oil or (if the crude oil is suitable) asphalt. Visbreaking is a process in which heavy atmospheric or vacuum-still bottoms are cracked at moderate temperatures to increase the production of distillate products and reduce the viscosity of the distillation residues. Capital cost functions for visbreaking and delayed coking cost functions are summarized in Table 24.22.

24.8.3 Catalytic Cracking

The atmospheric and vacuum gas oils as well as coker gas oil are used as feedstocks for catalytic cracking and hydrocracking units. Catalytic cracking breaks down the larger, heavier, more complex hydrocarbon molecules into simpler and lighter molecules. Catalytic cracking is accomplished through the use of a catalytic agent and is an effective process for increasing the yield of gasoline from crude oil. Fluid catalytic cracking cost curves for distillate and resid feed are given by $Cost(Catalytic\ cracking;\ distillate\ feed) = 24.67\ Capacity^{0.461}$ and $Cost(Catalytic\ cracking;\ resid\ feed) = 32.98\ Capacity^{0.510}$.

24.8.4 Catalytic Hydrocracking

Catalytic hydrocracking uses hydrogen and catalysts at high temperature and pressure to convert middle boiling or residual material to high-octane gasoline, reformer charge stock, jet fuel, and high-grade fuel oil. The process uses one or more catalysts, depending on product output, and can handle high-sulfur feedstocks without prior desulfurization. Capital investment costs for catalytic hydrocracking are computed at 1000 and 3000 scf/bbl hydrogen consumption.

24.8.5 Catalytic Hydrotreating

Impurities in hydrocarbons remain unchanged by the distillation process because distillation only segregates crude oil according to boiling point ranges. Catalytic hydrotreating treats petroleum fractions from distillation units and other petroleum (e.g., cat cracked naphtha, coker naphtha, gas oil, etc.) in the presence of catalysts and substantial quantities of hydrogen. If contaminants are not removed from the petroleum fractions as they travel through processing units, they can have detrimental effects on the equipment, catalysts, and quality of the finished products. Typically, hydrotreating is performed before processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock. Hydrotreating is also used before catalytic cracking to reduce sulfur and improve product yields as well as to upgrade middle-distillate petroleum fractions into finished kerosine, diesel fuel, and heating fuel oils. Desulfurization capital costs are computed for a naphtha feedstock, a distillate feedstock, and a residual feedstock.

24.8.6 Catalytic Reforming

Catalytic reforming converts low-octane naphthas into high-octane gasoline blending components called reformates. Depending on the properties of the naphtha feedstock and catalysts, reformates can be produced with very high concentrations of benzene, toluene, xylene, and other aromatics useful in gasoline blending and petrochemical processing. Hydrogen is separated from the reformate for recycling and use in other processes. The investment costs depend upon the semiregenerative and continuous processes applied. In semiregenerative reforming, the reforming unit is shut down at specified intervals for in situ catalyst regeneration. Continuous regeneration reforming is characterized by the continuous addition of the regenerated catalyst to the reactor. Continuous regeneration has been used in most of the new catalytic reformers built in the United States, although fixed-bed units are occasionally constructed depending on product requirements.

24.8.7 Isomerization

Isomerization alters the arrangement of atoms in hydrocarbon molecules. Isomerization is used to convert normal butane into isobutene (an alkylation process feedstock) and normal pentane and normal hexane into isopentane and isohexane (high-octane gasoline components). The first isomerization units in the early 1940s were characterized by high corrosion rates and catalyst consumption, and excessive sludge formation. Technological advances from catalytic reforming were adopted in the 1960s using low-temperature, dual-functional catalyst systems, which significantly improved operating economics and efficiency. Paraffin isomerization unit capital costs for butane and pentane/hexane feedstock for once-though and recycle processes are presented.

24.8.8 Alkylation

Alkylation is a process for chemically combining isobutene with olefin hydrocarbons in the presence of an acid catalyst, usually sulfuric or hydrofluoric acid. The product alkylate, an isoparaffin, has high octane value and is blended with motor and aviation gasoline to improve the antiknock value of the fuel. The investment cost of alkylation units are expressed in terms of alkylate production. The capital costs for sulfuric and hydrofluoric alkylation units are generally comparable; therefore, the investment curve can be applied for either unit. However, the composition of the costs varies with the technology. The sulfuric acid process has an expensive reactor section and requires refrigeration, whereas hydrofluoric alkylation uses feed driers, product treating, regeneration equipment, and more exotic metallurgy.

24.8.9 Hydrogen Production

Hydrogen recovery from catalytic reforming is often not enough to meet total refinery requirements, necessitating the manufacture of additional hydrogen or obtaining supply from external sources. High-purity hydrogen (95–99 %) is required for hydrodesulfurization, hydrocracking, and petrochemical processes. The steam reformation of natural gas accounts for most of the hydrogen produced, but catalytic reforming and partial oxidation processes are also applied. Steam reformation and catalytic processes are generally suitable for reforming light hydrocarbons and naphtha whereas partial oxidation processes are applied to a broader range of feedstocks, including heavy residual oils and low-value products.

24.8.10 Gas Processing

Wet gas streams from the crude tower, coker, and cracking units are separated in the vapor recovery section into fuel gas, liquefied petroleum gas (LPG), unsaturated hydrocarbons, normal butane, and isobutene. The fuel gas is burned as a fuel in refinery furnaces and the normal butane is blended into gasoline or LPG. The unsaturated hydrocarbons and isobutene are sent to the alkylation unit for processing. Amine plants remove acid contaminants from sour gas and hydrocarbon steams. Gas and liquid hydrocarbon streams containing carbon dioxide or hydrogen sulfide or both are charged to a gas absorption tower or liquid contactor where the acid contaminants are absorbed by counterflowing amine solutions.

24.8.11 Sulfur Recovery and Removal

The amount and type of sulfur in the feedstream, feed stability, product specifications, and refinery configuration will determine the choice of technologies used to remove and recover sulfur. Sulfur recovery converts hydrogen sulfide in sour gases and hydrocarbon streams to elemental sulfur. The most widely used recovery system is the Claus process, which uses thermal and catalytic-conversion reactions. The S-zorb process is also used in sulfur removal.

24.8.12 Lubricating Oil Blending Stocks

In some refineries, the heavy vacuum gas oil and reduced crude from paraffinic or naphthenic base crude oils are processed into lubricating oils. The vacuum gas oil and deasphalting stocks are first solvent-extracted to remove the aromatic compounds and then dewaxed to improve the pour point. They are then treated with special clays or high-severity hydrotreating to improve their color and stability before being blended into lubricating oils. The purpose of solvent extraction is to prevent corrosion, protect catalyst in subsequent processes, and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricant and grease stocks. Solvent dewaxing is used to remove wax from distillate or residual basestocks at any stage in the refining process.

24.8.13 Ether

Capital costs and utility consumption for methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME) production depend upon the number of stages involved. Capital costs are usually expressed in terms of total hydrocarbon feed (excluding alcohol); therefore, the *iso*-olefin content of the feedstock must be known for cost estimation. Many proprietary designs for making MTBE and TAME are available, but most of the processes are based on catalytic distillation, which can manufacture most of the higher ethers with the addition of one or two extra columns. A one- or two-stage design can be used for ether production, but because of the lower cost, a one-stage design is more common unless extremely high-purity raffinate is required.

24.9 LIMITATIONS OF ESTIMATION

Engineering cost estimates are widely available, but actual (finished) cost is preferred in analysis to avoid estimator bias and to assess actual system performance. Ideally, we would only use actual cost data, but because the sample sets are often too sparse, it is often necessary to supplement the data with engineering estimates.

The cost curves are meant to represent typical, or average, values and are presented as point estimates rather than in terms of intervals or ranges. Cost functions are meant to represent an “average” refinery, which of course also does not exist, but it is nonetheless useful in developing conceptual cost estimates in the early stage of assessment and design. Every cost estimate involves uncertainty due to differing qualities of equipment fabrication, design differences, location, market conditions, vendor profit, and other considerations. The cost curves can be assumed to have an accuracy limited to ±25 %. Working capital, inventories, start-up expense, the cost of land, site preparation, taxes, licenses, permits, and duties are not considered in the estimation. The cost curves presented are not appropriate for benchmarking studies.

The level of uncertainty in estimation can be reduced through a detailed front-end engineering design based on site-specific information. For definitive economic comparisons and estimation, other factors such as feedstock, production specification, operating conditions, design options, and technology options must be considered.

24.10 CONCLUSIONS

Refineries operate under the physical laws and engineering specification of the system, economic principles which guide investment and operating requirements, and man-made rules governing production activities and product specifications. Complex interrelationships exist among the physical laws by which a system operates, the product demands required by the market, and the commercial rules and regulations established for the system.

Petroleum refining is a mature industry with a well-established infrastructure and technology base using a complex array of chemical and physical processing facilities. Several factors affect the business and markets are subject to continuous change. A wide variety of public data sources are available to examine the status of the industry and assess market trends. Cost data are available sporadically, are significantly less transparent and subject to more uncertainty. The quality and availability of cost data vary widely and need to be used with caution with a view to their limitations.

Investment cost functions categorized according to technology, process feedstock, product output, and capacity were constructed for the main units of a refinery. Empirical estimates were derived using a power-law relation and regression analysis and developed based on one or more process-specific variables.

REFERENCES

[1] Chernow, R., *Titan—The Life of John D. Rockefeller, Sr.*, Random House, New York, 1998.

[2] Yergin, D., *The Prize: The Epic Quest for Oil, Money and Power*, Touchstone, New York, 1993.

[3] Schobert, H.J., *Energy and Society*, Taylor and Francis, New York, 2002.

[4] U.S. Department of Energy, Energy Information Administration, *Petroleum: An Energy Profile*, EIA, Washington, DC, 1999.

[5] OSHA Technical Manual, Chapter 2, "Refining Technology," in *Petroleum Refining Processes*, U.S. Department of Labor, Occupational Safety and Health Administration, Washington, DC, 2005, Sec. IV.

[6] U.S. Department of Energy, Energy Information Administration (EIA), *Petroleum Supply Monthly*, EIA, Washington, DC, 2009.

[7] BP, *Statistical Review of World Energy 2009*, 58th ed., www.bp.com.

[8] U.S. Department of Energy, Energy Information Administration, *The U.S. Petroleum Refining and Gasoline Market Industry*, Washington, DC, 1999.

[9] Kumins, L., Parker, L., and Yacobucci, B., *Refining Capacity—Challenges and Opportunities Facing the U.S. Industry*, PIRINC, New York, 2004.

[10] Pirog, R.L., *Refining: Economic Performance and Challenges for the Future*, CRS Report for Congress, RL 32248, Congressional Research Service, Library of Congress, Washington, DC, 2005.

[11] Peterson, D.J., and Mahnovski, S., *New Forces at Work in Refining, Industry Views on Critical Business and Operations Trends*, RAND Science and Technology, Santa Monica, CA, 2003.

[12] Pratt, J.A., *The Growth of a Refining Region*, JAI Press, Greenwich, CT, 1980.

[13] O'Connor, T., "Petroleum Refineries: Will Record Profits Spur Investment in New Capacity?" Testimony before the House Government Reform Committee, Subcommittee on Energy and Resources, United States House of Representatives, October 19, 2005.

[14] ENI, *World Oil and Gas Review 2005*, 5th ed., www.eni.it.

[15] Energy Intelligence Research, *The International Crude Oil Market Handbook*, Energy Intelligence, New York, 2006.

[16] Speight, J.G., *The Chemistry and Technology of Petroleum*, 3rd ed., Marcel Dekker, New York, 1998.

[17] Ruschau, G.R., and Al-Anezi, M.A., "Petroleum Refining: Corrosion Control and Prevention," in *Corrosion Costs and Preventive Strategies in the United States, Appendix U*, U.S. Department of Transportation, Washington, DC, 2001.

[18] Bacon, R., and Tordo, S., *Crude Oil Price Differentials and Differences in Oil Qualities: A Statistical Analysis*, ESMAP Technical Paper 081, Energy Sector Management Assistance Program, Washington, DC, 2005.

[19] Gary, J.H., Handwerk, G.E., and Kaiser, M.J., *Petroleum Refining: Technology and Economics*, 5th ed., CRC Press, Boca Raton, FL, 2007.

[20] Meyers, R.A., *Handbook of Petroleum Refining Processes*, 3rd ed., McGraw-Hill, New York, 2004.

[21] Leffler, W., *Petroleum Refining in Nontechnical Language*, 3rd ed., PennWell, Tulsa, OK, 2000.

[22] National Petroleum Council (NPC), *Observations on Petroleum Product Supply*, NPC, Washington, DC, 2004.

[23] Parkash, S., *Refining Process Handbook*, Elsevier, Amsterdam, 2003.

[24] Geman, H., *Commodities and Commodity Derivatives*, John Wiley & Sons, West Sussex, UK, 2005.

[25] National Petroleum Council (NPC), *U.S. Petroleum Products Supply: Inventory Dynamics*, NPC, Washington, DC, 1998.

[26] Pirog, R.L., *World Oil Demand and Its Effect on Oil Prices*, CRS Report for Congress, RL 32530, Congressional Research Service, Library of Congress, Washington, DC, 2005.

[27] Lichtblau, J., Goldstein, L., and Gold, R., "Commonalities, Uniqueness of Oil as Commodity Explain Crude Oil, Gasoline Price Behavior," *Oil & Gas J.*, June 28, 2004, p. 18.

[28] National Petroleum Council (NPC), *U.S. Petroleum Refining: Assuring the Adequacy and Affordability of Cleaner Fuels*, NPC, Washington, DC, 2000.

[29] O'Brien J.B., and Jensen, S., "A New Proxy for Coking Margins—Forget the Crack Spread," presented at the *National Petrochemical and Refiners Association*, San Francisco, CA, March 13–15, 2005, AM-09-55.

[30] U.S. Department of Energy, Office of Industrial Technologies (OIT), *Manufacturing Energy Consumption Survey*, OIT, Washington, DC, 2004.

[31] Ocic, O., *Oil Refineries in the 21st Century*, Wiley-VCH Verlag, Weinheim, Germany, 2005.

[32] North, D., "Refinery Utilities," in A.G. Lucas, Ed., *Modern Petroleum Technology*, *Vol. 2 Downstream*, John Wiley & Sons, West Sussex, UK, 2001.

[33] U.S. Department of Energy, Office of Industrial Technologies (OIT), *Energy and Environmental Profile of the U.S. Petroleum Refining Industry*, OIT, Washington, DC, 1998.

[34] U.S. Department of Energy, Energy Information Administration (EIA), *The Impact of Environmental Compliance Costs on U.S. Refining Profitability 1995–2001*, EIA, Washington, DC, 2003.

[35] American Petroleum Institute (API), *Technology Roadmap for the Petroleum Industry*, API, Washington, DC, 2000.

[36] Speight, J.G., *Environmental Analysis and Technology for the Refining Industry*, John Wiley and Sons, New York, 2005.

[37] U.S. General Accounting Office (GAO), *Energy Markets Effects of Mergers and Market Concentration in the U.S. Petroleum Industry*, GAO-04-96, Washington, DC, 2004.

[38] U.S. Department of Energy, Energy Information Administration (EIA), *Performance Profiles of U.S. Major Producers*, EIA, Washington, DC, 2008.

[39] American Petroleum Institute (API), *U.S. Oil and Natural Gas Industry's Environmental Expenditures 1995–2004*, API, Washington, DC, 2006.

[40] *Hydrocarbon Processing Refining Handbook*, Gulf Publishing, Houston, TX, 2004.

[41] Kaiser, M.J., and Gary, J.H., "Refinery Cost Functions in the U.S. Gulf Coast," *Petrol. Sci. Technol.*, Vol. 27, 2009, pp. 168–181.

[42] Maples, R.E., *Petroleum Refining Process Economics*, 2nd ed., PennWell, Tulsa, OK, 2000.

[43] Raseev, S., *Thermal and Catalytic Processes in Petroleum Refining*, Marcel Dekker, New York, 2003.

[44] Sadeghbeigi, R., *Fluid Catalytic Cracking Handbook*, 2nd ed., Gulf Publishing, Houston, TX, 2000.

[45] Gary, J.H., and Handwerk, G.E., *Petroleum Refining: Technology and Economics*, 4th ed., CRC Press, Boca Raton, FL, 2001.

[46] Peters, M.S., Timmerhaus, K.D., and West, R.E., *Plant Design and Economics for Chemical Engineers*, 5th ed., McGraw Hill, Boston, MA, 2003.

[47] Seider, W.D., Seader, J.D., and Lewin, D.R., *Product & Process Design Principles*, John Wiley and Sons, New York, 2004.

[48] Farrar, G.L., "How Nelson Cost Indices Are Compiled," *Oil & Gas J.*, December 30, 1985, p. 145.

[49] Farrar, G.L., "Interest Reviving in Complexity Factors," *Oil & Gas J.*, October 2, 1989, p. 90.

[50] U.S. Department of Energy, Energy Information Administration (EIA), *Annual Energy Review 2008*, DOE/EIA-0384, EIA, Washington, DC, 2008.

[51] Nelson, W.L., *Guild to Refinery Operating Cost* (*Process Costimating*), 3rd ed., Petroleum Publishing, Tulsa, OK, 1976.

[52] Nelson, W.L., "How the Nelson Refinery Construction-Cost Indexes Evolved," *Oil & Gas J.*, November 29, 1976, p. 68.

[53] Nelson, W.L., "Here's How Operating Cost Indexes are Computed," *Oil & Gas J.*, January 10, 1977, p. 86.

[54] Neumuller, R., "Method Estimates U.S. Refinery Fixed Costs," *Oil & Gas J.*, September 19, 2005, p, 43.

25

Financial Risk Management in Refinery Operations Planning

Miguel Bagajewicz[1]

25.1 INTRODUCTION

Refinery planning is a procedure that requires making decisions over various aspects of operations to maximize the gross refinery margin (GRM). Among these decisions are

- Crude selection under fluctuating price scenario and using different contract forms and spot market purchases,
- Crude transportation,
- Inventory management,
- Blending of crudes for operations,
- Processing conditions of the different equipment and utility usage to match product demands in quantity and quality,
- Product transportation to final consumers, and
- Product pricing.

The input data are equipment capacities, crude oil costs, processing costs, transportation costs, product demands, crude availability, crude prices and inventory costs, among others. Other limitations such as the capacity of the utility systems are also taken into account.

These decisions, which are made running different optimization models have to be done under uncertainty and hence companies incur financial risk.

25.2 PLANNING OF THE PETROLEUM SUPPLY CHAIN UNDER UNCERTAINTY

Uncertainty was introduced in refinery planning as early as the 1990s. Bopp et al. [1] handle natural gas purchases under conditions of uncertain demand and price, and Liu and Sahinidis [2] used two-stage stochastic programming to later also suggest the use of fuzzy programming to process the planning of a petrochemical complex. Guldimann and Wang [3] presented a large mixed integer linear programming (MILP) and a much smaller nonlinear programming (NLP) approximation of the MILP involving simulation and response surface estimation via regression analysis for the optimal selection of natural gas supply contracts by local gas distribution utilities.

In general, planning models for refinery operations fall under the more general category of optimization of multiperiod supply, transformation, and distribution (STD) systems. In this line of work, Escudero et al. [4] proposed an oil company modeling framework for STD optimization under uncertain product demand, spot supply cost, and spot selling price. Hsieh and Chiang [5] developed a manufacturing-to-sale planning system to deal with uncertain manufacturing factors. Neiro and Pinto [6] extended the single refinery model of Pinto et al. [7] to a corporate planning model that contains multiple refineries in which they examined different types of crude oil and product demand scenarios. An optimization model for the supply chain of a petrochemical company operating under uncertain operating and economic conditions was developed by Lababidi et al. [8]. In this work, uncertainties were introduced in demands, market prices, raw material costs, and production yields.

Reddy et al. [9] presented the first complete continuous-time MILP formulation for the short-term scheduling of operations in a refinery that receives crude from very large crude carriers via a high-volume single buoy mooring pipeline. Their objective was to develop the model that responds effectively and speedily to uncertain oil markets while maintaining reliable operations. An iterative algorithm was used to eliminate the crude composition discrepancy. The algorithm uses MILP solutions and obtains maximum-profit schedules for industrial problems with up to 7 days of scheduling horizon.

Some fundamental approaches for scheduling under uncertainty were determined and compared by Herroelen and Leus [10]. The various approaches consist of reactive scheduling, stochastic project scheduling, fuzzy project scheduling, robust (proactive) scheduling, and sensitivity analysis. They discussed the potentials of these approaches for scheduling under uncertainty projects with deterministic network evolution structure.

Csáji and Monostori [11] presented an approximate dynamic programming-based stochastic reactive scheduler that can control the production process online instead of generating an offline rigid static plan. The stochastic scheduling problem was formulated as a special Markov decision process. Homogeneous multiagent systems were suggested in which cooperative agents learn the optimal value function in a distributed way by using trial-based approximate dynamic programming (ADP) methods. After each trial, the agents asynchronously update the actual value function estimation. Finally, benchmark experimental results that illustrate the effectiveness of the ADP-based approach are shown.

Al-Redhwan et al. [12] addressed the problem of uncertainty in optimizing water networks in process industries to be able to accommodate the changes of wastewater flow rates and level of contaminants. A three-step methodology was developed. They first generated a deterministic optimization model. This model searches for the network configuration with minimal freshwater use and optimal

---

[1] School of Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, OK, USA

wastewater reuse or regeneration-reuse. The second step involved a sensitivity analysis in which uncertainty was introduced as maximum and minimum ranges in operating conditions. Finally, a stochastic formulation was developed based on the scenario-analysis stochastic programming approach. The optimization models are NLP problems that were effectively solved using the General Algebraic Modeling System (GAMS), coupled with various commercial solvers such as Conopt, Dicopt, Minos, etc. These models were tested on a typical refinery wastewater network.

Guillén et al. [13] considered the design and retrofit problem of a supply chain (SC) consisting of several production plants, warehouses, and markets and the associated distribution systems. A two-stage stochastic model was constructed to take into account the effects of the uncertainty in the production scenario. The problem objective (i.e., SC performance) is assessed by taking into account the profit over the time horizon and the resulting demand satisfaction. Finally, the SC configurations obtained by means of deterministic mathematical programming were compared with those determined by different stochastic scenarios representing different approaches to face uncertainty.

Liao and Rittscher [14] developed a measurement of supplier flexibility with consideration of demand quantity and timing reduction uncertainties. The measurement was extended to consider the uncertainty when the demand quantity is randomly changed. In addition, a multiobjective supplier selection model under stochastic demand conditions was developed. The model was determined with simultaneous consideration of the total cost, the quality rejection rate, the late delivery rate, and the flexibility rate, which involved constraints of demand satisfaction and capacity. In turn, Al-Qahtani and Elkamel [15] addressed the robustness of the planning of multisite refinery networks under uncertainty using two-stage stochastic programming.

It is believed that the best way to effectively perform planning under uncertainty is by using a two-stage stochastic programming as originally proposed by Liu and Sahinidis [2].

25.3 FINANCIAL RISK MANAGEMENT TECHNIQUES

Ierapetritou and Pistikopoulos [16] introduced integrated metric and estimated future plan feasibility together with the potential economic risk for two-period linear planning models. The metric used is the traditional maximum regret.

Mulvey et al. [17] studied and discussed components of the asset/liability management systems of three leading international firms in the United States: Towers Perrin, Frank Russell, and Falcon Asset Management. These companies applied asset/liability management for efficiently managing risk over extended time periods by dynamically balancing the firm’s asset and liabilities to achieve their objectives. Three components of asset/liability management were compared and described: (1) a multistage stochastic program for coordinating the asset/liability decisions, (2) a scenario generation procedure for modeling the stochastic parameters, and (3) solution algorithms for solving the resulting large-scale optimization problem.

Lowe et al. [18] looked into an international sourcing/production network. They proposed and illustrated a two-phase multiscreening approach that was used to help evaluate the strategy of having production facilities using Harvard Business School as a study case. Their approach involves a relatively simple one-year-ahead analysis in phase 1, followed by a more detailed analysis in phase 2. Afterward, new criteria of stochastic comparison (i.e., Pareto optimality, near-Pareto optimality, maximum regret, mean-variance efficiency, and stochastic dominance) were introduced. At last, they illustrated how excess capacity could provide flexibility by allowing a global manufacturing firm to shift production between various production facilities as relative costs change over time.

Gupta and Maranas [19] developed a model for incorporating market-based pollution abatement instruments in the technology selection decision of a firm. Multistage stochastic programming is used to model emission and market uncertainties while accounting for the availability of derivative instruments. The instruments help minimize total pollution abatement costs and predict the environmental liability. The model quantifies the benefits of the flexibility offered by these instruments. Management of environmental and financial risks was addressed by linking the optimization model with basic statistical and probabilistic techniques.

Cheng et al. [20] presented the method of risk management using a Markov decision process with recourse that considers decision-making throughout the process life cycle at different hierarchical levels. The formulation integrates design decisions and future planning by constructing a multiperiod decision process in which one makes decisions sequentially at each period. They were concerned with the following conflicting objectives: expected profit, expected downside risk, and process lifetime. The multiobjective Markov decision problem was finally decomposed using a rigorous multiobjective stochastic dynamic programming algorithm, and the Pareto optimal design strategy was obtained.

In addition, various methods were introduced into optimization and programming models to deal with the financial risk problem. The most popular is value at risk, which was proposed by Guldimann [21] and Jorion [22].

Barbaro and Bagajewicz [23] presented a methodology to include financial risk management in the framework of two-stage stochastic programming for planning under uncertainty. They adapted a known probabilistic definition of financial risk to use it in the framework. Their method is compared with the methods that intend to manage risk by controlling the second-stage variability. One of the major contributions of their work to the field of planning under uncertainty is the formal definition of financial risk as applied to these problems. On the basis of this definition, several theoretical expressions were developed that provide new insight into the tradeoffs between risk and profitability. Thus, the cumulative risk curves were constructed to be very appropriate to visualize the risk behavior of different alternatives. Moreover, they examined the concept of downside risk, and a close relationship with financial risk was discovered. They consequently suggested that downside risk be used to measure financial risk, considering that in that way there is no need to introduce new binary variables that increase the computational burden.

Aseeri and Bagajewicz [24] presented some new concepts and procedures for financial risk management. Upside potential (UP) or opportunity value (OV) as means to weigh opportunity loss versus risk reduction as well as a risk area ratio (RAR) are introduced and discussed to complement the use of value at risk. Upper and lower bounds for risk curves corresponding to the optimal stochastic solutions were developed, the use of the sampling average algorithm was studied, and the relation between two-stage stochastic models that manage risk as well as the use of chance constraints and regret analysis was discussed. These concepts are illustrated by introducing a stochastic planning model to optimize natural gas commercialization in Asia under uncertainty.

Al-Qahtani and Elkamel [15] independently presented a two-stage stochastic approach to the multisite refinery planning. They used a technique similar to the one presented by Aseeri and Bagajewicz [24], the sample average algorithm, but they assume that variance is representative of risk, which, as we shall see below, is not recommended.

In the next section, we review the background theory of two-stage stochastic programming for decision-making under uncertainty. We specifically focus on financial risk management and the measures of financial risk as well as the techniques used to manage it.

25.4 TWO-STAGE STOCHASTIC PROGRAMMING

This kind of problem is characterized by two essential features: the uncertainty in the problem data and the sequence of decisions. Liu and Sahinidis [2] as well as Barbaro and Bagajewicz [23] review in some detail the technique as applied to decision-making in investment and operations planning.

First, some model parameters are accounted for as random variables with a certain probability distribution. In turn, some of these decisions must be made with incomplete information about the future (these are called first-stage decisions or sometimes “here and now” decisions). Then, as some of the uncertainties are unveiled, the remaining decisions are made (called second-stage or recourse decisions). An example of a first-stage decision in refinery planning is placing an order for a certain amount of barrels of a particular crude. Such crude amounts will arrive in the future and a second-stage decision is how to blend the different crudes. Quite clearly, the level of usage and the type of crude blending usage envisioned at the time of the order is different from how the actual blending is performed later.

Among the two-stage stochastic models, the expected value of the cost (or profit) resulting from optimally adapting the plan according to the realizations of uncertain parameters is referred to as the recourse function. Solving this kind of model involves maximization or minimization of expected profits or expected cost. Expectations are obtained by representing uncertainties through several scenarios constructed via sampling.

The general form of a two-stage linear stochastic problem with fixed recourse and a finite number of scenarios (s) can be defined by Birge and Louveaux [25] as follows:

$$\left.\begin{array}{l} Max\ \mathrm{E}[Profit] = \sum_{s\in S} p_s q_s^{\mathrm{T}} y_s - c^{\mathrm{T}} x \\ \text{such that} \\ \qquad Ax = b \\ \quad T_s x + W y_s = h_s \quad s \in S \\ \\ \qquad x \ge 0 \quad x \in X \\ \qquad y_s \ge 0 \quad \forall s \in S \end{array}\right\} \tag{25.1}$$

In the above model, first-stage decisions are represented by variable x and second-stage decisions are represented by variable y_s, which has probability p_s. The objective function contains a deterministic term, $c^{\mathrm{T}}x$, and the expectation of the second-stage objective, $q_s^{\mathrm{T}}y_s$, taken over all realizations of the random event s. For a given realization of the random events, $s \in S$, the second-stage problem data q_s, h_s, and T_s become known, and then the second-stage decisions, $y_s(\mathrm{x})$, must be made.

The different scenarios are composed of instances of the uncertain parameters obtained by sampling the distributions. So far, this sampling was made assuming that the variables are independent; that is, each variable was sampled using its own distribution and no joint distributions were used. As this technique finishes its migration to industrial practice, better sampling methods and better assessment of joint parameter distributions will be needed. One such effort in the right direction was made by Park et al. [26], who used the geometric Brownian motion (GBM) stochastic oil price model [27,28]. In addition they used the well-known Black and Scholes equation, which underlies the assumption of the GBM.

25.5 FINANCIAL RISK

According to Barbaro and Bagajewicz [23], the financial risk related to a planning project can be defined as the probability of not meeting a certain acceptable targeted profit (when cost is minimized the target is a certain high cost). Several alternative point measures have also been used. For this, cumulative probabilities of profit are used. Once problem 25.1 is solved, one typically fixes the first-stage variable (x), which means that one has made the first-stage decisions, and then one can solve the following problem:

$$\left.\begin{array}{l} Max\ Profit(s) = q_s^{\mathrm{T}} y_s - c^{\mathrm{T}} x^* \\ \text{such that} \\ \qquad Ax = b \\ \quad T_s x^* + W y_s = h_s \quad s \in S \\ \\ \qquad y_s \ge 0 \quad \forall s \in S \end{array}\right\} \tag{25.2}$$

where x^* is the (now fixed) first-stage set of decisions. We note that the model is solved for each scenario. Because each scenario s has a probability $p(s)$, it is easy to make a histogram and obtain the probability distribution of profits ($f(x,\xi)$).

Originally, the models for robust planning under uncertainty [17] used the variance of the cost as a "measure" of the robustness of the plan (i.e., less variance corresponds to higher robustness), which was later also used to reduce risk. This practice is of value when the distributions of profit are symmetric, but it presents some problems otherwise. Thus, alternative definitions of risk, which look at only one side (the downside) of the distribution, were proposed.

We call the risk curve the cumulative probability curve corresponding to $f(x,\xi)$ (Figure 25.1). Thus, the risk of not making a certain aspiration level of profit, Ω, is given by the corresponding cumulative probability. Therefore, one formally writes $Risk(\Omega) = \mathrm{p}_{\Omega}$.

Another measure of risk is the downside risk introduced by Eppen et al. [29]. Unlike the risk, which is a probability, the downside risk is measured in dollars ($). This measure is defined as the integral of the profit positive deviations from the aspiration level $DRisk(x,\Omega)=\int_{-\infty}^{\Omega}(\Omega-\xi)f(x,\xi)d\xi$, where $\delta_s(x,\Omega)=Max\{\Omega-Profit_s(x),0\}$. For discrete scenarios, we write $DRisk(x,\Omega)=\sum_{s\in S}p_s\delta_s(x,\Omega)$. It was shown that the downside financial risk is equal to the area below the risk curve to the left of Ω (i.e., $DRisk(\Omega)=\int_{-\infty}^{\Omega}\zeta\, Risk(\zeta)d\zeta$) [23]. This is illustrated in Figure 25.2.

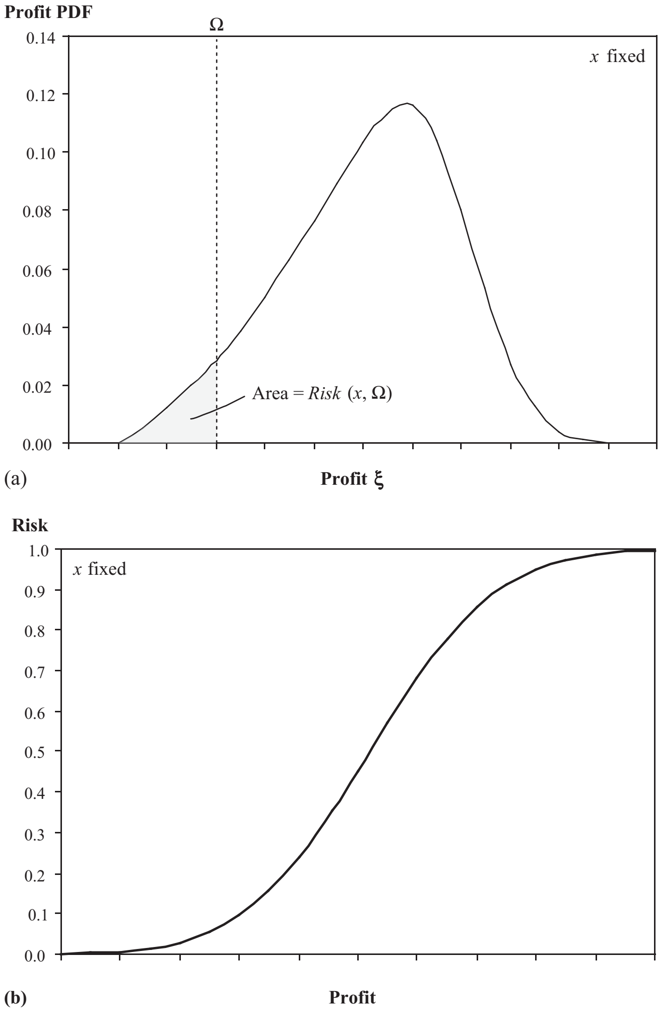


Figure 25.1—(a) Distribution of profits. (b) Risk curve: cumulative distribution.

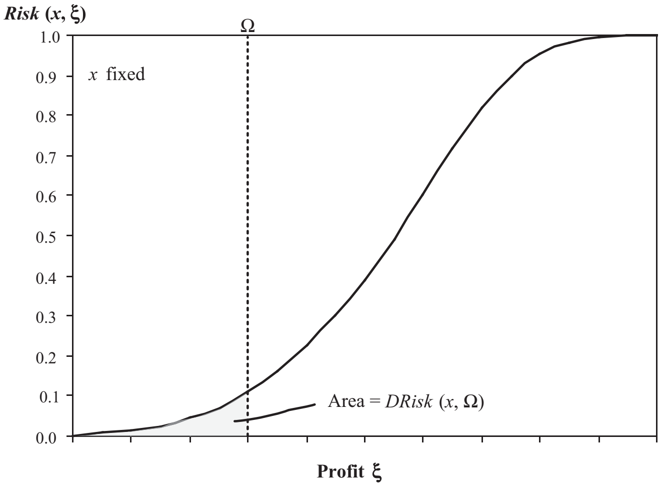


Figure 25.2—Probabilistic interpretation of downside risk.

The above two measures have the disadvantage that one needs to define an aspiration level to obtain a risk. Alternative measures that do not make use of an aspiration level are upper partial mean [30], the very popular value at risk [22], and the area ratio [24].

The upper partial mean (UPM) is defined as the integral of all negative deviations from the mean value; that is, $UPM=\int_{-\infty}^{\bar{P}}p(\varepsilon)\Delta(\varepsilon)d\varepsilon$, where $\bar{P}=\int_{-\infty}^{\infty}\varepsilon p(\varepsilon)d\varepsilon$ is the average profit and $\Delta_s=\bar{P}-q_s^Ty_s$. For discrete scenarios $UPM=\sum_{s\in S}p_s\Delta_s$, $\bar{P}=\sum_{k\in s}p_kq_k^Ty_k$, and $\Delta_s=\max\{0;\bar{P}-q_s^Ty_s\}$. Quite clearly, this is similar to downside risk, except that the aspiration value is the mean value.

In turn, value at risk (VaR) is defined as the expected loss for a certain confidence level usually set at 5 % [22]. A more general definition of VaR is given by the difference between the mean value of the profit and the profit value corresponding to the p-quantile (value at p risk). VaR has been used as a point measure very similar to the variance; it usually measures the deviation of the profit at 5 % risk from the expected value.

Aseeri and Bagajewicz [24] proposed that VaR be compared to a similar measure, the UP (upside potential) or OV (opportunity value), defined in a similar way to VaR but at the other end of the risk curve with a quantile of $(1-p)$ as the difference between the value corresponding to a risk of $(1-p)$ and the expected value (see Figure 25.3). They discussed the need of the UP for a good evaluation of the project.

To ameliorate the fact that VaR and UP are point measures that do not represent the behavior of the entire risk curve but only its values at certain points, Aseeri and Bagajewicz [24] proposed the risk area ratio (*RAR*). This ratio requires the use of the maximum expected profit risk curve (defined by x^*) and any other alternative one (defined by x') that is evaluated. This area ratio is calculated as the ratio of the opportunity area (*O_Area*), enclosed by the aforementioned two curves above their intersection, to the risk area (*R_Area*), enclosed by the two curves below their intersection (see Figure 25.4).

$$RAR=\frac{O\_Area}{R\_Area} \tag{25.3}$$

Note that this is only true if the second curve is minimizing risk in the downside region. If risk on the upside is to

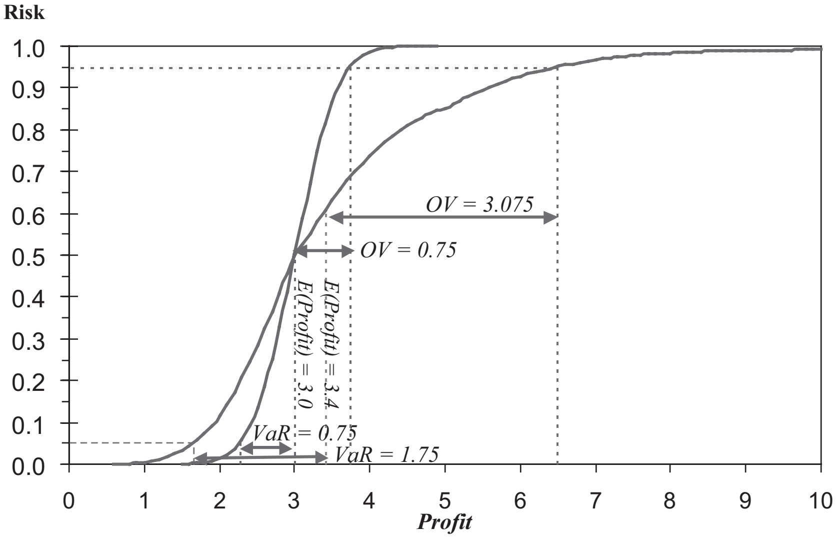


Figure 25.3—Upside potential (*UP*) or opportunity value (*OV*) versus value at risk (*VaR*).

be minimized, then the relation is reversed (i.e., *O_Area* is below the intersection and *R_Area* is above it).

The UPM and VaR can be used as measures of robustness, but they have limitations that make them inappropriate measures to manage financial risk within an optimization model. Although it has not been demonstrated formally, there are reasons that support the idea that the area ratio is the same. The reason relies on the fact that the nonoptimal second-stage decision would be chosen. Because of the way the UPM is defined, a solution may falsely reduce its variability just by not choosing optimal second-stage decisions. Making nonoptimal second-stage decisions reduces the expected profit, allowing the positive deviation between the expected second-stage profit and the profit for that scenario (Δ_s) to be zero for some scenarios that otherwise would have a profit lower than the actual expected value and therefore $\Delta_s > 0$. Because nobody would want to obtain a lower profit when a higher value is already attainable, operating with nonoptimal second-stage policies does not make any sense from a financial point of view. This is discussed in detail by Takriti and Ahmed [31], who present sufficient conditions for the variability measure of a robust optimization to ensure that the solutions are optimal in profit.

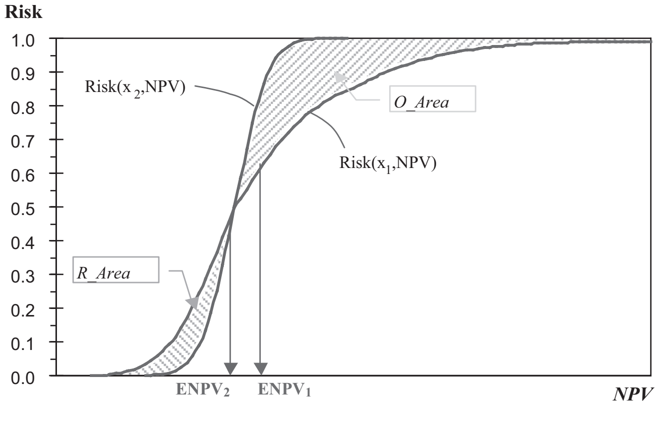


Figure 25.4—Risk area ratio. *Source:* [24].

Although they should not be incorporated in models that simultaneously compute and manage financial risk, the UPM, VaR, and the area ratio can be efficiently used to assess financial risk.

Earlier perspectives to evaluate risk include the work of Ierapetritou and Pistikopoulos [16], who proposed to use regret functions as an indirect measure of financial risk. For any realization of uncertain parameters, the regret function measures the difference between the objective function resulting from the actual plan or design and the plan that is optimal for that realization of uncertain parameters. The idea is then to find plans that have low regret for the set of feasible uncertain parameters. This approach has two major difficulties. First, financial risk is only evaluated indirectly because the regret functions only measure the potential losses of the actual plan in comparison with a hypothetical plan that is optimal only for a specific uncertainty realization (no information is given about the feasibility of that plan under other circumstances). Thus, the regret functions do not provide any information about the financial risk. The second disadvantage of this approach is that to construct each regret function a separate optimization problem has to be solved for each possible uncertainty realization. This greatly increases the computational complexity of the problems.

An alternative approach, recently suggested by Cheng et al. [20], is to rely on a Markov decision process modeling the design/production decisions at each epoch of the process as a two-stage stochastic program. The Markov decision process used is similar in nature to a multistage stochastic programming in which structural decisions are also considered as possible recourse actions. Their solution procedure relies on dynamic programming techniques and is applicable only if the problems are separable and monotone. In addition, they proposed to depart from single objective paradigms and use a multiobjective approach rightfully claiming that cost is not necessarily the only objective and that other objectives are usually also important, such as social consequences, environmental impact, process sustainability, etc. Among these other objectives, they include risk (measured by downside risk, as introduced by Eppen et al. [29]), which under the assumption that decision-makers are risk-averse, they claim it should be minimized. Although some level of risk could be tolerable at low profit aspirations to get larger gains at higher ones, thus promoting a risk-taking attitude, this assumption has some important additional limitations. As will become apparent later in this chapter, because downside risk is not only a function of the first-stage decisions but also of the aspiration or target profit level, minimizing downside risk at one level does not imply its minimization at another. Moreover, minimizing downside risk does not necessarily lead to minimizing financial risk for the specified target. Thus, treating financial risk as a single objective presents some limitations, and we propose that risk be managed over an entire range of aspiration levels.

Applequist et al. [32] proposed to manage risk at the design stages by using the concept of risk premium. They observed that for various investments, the rate of return correlates linearly with the variability. The coefficient of such dependence is called risk premium. On the basis of this observation, they suggest benchmarking new investments against the historical risk premium mark. Thus, they propose a two-objective problem in which the expected net present value and the risk premium are maximized. The technique relies on using the variance as a measure of variability and therefore it equally penalizes/rewards scenarios at both sides of the mean, which is the same limitation that is discussed above. Finally, Li et al. [33] make use of chance constraints, which have been shown to be less efficient than two-stage stochastic programming—in fact, a special case of it as proved by Aseeri and Bagajewicz [24].

25.6 COMPUTATIONAL APPROACHES

The scenarios need to be generated using appropriate sampling procedures. The simple approach is to treat the uncertain parameters as independent, which allows for simple sampling procedures once their distribution is known. However, in many cases, the variables are not statistically independent; for example, in the case of demands and prices, there are trends they follow in time, etc. To this date, although many of these problems can be efficiently sorted through standard statistical procedures, the direct application to data related to refinery planning has not merged the academic and practical efforts.

The solution of problem 25.1 directly as it is posed presents some computational challenges, even for this linear formulation. Indeed, a reasonably small number of scenarios is approximately 200, and this gives rise to optimization problems containing thousands of second-stage variables. To address this issue a special decomposition algorithm was used—the sampling algorithm as presented by Verweij et al. [34].

In the sampling algorithm, the deterministic model is run for each scenario. After these solutions are obtained, the first-stage variables of each of these solutions, called "designs," are fixed, and the deterministic model is run with them fixed for all of the scenarios again. Thus, each of these runs performed with the first-stage variables fixed provides a profit for each scenario from which a risk curve can be constructed. The result tends asymptotically to such optimum, which was proven by Aseeri and Bagajewicz [24]. Once all risk curves are generated the curve with the highest expected gross refinery margin (EGRM) is chosen. The curves that are dominated by this highest EGRM (completely to the left of the highest EGRM curve) are disregarded and the others (nondominated curves) are selected as alternative solutions (Figure 25.5)

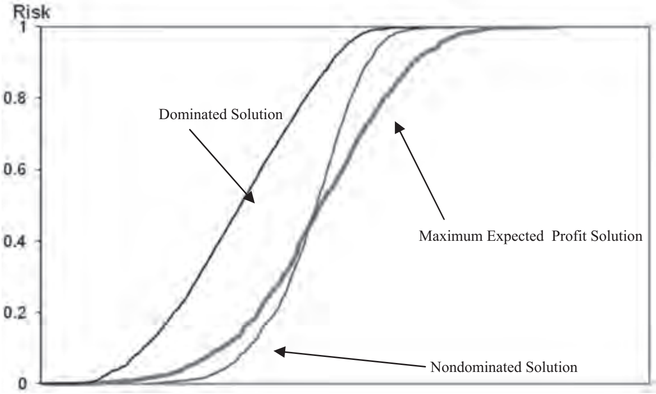


Figure 25.5—Maximum expected solution, dominated and nondominated solutions.

In addition, Aseeri and Bagajewicz [24] proposed the construction of an upper bound curve. The upper bound risk curve is defined as the curve constructed by plotting the set of net present values (NPV) for the best design under each scenario (i.e., by using all "wait and see" solutions). Figure 25.6 shows the upper bound risk curve and curves corresponding to possible and impossible solutions. The risk curve for any feasible design is positioned entirely above (to the left of) the upper bound risk curve [24].

25.7 PRICING

Consumer behavior is best understood as having two components: preferences for certain products independent of price and budget constraints that make them most of the time buy less preferred products. On the basis of this information, one can put consumer preferences and budget constraints together to determine consumer choices. This is a well-established theory [35,36].

Bagajewicz [37] presented a methodology that puts together a price-demand-preferences relationship that is based on a constant elasticity of substitution model with

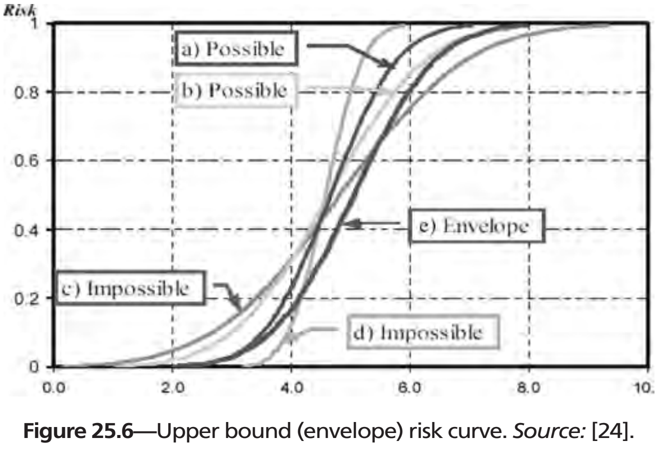


Figure 25.6—Upper bound (envelope) risk curve. *Source:* [24].

a profit-based model that determines the right product qualities that maximize profit. Usually these qualities are not those corresponding to the most preferred product. Lakkhanawat and Bagajewicz [38] used the following two expressions for the price demand relationships:

$$p_1(d_1)^{1-\rho} = \left(\frac{\alpha}{\beta}\right)^{\rho} p_2 \left[\frac{Y - p_1 d_1}{p_2}\right]^{1-\rho} \tag{25.4}$$

$$(d_1)^{1-\rho} = \left(\frac{\beta}{\alpha}\right)^{\rho} (D - d_1)^{1-\rho} \tag{25.5}$$

In these models, d_1 and d_2 are the demand of the refinery's product and that for the competition's same products, p_1 is the refinery product selling price and p_2 is that of the competitor, Y is the consumer budget, D is the maximum possible demand, and ρ is a parameter related to the elasticity of substitution. Finally, the parameter β is a measure of how much a consumer prefers product 1 to product 2 and α is a measure of how much the consumer population is aware of the quality of product 1.

Lakkhanawat and Bagajewicz [38] used α and β to be equal to 1; that is, consumers are equally aware of all products and they have no specific preferences. This is usually (not always) the public attitude toward refinery products, resulting in a purchasing decision that is based on budget and price.

Both are derived using the constant elasticity of substitution model slightly modified to include hedonic and information constraints [37]. The first correspond to the case in which the budget of the consumers (Y) is binding; that is, the consumer reaches the limit of the budget allocated to the product. The second is when the budget exceeds the purchasing needs.

25.8 CASE STUDIES

Because the technique is starting to popularize, there are only a few articles discussing financial risk in refinery operations. Pongsakdi et al. [39] were the first to apply the two-stage stochastic framework to financial risk management in refinery operations. They considered crude purchases as the first-stage decisions under uncertain product demands and prices. The second-stage decisions are the existing purchased crude blending and the flows through the different units to meet the demands. Later, Lakkhanawat and Bagajewicz [38] extended the model to include decisions on product pricing. In both cases, the refinery model used is linear; that is, the yields of the different units are constant. To this date, only one nonlinear model (in which the yields of the different units are variable) that includes financial risk management has been developed by Bagajewicz and Uribe [40]. Very recently, Park et al. [26] applied the technique to consider long-term contracts as first-stage variables. Their second-stage decisions are spot and future contracts as well as the flow through units. The uncertainty is only in the crude and product prices. We comment on the results of the work of Lakkhanawat and Bagajewicz [24] and we later briefly discuss the work of Bagajewicz and Uribe [40], who showed how to use a commercial software to perform financial risk management.

25.9 COMPARISONS WITH PRICING MODELS

Lakkhanawat and Bagajewicz [24] showed the differences between deterministic models with and without pricing. They also showed the advantage of stochastic models with and without pricing.

Figure 25.7 shows a simplified scheme of the refinery. It has two atmospheric distillation units (CDU2 and CDU3), two naphtha pretreating units (NPU2 and NPU3), one light naphtha isomerization unit (ISOU), two catalytic reforming units (CRU2 and CRU3), one kerosine treating unit (KTU), one gas oil hydrodesulfurization (GO-HDS), and one deep gas oil hydrodesulfurization (DGO-HDS). The products are liquefied petroleum gas (LPG), gasoline RON 91 (SUPG), gasoline RON 95 (ISOG), jet fuel (JP-1), high-speed diesel (HSD), fuel oil 1 (FO1), fuel oil 2 (FO2), and low-sulfur fuel oil (FOVS). Fuel gas (FG) and some amount of FOVS produced from the process are used as an energy source for the plant. There are three product pools for blending products: gasoline pool (GSP), diesel pool (DSP), and fuel oil pool (FOP).

There are six crude oil types for feeding the refinery: Oman, Tapis, Labuan, Seria Light, Phet, and Murban. The refinery produces eight commercial products (LPG, SUPG, ISOG, JP-1, HSD, FO1, FO2, and FOVS) using two crude distillation units (CDU2 and CDU3) and six productive units (NPU2, NPU3, CRU2, CRU3, ISOU, GO-HDS, DGO-HDS, KTU). Data of all units and commodities (crude oils, intermediates, and products), their availability, demands and prices, as well as the production yields and unit capacity can be found in the original article. Finally, the maximum plant production capacity is 120 kbbl/day, the horizon plan has three periods, and some small restrictions are added.

The demand in each period was considered to be satisfied by the production. Uncertainty was introduced in market demand and price for the general stochastic model without pricing. For the model with pricing decision added, uncertainty was taken into account in consumer budget and the total demand of each product.

Results of the general deterministic model using mean values show a GRM of $9.574 million (U.S.) using 754 variables and 655 constraints. Details are given in Table 25.1.

From the general deterministic model result, Crude LB, PHET, and MB are purchased at the maximum available quantity. Crude PHET is fed to CDU2 only because of the limitation of unit. In addition PHET is not suitable for the production of FO1 and FO2 (low pour point fuel oil) from CDU3 because it has the high pour point and low viscosity factor at 50°C (V50) in the fuel oil portion. The smallest amount of crude oil used is that of TP crude because of its highest cost. It is chosen in time period 2 because of the higher product price in this period.

When pricing is introduced, the optimal set of first-stage decisions changes. For the pricing model, we also chose an elasticity of substitution $\sigma_{ES} = -1$, which leads to equal demands for equal prices. In fact, our formula simplifies to the very well known $p_1 d_1 = p_2 d_2$. Other values of ρ can be used if the elasticity is better determined. For example, it is a well-known fact that different motor fuels have different degrees of elasticity. This ought to slightly change the results of our example without altering the main

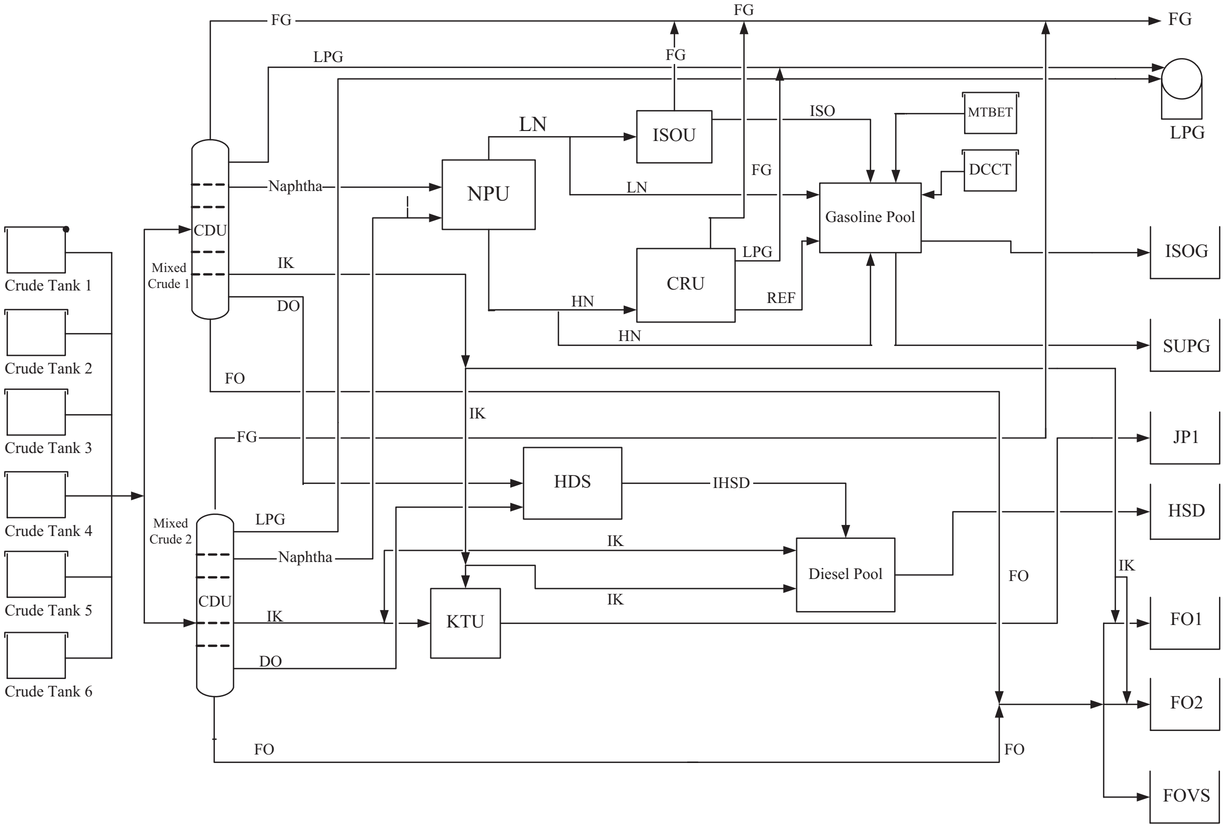


Figure 25.7—Refinery flow diagram.

message (that pricing has a big influence in planning). The competition product prices, the total demand of product, and the consumer budgets with their standard deviations are shown in the original paper. The results of crudes to purchase are shown in Table 25.2. Resulting prices and corresponding demands are shown in the original paper. Finally, an EGRM of $10.712 million (U.S.) is predicted. Because of the price manipulations, this result is not surprisingly higher than the one without pricing.

The stochastic model takes into account the uncertainty in demand and price of products and was solved using 200 scenarios. The demand and price were randomly generated independently by sampling from normal distributions [39]. Results of purchased oil (first-stage decision) are shown in Table 25.3.

The stochastic model with pricing decisions takes into account that the total demand of products and the consumer budget are uncertain. The volume of petroleum purchased of this model is shown in Table 25.4.

Figure 25.8 shows the risk curves of the stochastic solution and the deterministic solution. The stochastic solution is the highest EGRM taken from all solutions obtained.

TABLE 25.1—Oil Purchased from the Deterministic Model without Pricing

Crude Oil	Available Quantity	Period 1 (m³)	Period 1 (%)	Period 2 (m³)	Period 2 (%)	Period 3 (m³)	Period 3 (%)
OM	No limit	176,065	36.30	211,937	37.03	117,966	29.63
TP	No limit	0	0.00	17,004	2.97	0	0.00
LB	95,392	95,392	19.67	95,392	16.67	95,392	23.96
SLEB	95,392	60,938	12.56	95,392	16.67	95,392	23.96
PHET	57,235	57,235	11.80	57,235	10.00	57,235	14.38
MB	95,392	95,392	19.67	95,392	16.67	32,158	8.08
Total		485,022	100.00	572,353	100.00	398,143	100.00
Total (kbbl/day)		101.69		120.00		83.47	
GRM	$9.574 million (U.S.)						

TABLE 25.2—Oil Purchased from the Deterministic Model with Pricing

Crude Oil	Available Quantity	Period 1		Period 2		Period 3	
		(m^3)	(%)	(m^3)	(%)	(m^3)	(%)
OM	No limit	175,969	36.1235	211,937	37.0291	117,965	29.629
TP	No limit	0	0	17,004	2.97094	0	0
LB	95,392	63,144	12.9623	95,392	16.6667	95,392	23.9593
SLEB	95,392	95,392	19.5824	95,392	16.6667	95,392	23.9593
PHET	57,235	57,235	11.7494	57,235	10	57,235	14.3756
MB	95,392	95,392	19.5824	95,392	16.6667	32,157	8.07679
Total		487,133	100	572,353	100	398,142	100
Total (kbbl/day)		102.13		120.00		83.47	
GRM	$10.712 million (U.S.)						

TABLE 25.3—Oil Purchased from the Stochastic Model without Pricing

Crude Oil	Available Quantity	Period 1		Period 2		Period 3	
		(m^3)	(%)	(m^3)	(%)	(m^3)	(%)
OM	No limit	211,937	37.03	211,937	37.03	126,125	30.29
TP	No limit	17004.3	2.97	17,004	2.97	0	0.00
LB	95,392	95,392	16.67	95,392	16.67	95,392	22.91
SLEB	95,392	95,392	16.67	95,392	16.67	95,392	22.91
PHET	57,235	57,235	10.00	57,235	10.00	57,235	13.75
MB	95,392	95,392	16.67	95,392	16.67	42,202	10.14
Total		572,353	100	572,353	100	416,347	100
Total (kbbl/day)		120		120		87.29	
GRM	$15.131 million (U.S.)						

TABLE 25.4—Oil Purchased from the Stochastic Model with Pricing

Crude Oil	Available Quantity	Period 1		Period 2		Period 3	
		(m^3)	(%)	(m^3)	(%)	(m^3)	(%)
OM	No limit	207,796	37.40	211,937	37.03	105,350	26.41
TP	No limit	4,422	0.80	17,004	2.97	12,857	3.22
LB	95,392	95,392	17.17	95,392	16.67	95,392	23.92
SLEB	95,392	95,392	17.17	95,392	16.67	95,392	23.92
PHET	57,235	57,235	10.30	57,235	10.00	57,235	14.35
MB	95,392	95,392	17.17	95,392	16.67	32,601	8.17
Total		555,630	100	572,353	100	398,828	100
Total (kbbl/day)		116.49		120.00		83.62	
GRM	$8.049 million (U.S.)						

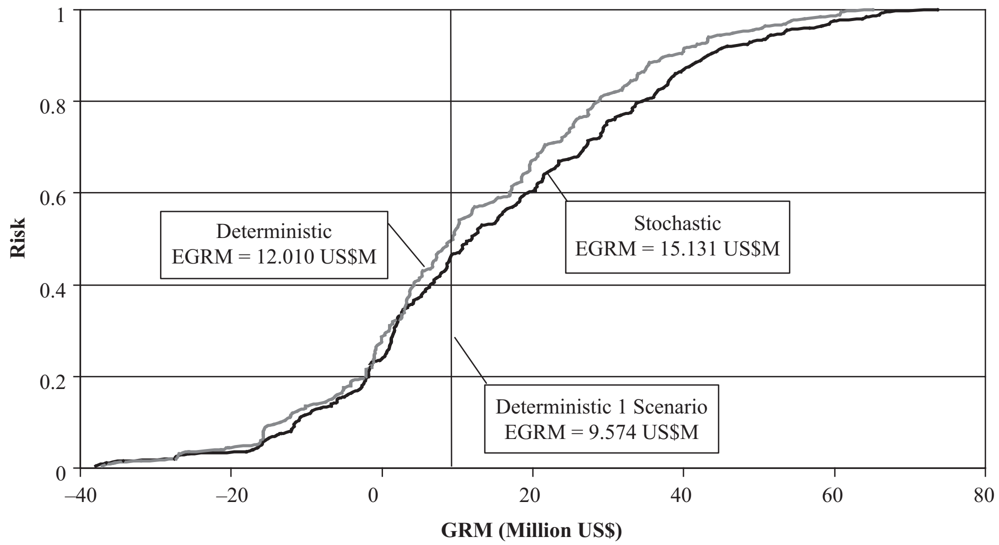


Figure 25.8—Risk curves of the deterministic and stochastic model solutions without pricing.

The deterministic risk curve is constructed by running the stochastic model under each scenario with the first-stage variable fixed to that of the deterministic model result. The EGRM obtained from the deterministic model under 200 scenarios of uncertain parameters is different from that of the deterministic model using mean values. This is an indication of the nonsymmetric nature of the distributions obtained. Finally, the deterministic solution provides a lower EGRM than the stochastic solution but a slightly higher risk.

The solutions shown in Table 25.4 suggest the higher amount of crude oil purchased in time period 1. The types of crude oil purchased from the stochastic pricing model are the same as those from the deterministic pricing model. From the results, TP is selected in time period 1 and 3 because of the higher demand of fuel oil in time period 1 and high-speed diesel in time period 3. This is because TP gives the high fraction in fuel oil and diesel oil intermediates. The solution obtained by the deterministic model using the mean values of total demand of product and consumer budget is evaluated against the same scenarios of the stochastic model by fixing the first-stage variables (amount of crude oil purchased) and computing the second-stage ones with the stochastic formulation. The risk curve of the deterministic pricing model against all scenarios is compared with the risk curve of the stochastic pricing model as shown in Figure 25.9. This plot shows that the stochastic solution provides a higher expected GRM than the deterministic solution. In addition, the stochastic model provides a solution with lower risk of negative margin.

The EGRM suggested by the stochastic planning model with pricing is lower than that of the stochastic model without pricing. This is because of the difference in how

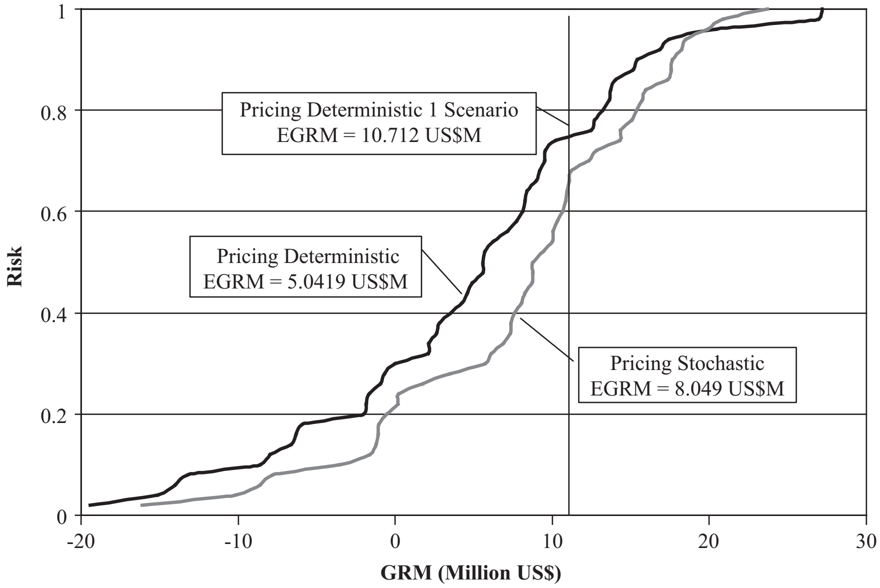


Figure 25.9—Risk curves of the deterministic and stochastic pricing model solutions.

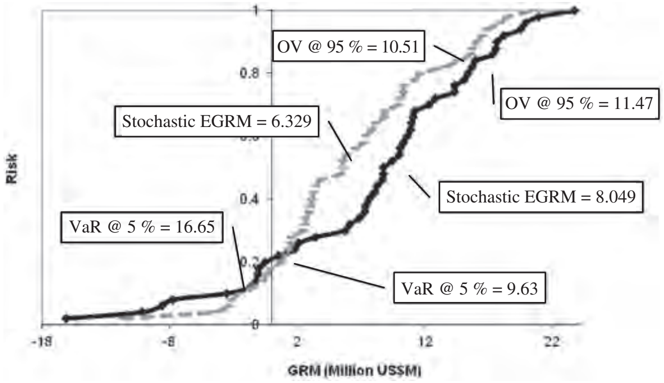


Figure 25.10—Risk curves of the stochastic pricing solution and one alternative (less risky) solution.

the demand and price of product are generated. In the general stochastic model, demand and price of product are generated independently for each scenario as the uncertain parameters and are usually considered independent. However, in the stochastic model with pricing, the demand and price are model variables that are related.

25.10 FINANCIAL RISK MANAGEMENT

Although stochastic models optimize the total expected GRM, they do not provide any control of their variability over the different scenarios; that is, they assume that the decision-maker is risk neutral. Different attitudes toward risk may actually be encountered. In this section, approach to manage financial risk is applied to compare the results.

The alternative plan that can reduce risk was considered. Figure 25.10 shows the risk curves of this plan compared with the stochastic solution. This plan suggests a lower amount of crude oil purchased in time period 1 and 3 as shown in Table 25.5.

From Figure 25.10, decreasing the crude oil purchased resulted in lower risk at low targets but with a lower chance to make a higher profit. VaR (at 5 %) and OV (at 95 %) for the two curves in Figure 25.10 are shown in Table 25.6. The VaR of the alternative plan reduces from 16.65 of the stochastic solution to 9.63 or 42 %, but the OV is also reduced from 11.47 to 10.51 or 8 %. Therefore, this plan may be preferred by a risk-averse decision-maker.

TABLE 25.6—Value at Risk and Opportunity Value for the Alternative Solution with Lower Risk

Plan	VaR (5 %)	OV (95 %)
Stochastic solution	16.65	11.47
Alternative solution	9.63	10.51

The alternative plan that suggests a higher OV was also considered. Figure 25.11 shows the risk curves of the alternative plan with a higher opportunity of profit compared with the stochastic solution. The amount of crude oil purchased corresponding to this alternative plan is shown in Table 25.7.

The alternative plan has an OV of 14.15, much higher than the 11.47 of the stochastic solution with pricing. It increases approximately 23 %. The VaR of the alternative design also increases from 16.65 to 17.44 or 4.7 %. The VaR and OV of this alternative plan are shown in Table 25.8. This alternative solution with higher opportunity of profit may be preferred by the risk-taker decision-makers who prefer a higher chance of getting higher profit.

Finally, Figure 25.12 shows the upper bound risk curve compared to the risk curves of the stochastic solution and the two alternative plans. The stochastic solution curve and both alternative curves are entirely positioned on the left side of the upper bound risk curve, as expected. The position of the upper bound also indicates that there could be room for solutions with smaller VaR, but not so much room for solutions with higher OV.

25.11 USE OF COMMERCIAL SOFTWARE

Most commercial models (PIMS, RPMS, PETRO, etc.) perform refinery planning under deterministic conditions; that is, they do not consider uncertainty in process, demands, refinery parameters, etc., and as a consequence, they are unable to perform risk management.

TABLE 25.5—Oil Purchased from the Stochastic Model with Pricing for an Alternative (Less Risky) Solution

Crude oil	Available Quantity	Period 1		Period 2		Period 3	
		(m³)	(%)	(m³)	(%)	(m³)	(%)
OM	No limit	169,801.15	36.31	211,937.01	37.03	132,318.95	35.44
TP	No limit	0.00	0.00	17,004.28	2.97	0.00	0.00
LB	95,392	95,392.20	20.40	95,392.20	16.67	22,752.17	6.09
SLEB	95,392	49,767.31	10.64	95,392.20	16.67	95,392.20	25.55
PHET	57,235	57,235.32	12.24	57,235.32	10.00	57,235.32	15.33
MB	95,392	95,392.20	20.40	95,392.20	16.67	65,678.77	17.59
Total		467,588.18	100	572,353.21	100	373,377.41	100
Total (kbbl/day)		98.03		120.00		78.28	
GRM	6.329 US$M						

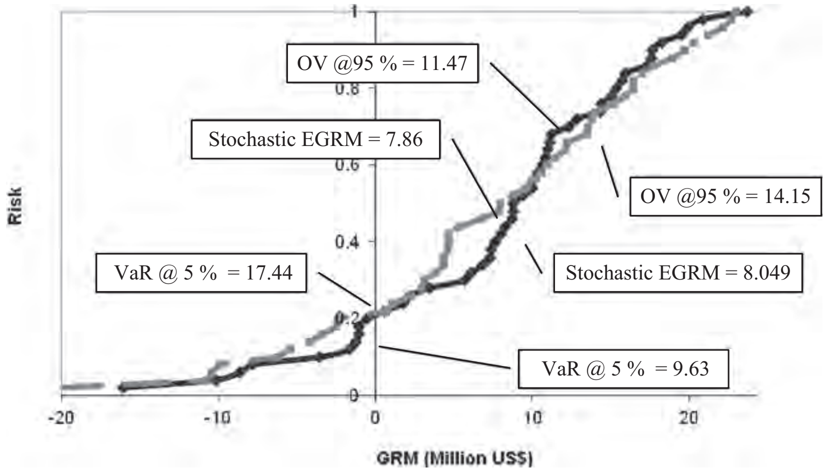


Figure 25.11—Risk curves of the stochastic pricing solution and the alternative solution with higher opportunity value (OV).

Bagajewicz and Uribe [40] showed that all of this procedure can be implemented using commercial software. They used PIMS' sample model PVOLSAMP [41]. This model is a volume-based multiperiod model of a 100,000-bbl/day refinery that has the following process units: two atmospheric distillation units (CDU1, CDU2, and CDU3) and three operational modes, one naphtha splitter (NSP) and a naphtha hydrotreater (NHT), one low-press reformer (LPR), one kerosine (KHT) and a distillate hydrotreater (DHT), one catalytic cracking unit (CCU), one butane isomerization (IS4), one sulfuric acid alkylation (SFA), one hydrocracker distillate, one delayed coking (DLC), one delayed coking multipath (DCX), one hydrogen plant (HYD), one plant fuel system (PFS), one amine sulfur removal unit (AMN), one sulfur recovery unit (SRU), one tail gas treating unit (TGT), one saturate gas plant (SGP), unsaturated gas plant (UGP), one utility generation unit, and products blending. The goal of the refinery is to make the following products: LPG, unleaded regular gasoline (URG), unleaded premium gasoline (UPR), leaded regular gasoline (LRG), kerosine/jet (JET), diesel (DSL), low-sulfur fuel oil (LSF), high-sulfur fuel oil (HSF), coke (coke), and crude atmospheric residue (ATB). The CDU1 and CDU2 can operate to obtain fuels, and the CDU2 is operated to get lube. The blended product specifications are shown in the original article.

The decision variables we consider are crude oil purchase decisions, process unit operation parameters and internal flows, inventory management, and blending over time periods. The values of crude costs and product prices were taken from historical data published by the United States energy information administration webpage (http://www.eia.doe.gov/). The following data between parentheses indicate the maximum demand and standard deviation for products: LRG (5.00, 0.34), URG (45.00, 3.09), UPG (200.00, 8.00), Kero/JET (10.00, 1.31), diesel (22.00, 2.88), HSF (5.50, 0.33), and ATB (1.20, 0.07).

The deterministic optimization model (2281 constraints and 2317 variables) was run using mean values. Results show a GRM of $301 million (U.S.) per 3-month period with less than 30 s of execution time on a workstation M65 (Intel Core 2, 2 GHz, 2 GB RAM). We then solved the stochastic model using our procedure. To compare, we then take the deterministic solution and evaluate its

TABLE 25.7—Oil Purchased by the Alternative Solution with Higher Opportunity Value

Crude Oil	Available Quantity	Period 1		Period 2		Period 3	
		(m³)	(%)	(m³)	(%)	(m³)	(%)
OM	No limit	181,862.96	36.17	212,345.86	37.10	123,206.99	32.38
TP	No limit	0.00	0.00	16,595.42	2.90	0.00	0.00
LB	95,392	72,933.12	14.50	95,392.20	16.67	56,023.10	14.72
SLEB	95,392	95,392.20	18.97	95,392.20	16.67	95,392.20	25.07
PHET	57,235	57,235.32	11.38	57,235.32	10.00	57,235.32	15.04
MB	95,392	95,392.20	18.97	95,392.20	16.67	48,667.57	12.79
Total		502,815.80	100	572,353.20	100	380,525.17	100
Total (kbbl/day)		105.42		120.00		79.78	
GRM	7.863 US$M						

TABLE 25.8—Value at Risk and Opportunity Value for the Alternative Solution with Higher Opportunity Value

Plan	VaR (5 %)	OV (95 %)
Stochastic solution	16.65	11.47
Alternative solution	17.44	14.15

performance over the 600 scenarios used. The uncertain parameters are crude oil cost, products demand, and prices. We assume that this information is a forecast and it is available as a probability density function.

After implementing the procedure, the downside risk and VaR (at 5 %) are computed. Figure 25.13 shows the risk curves for the best stochastic solution and the performance of the deterministic solution.

Results indicate that the stochastic solution has an expected GRM of $411 million, a significant increase over the deterministic value. When the decisions of the deterministic model are evaluated over the uncertainty space, the expected GRM is $397 million.

25.12 CONCLUSIONS

Refinery planning under uncertain conditions has just left academic circles and is starting to make its way into industrial practice. In this chapter, we showed how refinery planning models incorporating pricing are able to manage risk and make more accurate predictions as well as a more realistic set of first-stage decisions (purchase of crudes in the cases explored).

Optimization results from the planning model without pricing are more optimistic than those of the pricing one. This is because the price and demand of the planning model without pricing were generated randomly and

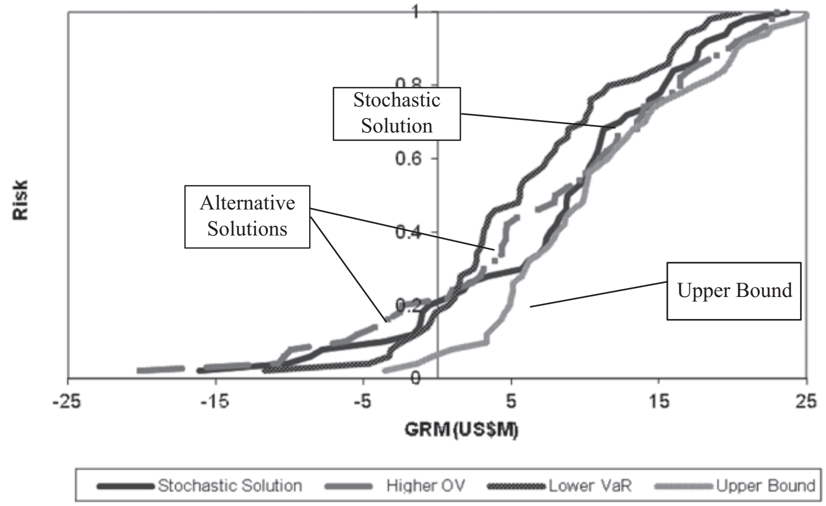


Figure 25.12—Upper bound risk curve for the stochastic and alternative solution.

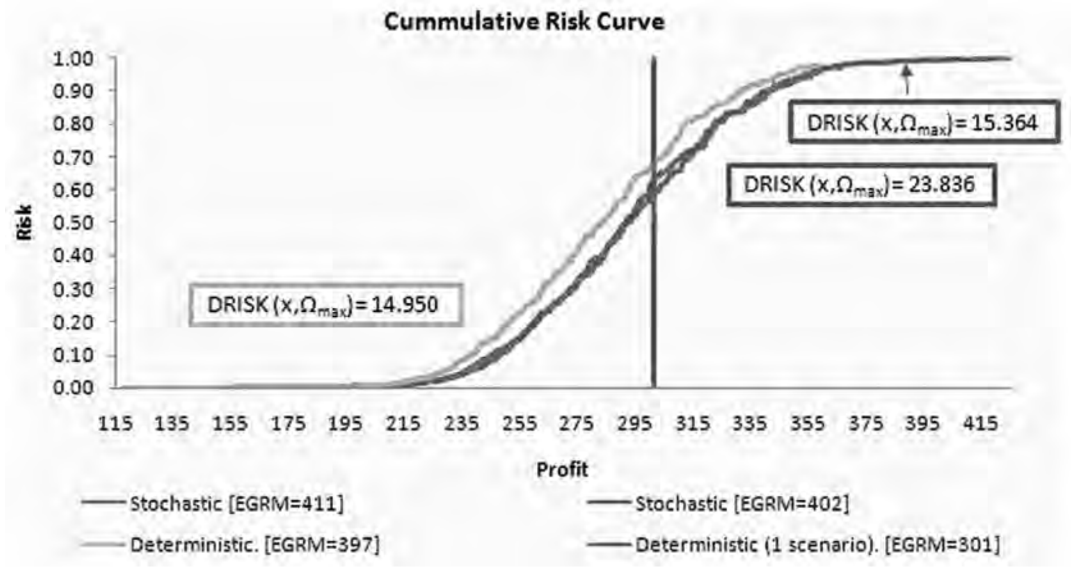


Figure 25.13—Risk curves obtained recursively using PIMS.

independently instead of predicted from the price-demand relation as in the planning model with pricing.

Results show that when the uncertainty is considered, the risk curves of the deterministic solutions provided a lower expected GRM and higher risk than those of the stochastic solutions. Some concepts of the financial risk management were presented including the upper bound risk curve, the OV, and the VaR to compare the best stochastic result with the other alternative solutions.

REFERENCES

[1] Bopp, A.E., Kannan, V.R., Palocsay, S.W., and Stevens, S.P., "An Optimization Model for Planning Natural Gas Purchases, Transportation, Storage and Deliverability," *Omega,* Vol. 24, 1996, pp. 511–522.

[2] Liu, M.L., and Sahinidis, N.V., "Optimization in Process Planning under Uncertainty," *Ind. Eng. Chem. Res.,* Vol. 35, 1996, pp. 4154–4165.

[3] Guldimann, J.M., and Wang, F., "Optimizing the Natural Gas Supply Mix of Local Distribution Utilities," *Eur. J. Oper. Res.*, Vol. 112, 1999, pp. 598–612.

[4] Escudero, L.F., Quintana, F.J., and Salmerón, J., "CORO, a Modeling and an Algorithmic Framework for Oil Supply, Transformation and Distribution Optimization under Uncertainty," *Eur. J. Oper. Res.*, Vol. 114, 1999, pp. 638–656.

[5] Hsieh, S., and Chiang, C.C., "Manufacturing-to-Sale Planning Model for Fuel Oil Production,“ *Adv. Manuf. Technol.*, Vol. 18, 2001, pp. 303–311.

[6] Neiro, S.M.S., and Pinto, J.M., 2003, "Supply Chain Optimization of Petroleum Refinery Complexes," FOCAPO Proceedings, Coral Springs, FL, 2003, pp. 59–72.

[7] Pinto, J.M., Joly, M., and Moro, L.F.L., "Planning and Scheduling Models for Refinery Operations," *Comp. Chem. Eng.*, Vol. 24, 2000, pp. 2259–2276.

[8] Lababidi, H.M.S., Ahmed, M.A., Alatiqi, I.M., and Al-Enzi, A.F., "Optimizing the Supply Chain of a Petrochemical Company under Uncertain Operating and Economic Conditions," *Ind. Eng. Chem. Res.*, Vol. 43, 2004, pp. 63–73.

[9] Reddy, P.C.P., Karimi, I.A., and Srinivasan, R., "A New Continuous-Time Formulation for Scheduling Crude Oil Operations," *Chem. Eng. Sci.*, Vol. 59, 2004, pp. 1325–1341.

[10] Herroelen, W., and Leus, R., "Project Scheduling under Uncertainty: Survey and Research Potentials," *Eur. J. Oper. Res.*, Vol. 165, 2005, pp. 289–306.

[11] Csáji, B., and Monostori, L., "Stochastic Reactive Production Scheduling by Multi-Agent Based Asynchronous Approximate Dynamic Programming," in: *Multi-Agent Systems and Applications IV (CEEMAS 2005), Lecture Notes in Artificial Intelligence*, 3690, Springer, Germany, 2005, pp. 388–397.

[12] Al-Redhwan, S.A., Crittenden, B.D., and Lababidi, H.M.S., "Wastewater Minimization under Uncertain Operational Conditions," *Comp. Chem. Eng.*, Vol. 29, 2005, pp. 1009–1021.

[13] Guillén, G., Mele, F.D., Bagajewicz, M.J., Espuña A., and Puigjaner, L., "Multiobjective Supply Chain Design under Uncertainty," *Chem. Eng. Sci.*, Vol. 60, 2005, pp. 1535–1553.

[14] Liao, Z., and Rittscher, J., "A Multi-Objective Supplier Selection Model under Stochastic Demand Conditions," *Int. J. Prod. Econ.*, Vol. 105, 2007, pp. 150–159.

[15] Al-Qahtani K., and Elkamel, A., "Robust Planning of Multisite Refinery Networks: Optimization under Uncertainty," *Comp. Chem. Eng.*, Vol. 34, 2010, pp. 985–995.

[16] Ierapetritou, M.G., and Pistikopoulos, E.N., "Simultaneous Incorporation of Flexibility and Economic Risk in Operational Planning under Uncertainty," *Comp. Chem. Eng.*, Vol. 18, 1994, pp. 163–189.

[17] Mulvey, J.M., Rosenbaum, D.P., and Shetty, B., "Strategic Financial Risk Management and Operations Research," *Eur. J. Oper. Res.*, Vol. 97, 1997, pp. 1–16.

[18] Lowe, T.J., Wendell, R.E., and Hu, G., "Screening Location Strategies to Reduce Exchange Rate Risk," *Eur. J. Oper. Res.*, Vol. 136, 2002, pp. 573–590.

[19] Gupta, A., and Maranas, C., "Market-Based Pollution Abatement Strategies: Risk Management Using Emission Option Contracts," *Ind. Eng. Chem. Res.*, Vol. 42, 2003, pp. 802–810.

[20] Cheng, L., Subrahmanian E., and Westerberg, A.W., "Design and Planning under Uncertainty: Issues on Problem Formulation and Solution," *Comp. Chem. Eng.*, Vol. 27, 2003, pp. 781–801.

[21] Guldimann, T., "The Story of Risk Metrics," *Risk*, Vol. 13, 2000, pp. 56–58.

[22] Jorion P., *Value at Risk. The New Benchmark for Managing Financial Risk*, 2nd ed., McGraw Hill, New York, 2000.

[23] Barbaro, A., and Bagajewicz, M.J., "Managing Financial Risk in Planning under Uncertainty," *AIChE J.*, Vol. 50, 2004, pp. 963–989.

[24] Aseeri, A., and Bagajewicz, M., "New Measures and Procedures to Manage Financial Risk with Applications to the Planning of Gas Commercialization in Asia," *Comp. Chem. Eng.*, Vol. 28, 2004, pp. 2791–2821.

[25] Birge, J.R., and Louveaux F., *Introduction to Stochastic Programming*, Springer, New York, 1997.

[26] Park J., Park, S., Yun, C., and Kim, Y., "Integrated Model for Financial Risk Management in Refinery Planning," *Ind. Eng. Chem. Res.*, Vol. 49, 2010, pp. 374–380.

[27] Rutherford, S. "Deep Water Real Options Valuation: Waiting for Technology," Paper SPE 77584 presented at the SPE Annual Technical Conference and Exhibition, San Antonio, TX, 2002.

[28] Dezen, F., Morooka, C., "Field Development Decision Making Under Uncertainty: A Real Option Valuation Approach," Paper SPE 69595 presented at the SPE Latin American and Caribbean Petroleum Engineering Conference, Buenos Aires, Argentina, March 25–28, 2001.

[29] Eppen, G.D., Martin, R.K., and Schrage L., "A Scenario Approach to Capacity Planning," *Oper. Res.*, Vol. 37, 1989, pp. 517–527.

[30] Ahmed, S., and Sahinidis, N.V., "Robust Process Planning under Uncertainty," *Ind. Eng. Chem. Res.*, Vol. 37, 1998, pp. 1883–1892.

[31] Takriti, S., and Ahmed, S., "On Robust Optimization of Two-Stage Systems," *Mathematical Programming*, 2004, Ser. A 99: 109–126.

[32] Applequist G., Pekny, J.F., and Reklaitis, G.V., "Risk and Uncertainty in Managing Chemical Manufacturing Supply Chains," *Comp. Chem. Eng.*, Vol. 24, 2000, p. 2211.

[33] Li, W., Hui, C., Li, P., and Li, A.-X., "Refinery Planning under Uncertainty," *Ind. Eng. Chem. Res.*, Vol. 43, 2004, pp. 6742–6755.

[34] Verweij, B., Ahmed, S., Kleywegt, A. J., Nemhauser, G., and Shapiro A., "The Sample Average Approximation Method Applied to Stochastic Routing Problems: A Computational Study," *Comp. Appl. Optimiz.*, Vol. 24, 2001, pp. 289–333.

[35] Hirshleifer, J., and Hirshleifer, D., *Price Theory and Applications*, South-Western CENGAGE Learning, Mason, OH, 1998.

[36] Varian, H., *Microeconomic Analysis*, W.W. Norton & Company, New York, 1992.

[37] Bagajewicz, M., "On the Role of Macroeconomics, Multi-Scale Planning and Finances in Product Design," *AIChE J.*, Vol. 53, 2007, pp. 3155–3170.

[38] Lakkhanawat, H., and Bagajewicz, M., "Financial Risk Management with Product Pricing in the Planning of Refinery Operations," *Ind. Eng. Chem. Res.*, Vol. 47, 2008, pp. 6622–6639.

[39] Pongsakdi, A., Rangsunvigit, P., Siemanond, K., and Bagajewicz, M., "Financial Risk Management in Planning of Refinery Operations," *Int. J. Product. Econ.*, Vol. 103, 2006, pp. 64–86.

[40] Bagajewicz M., and Uribe, A., "Financial Risk Management in Refinery Operations Planning Using Commercial Software," XIV Latin Ibero-American Congress on Operations Research (CLAIO 2008), 2008.

[41] Aspen PIMS, "Training Manual," Course number SP810.145.04. Bogotá, Colombia, 2004.

NOMENCLATURE

Sets

S: Set of scenarios

Variables:

x: vector of first-stage variables
y_s: vector of second-stage variables for scenario $s \in S$
p_s: probability of scenario $s \in S$
c: vector of first-stage costs
q_s: vector of second-stage costs for scenario $s \in S$
T_s : Technology Matrix for first stage
W: Technology Matrix for second stage
$f(x,\xi)$: Probability distribution of profits

26

Process Modeling and Simulation of Refineries

Maria J. Guerra[1], Pablo Jiménez-Asenjo[2], Antonio López-Rodríguez[3], and José L. Peña Díez[3]

NOMENCLATURE

AIChE	American Institute of Chemical Engineers
APC	Advanced process control
BRP	Basis refinery production
CFD	Computational fluid dynamics
DCS	Distributed control system
DDB	Dortmund Data Bank
DIPPR	Design Institute for Physical Properties
EOS	Equation of state
FCC	Fluid catalytic cracking
GC	Gas chromatography
HDS	Hydrodesulfurization
HQ	Headquarters
KPI	Key performance indicator
LIMS	Laboratory information management system
LP	Linear programming
MPP	Monthly production plan
MS	Mass spectroscopy
MTHS	Molecular-type homologous series
NIR	Near-infrared
NMR	Nuclear magnetic resonance
PCA	Principal component analysis
PI	Plant information
PLS	Partial least squares
PFD	Process flow design
PR	Peng–Robinson
RPP	Refinery processing plan
SOL	Structure-oriented lumping
SRK	Soave-Redlich-Kwong
TBP	True boiling point
UPM	Unit performance monitoring

26.1 INTRODUCTION

Market competition in the refining industry is motivating companies to optimize their processes to maximize margins and make better products while meeting more stringent constraints to comply with safety and environmental regulations. A deep understanding of the basics of the process, from thermodynamics and kinetics fundamentals to process control and the effect of feed qualities on product specifications, is critical for continuous plant operation improvement. Simulation models allow refinery engineers to take into account those factors and anticipate the optimal operating conditions for the different refinery units to achieve the target.

Process simulation technologies have been widely used in refinery applications for several decades. However, through the incredible evolution undergone by refining models during the last decades, process simulation has become an indispensable tool in the operation of refineries, covering disciplines such as process design and revamping, process control, plant planning and optimization, process safety, operator training, and decision support for the refinery operation.

The first references to process simulation appeared in the 1950s. Chemical engineering was one of the first disciplines to take advantage of the new possibilities offered by the introduction of digital computing, and there are references about computer simulation being applied to model distillation processes [1]. Although the new simulation tools were initially used almost exclusively in engineering applications and thermodynamic calculations in the scientific community, refining companies started to implement the use of flowsheeting simulation packages in subsequent decades.

There are excellent reviews in the literature covering the evolution of process engineering simulation tools during this period in the context of technological developments in computing technologies [2–4]. The close relationship between these two technologies has resulted in the progressive change in the focus through time. The original objective in model development was algorithm improvement to overcome hardware limitations in computing power. The development of personal computing technologies in recent decades made steady-state simulation widely accessible, but industrial-scale large process modeling, and especially dynamic simulation, had limited applications still in the 1990s, with some examples of industrial problems requiring long computing times even using high-performance computing capacity [5]. In this decade, CPU computing time limitations lost their focus toward an improvement in software interfaces, integration, and interoperability.

This change is questioning a classic paradigm related to the high level of specialization required by simulation model developers. Simulation engineers were expected to have not only a deep understanding of process engineering and model development methodologies, but also strong skills in other disciplines such as advanced thermodynamics and mathematics. With current advances in commercial tools, this level of expertise, although recommended, is not always applied. The ease of use of new simulation packages has led to widespread application of simulation models that may be very complex and allow for very sophisticated representations of a refinery, although simplifying the access to the

---

[1] AspenTech, Ltd., Reading Berkshire, UK
[2] KBC Advanced Technologies, Walton on Thames, Surrey, UK
[3] Repsol S.A., Madrid, Spain

complexity of thermodynamic models, process unit models, and mathematical algorithms integrated in the software.

However, referring to a quote attributed to Pablo Picasso—"Computers are useless; they can only give you answers"—simulation engineers must not forget that even with these new tool capabilities, the user's knowledge and experience are critical for the proper definition of the model and the correct interpretation of the results. A "simulation culture," supported by management, is present in companies applying simulation technologies in their daily activities. Against the traditional approach of one different model for each application, the new trend is toward using a single consistent model in different applications through the whole production chain, and this requires highly specialized integrated teams to obtain the maximal benefits.

It is beyond the scope of this chapter to present an exhaustive review of commercial simulation tools. The main software packages, some of them shown in Figure 26.1, were partially covered in Chapter 24, and their features may be easily found in simulation software reviews [6] and through the webpages of the main providers. This chapter will illustrate how refining companies may obtain economic benefits through the integrated application of simulation models in the entire production chain.

The first part of the chapter focuses on some of the key aspects in building simulation models for refining processes, with special emphasis given to adequate technologies for fast and flexible updated stream characterization and rigorous thermodynamic model selection, which is critical to guarantee model reliability. The second section reviews applications of simulation models in different areas of current refinery operation, with special focus on planning, engineering, and control applications.

26.2 BUILDING REFINERY MODELS

Current commercial process simulation packages usually include tools and built-in expert systems to support users in efficiently building models. However, the development of a simulation model is a wider process, ranging from the conceptual design of the model to its calibration and maintenance, in which many of the user decisions may determine the final success of the model.

Figure 26.2 schematically summarizes the main phases in the model development workflow.

- *Problem definition:* Model objective and mathematical description of the problem (physical and chemical constraints). Final objective, existing modeling environments, or resource availability may influence the decision about the type of model to be used.
- *Input data analysis:* Data gathering, energy and material balance consistency check, and adequate feed characterization are some of the key issues in this phase.
- *Model development and calibration:* Model building according to the defined specifications and calibration to match the real plant according to available data.
- *Result analysis:* Define case studies following the objective defined for the model. Analysis of different scenarios to check model consistency.

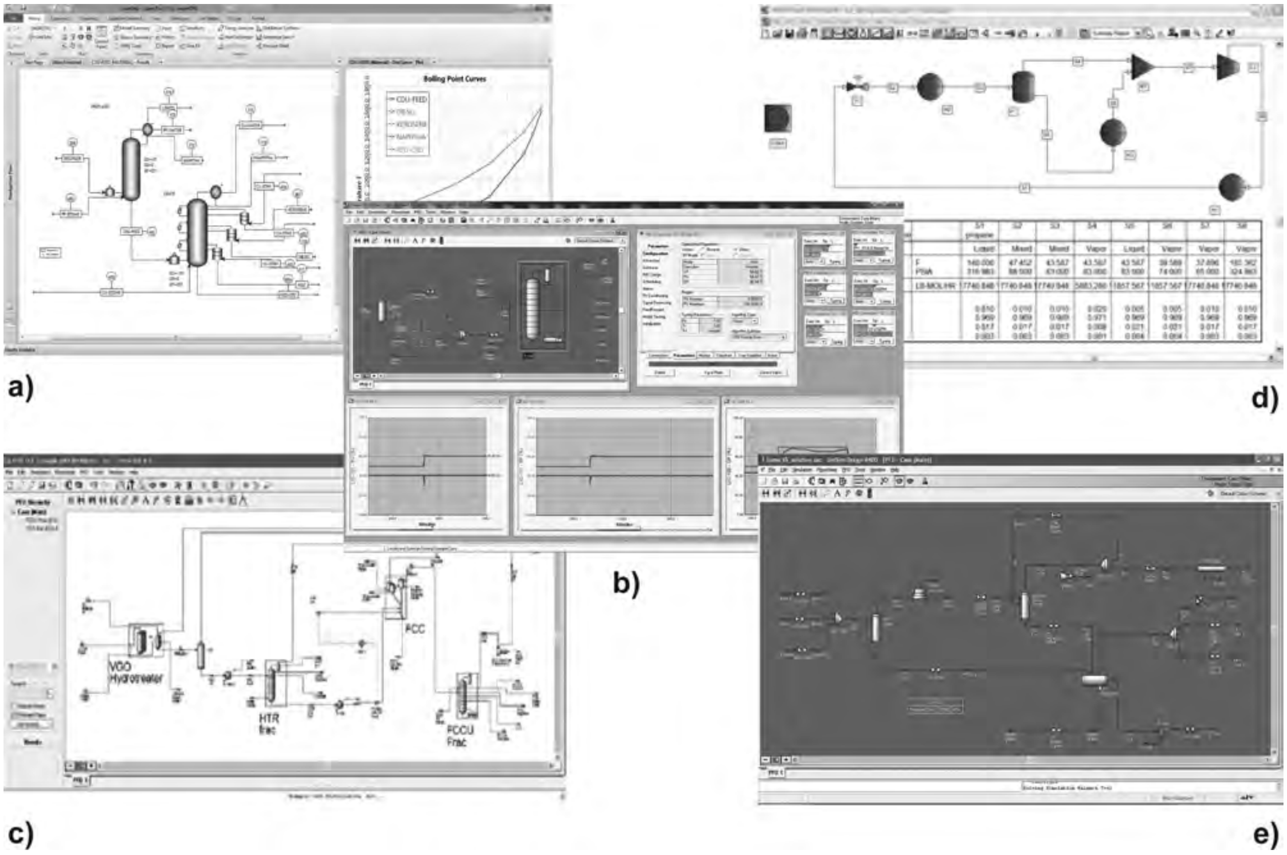


Figure 26.1—Several commercial simulation packages: (a) Aspen Plus® and (b) HYSYS® courtesy of Aspen Technology Inc.; (c) Petro-SIM® courtesy of KBC Advanced Technologies PLC; (d) Pro/II® courtesy of Invensys PLC, and (e) UniSim® Design courtesy of Honeywell International Inc.

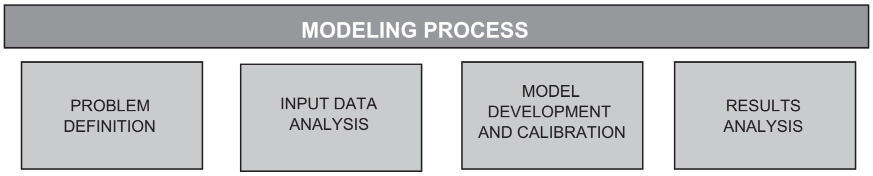


Figure 26.2—Process modeling workflow.

During the development of a refinery unit model, simulation engineers need to turn all of their knowledge about the process into information to be specified along the following elements, which linked together represent the heart of the simulation model:

- The definition of the chemical components to be used, including pseudocomponents, to represent refinery mixtures and their corresponding physical properties;
- The thermodynamic models to describe stream phase equilibrium and physical properties; and
- The individual unit operation models such as distillation, heat exchangers, reactor models, etc., to reproduce the unit behavior.

This section discusses some key aspects from these elements that may influence the success of refinery models, such as the complexity of crude oil streams description, and the challenge of choosing appropriate thermodynamic and physical property estimation models. A brief description about the features and model development techniques for the most common processing units at a refinery is also included.

26.2.1 Crude Oil and Petroleum Streams Description

Input data are critical to guarantee model success. A well-known axiom in process modeling correlates reliability of simulation results with input information quality. Improvements in accuracy and robustness in modern process instrumentation may reduce uncertainty in process variable quality. However, adequate stream description of systems with the complexity of crude oils or petroleum fractions continues to be a challenge.

As reviewed in Chapter 2, a crude oil is a very complex mixture containing thousands of discrete compounds, ranging from simple, short-chain structures to complex, multichain, multiring hydrocarbons. The exponential increase in the number of isomers as a function of carbon number, shown in Figure 26.3, results in the technical unfeasibility to identify, quantify, and represent each individual crude oil component in a simulation model.

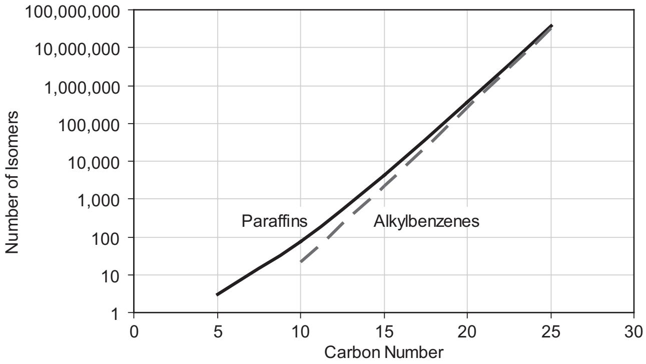


Figure 26.3—Structural isomers from homologous hydrocarbon series.

Extensive laboratory analyses need to be performed and integrated to represent crude oil streams with the level of detail required by current simulation models. Lumping methodologies must be designed to transform petroleum properties as obtained in the laboratories in a reduced number of components (pseudocomponents) capable to be used in simulation models while representing the complexity of the mixture. These critical steps will be covered in this section.

26.2.1.1 CHARACTERIZATION TECHNOLOGIES

Characterization technologies are moving from conventional laboratory distillation to advanced techniques capable of obtaining compositional representations of petroleum streams up to the molecular level. However, most of these technologies are still under development and are not accessible as routine analysis in most refinery laboratories because of their complexity and cost. Standard crude oil characterization continues to be based on the measurement of crude oil bulk properties, batch distillation of the crude oil (true boiling point [TBP]), and property distribution through distillation cuts; this is commonly referred to as crude oil assay.

Crude oil assays and the main properties and specifications for petroleum fractions and products are discussed in Chapter 4 and more comprehensively in previous ASTM publications [7] and other references [8,9]. The method relies on standardized batch atmospheric and vacuum distillations to generate narrow boiling distillation cuts that are further analyzed in depth to determine physical and transport properties as well as compositional information related to product specifications.

Current analytical techniques reach a complete molecular description of the light fractions of a crude oil (below C_{10}–C_{12}), very detailed analysis of middle and vacuum distillates (until C_{25}–C_{30}), and limited characterization for heavier fractions. This crude oil description cannot be performed with a single technique but is the result of a combination of techniques addressing bulk properties and chemical structure analysis.

Intensive experimental workload and the long time required to generate a crude oil assay make it not appropriate for routine analysis. The crude oil assay is usually maintained in the crude oil refinery model database until a significant change in quality is identified, or with predefined regularity, normally a few years, depending on the company strategy. During that period, crude oils may exhibit variations and trends in quality, as shown in Figure 26.4.

This approach may be acceptable for process design applications in which time is usually not a constraint and updated assays may be proposed if required. However, short-term planning and especially advanced control applications heavily depend on recent, accurate, and reliable data. New analytical technologies and alternative characterization techniques are required to overcome this limitation and extract all of the potential value from refinery simulation models [10].

The increasing use of online analyzers in refinery applications is described in Chapters 14 and 28. Although the main application is product quality control, near-infrared (NIR) spectroscopy and nuclear magnetic resonance (NMR) may be applied for feed characterization in online optimization models. Offline applications include advanced technologies like two-dimensional gas chromatography (GC×GC) (Figure 26.5) and mass spectroscopy (MS). These promising technologies allow full crude oil compositional characterization, but they are not available as routine analysis in refinery laboratories.

Finally, a third group includes chemometric techniques. These methodologies are capable of generating a fast and reliable updated crude oil assay that is based on existing information, and they are especially appropriate to update short-term planning based on limited experimental analysis from received cargos.

26.2.1.2 LUMPING METHODOLOGIES

Even with the existing limitations in analytical techniques, it is possible to obtain a combination of crude oil molecular description and physicochemical properties to a level of detail that might not be handled directly by

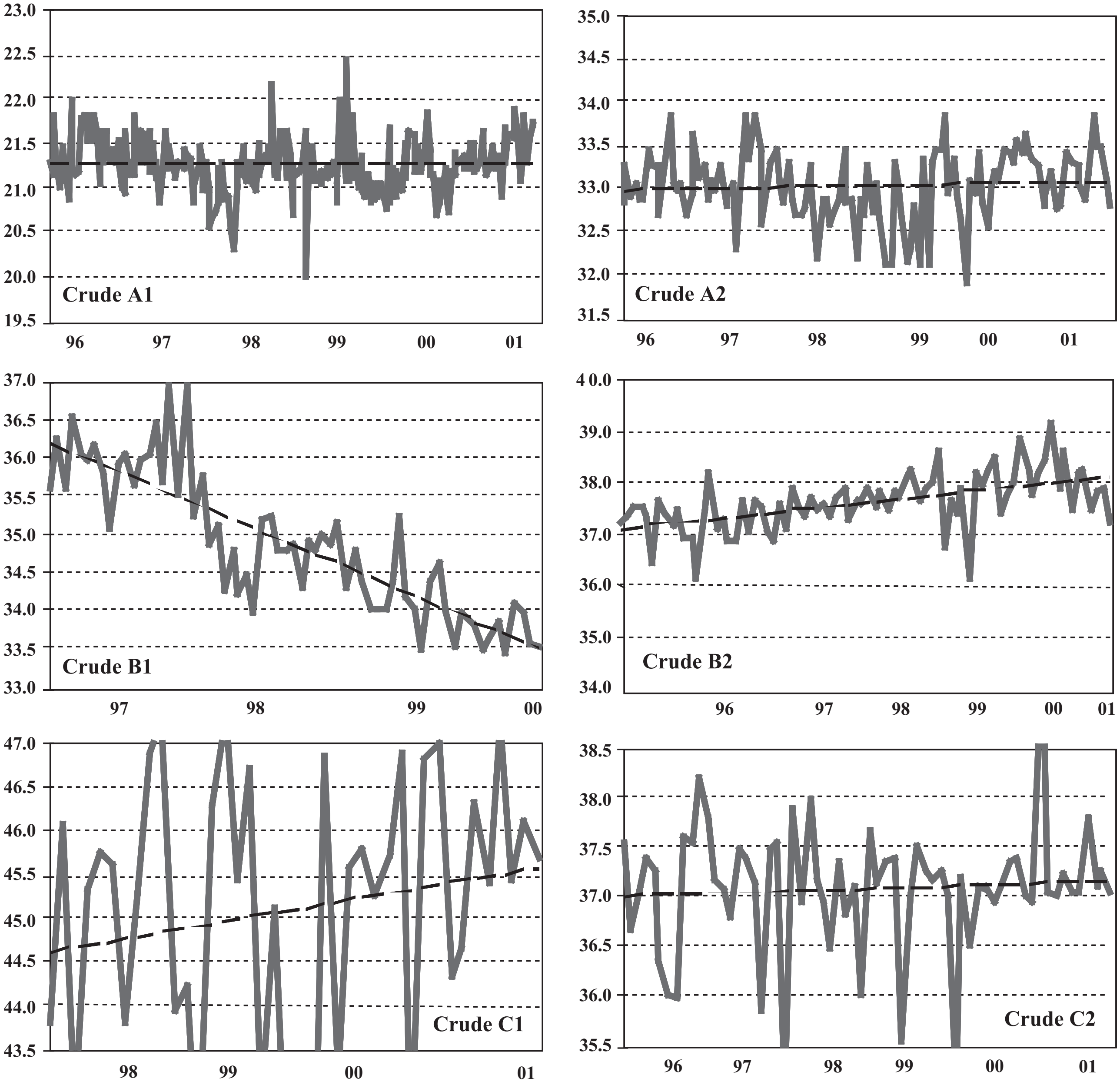


Figure 26.4—Examples of quality variations in several crude oils. *Source:* Figure used with permission from [10].

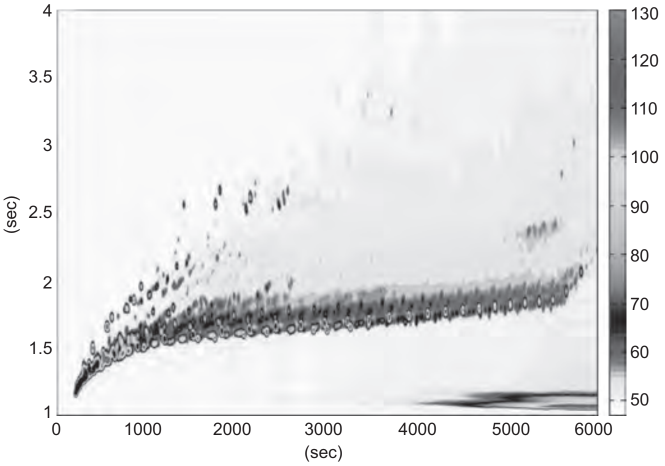


Figure 26.5—Advanced crude oil characterization by GC×GC. *Source:* Figure used courtesy of Schlumberger Ltd.

simulation models. The common practice is to transform this mixed information in a relatively small number of components (pseudocomponents) describing the model feedstocks and products through the physical and quality properties to be addressed according to the purpose of the model. Therefore, different lumping methodologies have been proposed for refinery separation and reaction simulation models.

A traditional lumping approach that is based on volatility has been used for decades to generate pseudocomponents for process modeling when distillation was the core refinery model and product specifications were typically defined in terms of boiling points. A pseudocomponent represents all of the compounds boiling within a given temperature range and may contain from a few hydrocarbons to thousands of real components. A wide boiling range feedstock such a crude oil is typically represented by a group of 50–100 pseudocomponents, and only the lightest end is integrated in the feed definition as pure components from chromatography data.

Process models need to predict not only distribution of product yields but also quality specifications that are based on physical properties and composition. Therefore, these properties must be defined for each pseudocomponent on the basis of laboratory data from the crude oil assay (e.g., boiling point, specific gravity, viscosity, octane and cetane numbers, cold properties, refractive index, aromatics, sulfur and metal content, etc.). The method to transform bulk analysis from TBP distillation cuts into a distribution of pseudocomponent properties is critical for successful model development. Figure 26.6 illustrates the lumping process to represent a product stream by a group of pseudocomponents with detailed characterization.

In addition, physical and chemical properties such as critical temperatures and pressures and acentric factor are required in equation-of-state models for phase equilibrium calculations. These parameters can be estimated from a few characterization parameters, usually boiling point and specific gravity, through industry-standard empirical correlations included in most process simulation packages [11–13]. These correlations also allow the prediction of other physical properties that are not available from laboratory data.

Alternative approaches considering continuous mixtures definition, especially for C_7+ characterization, have received considerable interest in recent decades. Originally proposed for upstream reservoir fluid characterization, this method relies on a distribution function to represent a continuous reference property, such as boiling point [14,15]. The extension of this basic approach to molecular-based models, representing combined distribution functions for hydrocarbons with different chemical structure, and the natural correlation of physical properties with carbon numbers [16,17] provide a robust framework to represent very complex systems, as demonstrated by Peng [18]. She proposed a characterization method, based on MTHS (molecular-type homologous series) matrix representation, that was suitable for refinery modeling [19].

Lumping processes based on volatility are not appropriate for other separation processes involving liquid-liquid equilibrium, such as solvent extraction. In this case,

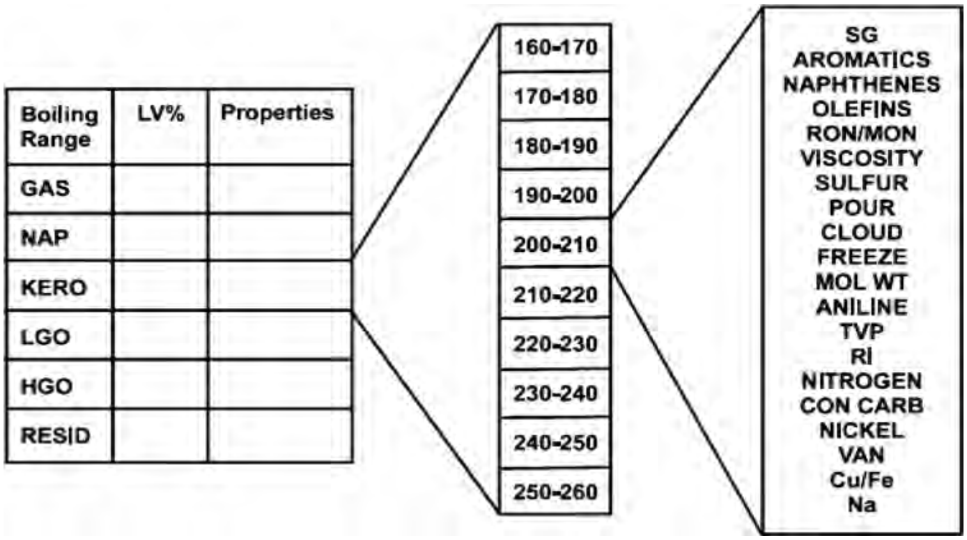


Figure 26.6—Example of a pseudocomponent definition in kerosine boiling range. *Source:* Figure used courtesy of KBC Advanced Technologies PLC.

alternative pseudocomponents must be defined in terms of chemical composition instead of or in addition to boiling ranges. Model molecules with structure defined from laboratory analyses have demonstrated satisfactory results in predicting phase distribution and product physicochemical properties [20,21].

As refinery simulation began to integrate chemical reactor models from conversion processes such as catalytic reforming, hydrotreating, hydrocracking, or fluid catalytic cracking (FCC), conventional lumping processes became obsolete, with models dealing with molecules instead of boiling ranges. With this trend in "molecule management" [22], not only several pseudocomponents must be obtained within a boiling range by their chemical nature (paraffinic, naphthenic, aromatics, etc.) but the relationship between them must also be defined for all of the components involved in the kinetic reactions. Although there are simplified reactor models that may be used in certain refinery applications using bulk stream characterization, accurate reactor modeling requires these advanced lumping techniques.

The earliest effort to apply a fundamental kinetic approach for modeling a reactor unit was the 1953 work of Standard Oil on the FCC process [23], which was extended in the following years to other refining processes [24,25]. The common idea of these lumping processes assumed that structurally similar compounds were kinetically equivalent, and the models developed proved to be useful prediction tools during tests with experimental data.

Quann and Jaffe proposed a new method, called structure-oriented lumping (SOL), for describing the composition, reactions, and properties of complex hydrocarbon mixtures [26]. SOL represents individual hydrocarbon molecules as a vector of incremental structural features, in a similar approach to group contribution methods. The method was later extended to heavy fractions [27] and provided a theoretical foundation for molecular-based modeling of nearly all refinery processes. The complexity of the proprietary technology (considering all potential homologous series from hydrocarbon structures with boiling temperatures up to 800K; a SOL mixture has ~5000–6000 components) has not prevented similar lumping algorithms from being implemented in process simulation software.

The algorithms included in similar lumping techniques have several problems associated with discrete and broad boiling lumps. One commercial implementation introduced the carbon-number-based pseudocomponents in reactor models [28]. Each carbon lump includes paraffinic, naphthenic, and aromatic structures, and each carbon structure has a defined route to lighter products as shown in Figure 26.7. Using this "continuum" approach, model reliability is enhanced for prediction situations outside of the calibration data.

Even with these advanced methodologies, there are still limitations in stream description for process modeling, especially in the heavier fractions. Integration of new analytical techniques and increased computing capacity will enhance the detail allowed in lumping techniques, and true molecular modeling might be feasible for refinery modeling.

26.2.2 Thermodynamic Models

Thermodynamic models are one of the key components of process simulation packages because the results of a simulation model largely depend on the algorithms used for the calculation of phase equilibrium and physical and transport properties for the process streams, which are used as intermediate variables for all process unit models [29,30]. According to some estimations, more than 70 % of the code included in commercial process simulators is dedicated to thermodynamic models and physical property prediction subroutines.

Widespread use of process modeling technologies leave simulation engineers having to deal with an enormous variety of thermodynamic models with endless options. Wise model selection and property correlation fine-tuning may require highly specialized expertise to achieve proper accuracy and reliability. To manage the gap from potential limitations in advanced thermodynamic skills, most commercial simulation software includes built-in expert systems

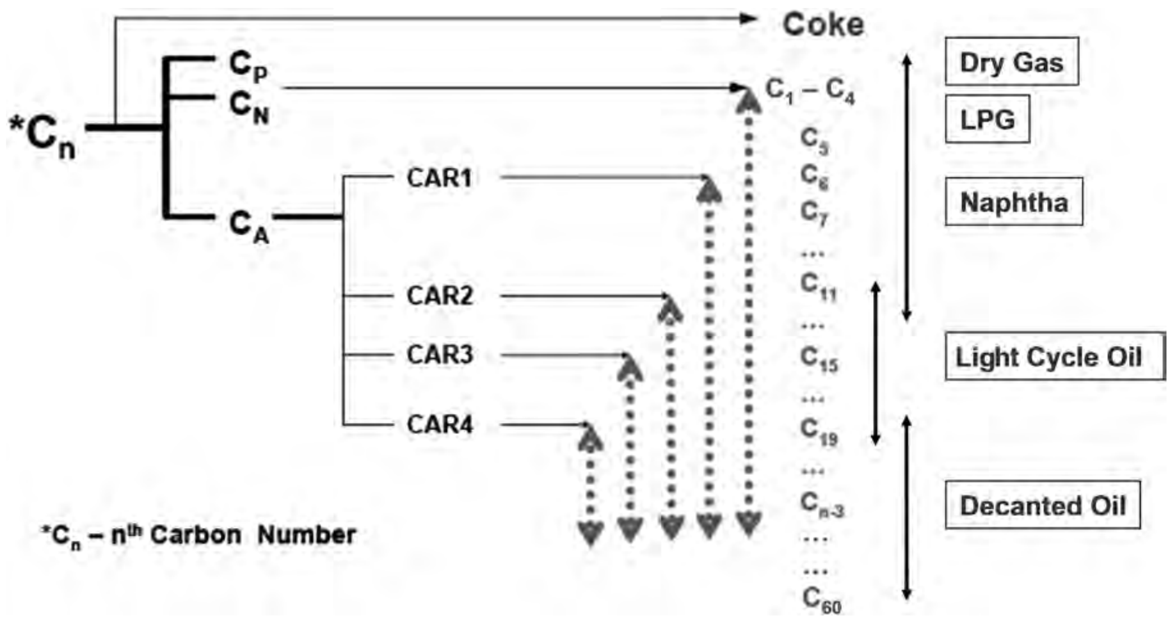


Figure 26.7—Reaction network in FCC reactor simulation. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

to assist in the thermodynamic model selection, based on the nature of the components present in the simulation and the expected operating conditions, using predefined property packages.

These property packages, designed for typical industrial problems, perform all of the necessary calculations, as reviewed by Satyro [31], to model the thermophysical behavior of process streams through the determination of

- Number of fluid phases from composition and two variables from the degrees of freedom in the system (usually temperature and pressure);
- Composition of each phase at equilibrium;
- Molar enthalpy, entropy, and heat capacity of each phase; and
- Interfacial properties and transport (rate-related) properties for each phase.

In the simulation of most unit operations, the equilibrium of components between different phases is the key calculation once the individual component physical properties are available. Because the thermodynamics of most refinery processes are not too complicated (hydrocarbons behave quite ideally and their relative volatilities are nearly independent of pressure), equations of state (EOS) constitute the most useful thermodynamic method used to accurately predict equilibrium for hydrocarbon systems.

Soave-Redlich-Kwong (SRK) and Peng–Robinson (PR) are the most widely used EOS in refinery modeling, although it is worth noting that the Grayson-Streed method is a semiempirical method that is still widely used in the simulation of vacuum columns and hydrogen-rich systems. There are additional factors to consider to obtain the most accurate results using EOS, such as binary interaction parameters. These parameters represent the nonideality of the pairs of components and are obtained through regression of experimental equilibrium data. It is important to guarantee the accuracy of such parameters when using simulation models, although most of the commercial packages include exhaustive interaction parameter databases from respected sources such as the Design Institute for Physical Properties (DIPPR) from AIChE [32] or the Dortmund Data Bank (DDB) from the University of Dortmund [33].

There are cases in which EOS are not suitable, and alternative sets of thermodynamic models must be applied. Systems with more polar compounds with stronger interactions (such as mixtures with water, CO_2, H_2S) may require the use of activity models to predict phase equilibrium [34]. More complex thermodynamic models are also required for electrolyte simulations [35] or when more than one liquid phase is expected, such as in liquid-liquid extraction [36].

Although current commercial packages include multiple user support tools to help in selecting the appropriate thermodynamic model, many authors have emphasized that current users dedicate a minimum of the time invested in developing the model to analyze the thermodynamic aspects of the process. The serious problems that may be encountered if this simulation element is not properly treated are well documented through many literature examples [37–39].

26.2.3 Steady-State Model Building

Despite the significant advances in computing power that made dynamic simulation feasible for most simulation users, steady-state models still account for most process engineering, planning, and production models in refinery applications. Although the technology applied in key refinery processes such as distillation units has not changed significantly over the last decades, there has been significant progress in reactor model integration, especially conversion units. Some considerations about development techniques and a description of the main features of refinery unit models are discussed.

26.2.3.1 REFINERY UNIT MODEL DEVELOPMENT

In general, the development of every refinery unit model involves two well-defined phases:

1. In calibration mode, information regarding the feed, products, and operating conditions is known, and the model is run to calculate the calibration factors.
2. In prediction mode, the feed, operating conditions, and calibration factors (from a previous calibration run mode) are known. The model is able to predict the output (e.g., product qualities and yields) for different scenarios.

The initial model setup involves the calibration step, because the model relies on calibration factors to accurately represent the unit. The equations are tuned to allow for the prediction of the output when the unit is run for future scenarios.

Figure 26.8 represents the way the calibration and prediction modes are linked. The straight arrows symbolize

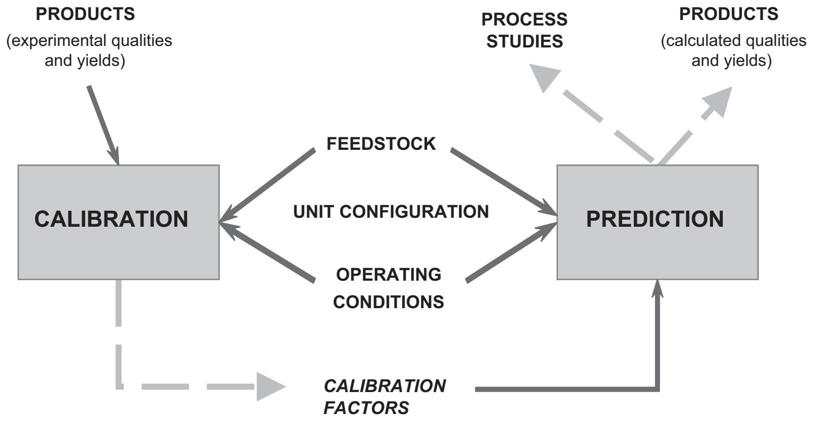


Figure 26.8—Flow of information in prediction and calibration modes during model development.

the information input into the model whereas the dotted arrows correspond to model outputs.

To perform the calibration of unit models, it is necessary to establish a procedure that allows for the selection of quality data. The information is usually gathered from the refinery plant information (PI) system and from the laboratory analysis of intermediate feeds, which is stored in the laboratory information management system (LIMS). The quality of the information is used to verify the condition of the instruments.

26.2.3.2 REFINERY UNIT MODEL FEATURES

This subsection covers some of the most relevant features for distillation and reactor models as the main refinery units to be modeled. A more detailed description of steady-state models may be found in excellent dedicated publications [40,41].

26.2.3.2.1 Distillation Models

The most widely used method to model distillation columns is the tray-by-tray method. This method calculates the vapor liquid equilibrium in a series of linked equilibrium stages or theoretical trays. This set of equations is solved with the heat and material balances for every tray as well as for the whole column. The typical algorithm used to solve this complex mathematical problem is the inside-out method with several improvements provided by commercial process simulators.

The information required to build a distillation model and how important its quality is for developing a representative model of the actual column behavior starts with an accurate representation of the feedstock, especially in the case of complex distillation columns such as crude, vacuum, or other main fractionators. Many cases of model failures are related to poor feedstock description. Section 26.2.1 of this chapter covers recommended feedstock description techniques.

Because there is always some uncertainty in the quality of the feed sampling as well as in the laboratory analysis, it is usually recommended to create the wide-distillation column feed as a blend of all of the column products from their individual analysis. This back-blended feed truly represents the products of the column at a given time. This will also ensure that any modeling issue will not be related to the input data. All column product analyses are required to build an accurate feed. The minimum information required is a distillation curve; the density of all distillates, including the heaviest products; and the chromatographic analysis of lighter streams. Additional product properties are useful in validating and adding value to the simulation model.

It is also strongly recommended to calculate and close the unit material balance with accurate raw flow rate measurements (within ±2 %). Otherwise, although the model can still be built if the rest of the information is available, the user will not be able to troubleshoot the model if it does not satisfactorily predict column performance.

Another piece of information required is the column configuration. The process flow design (PFD) is necessary to build the correct column topology: number of trays, draws and feed locations, condenser type, reboiler configuration, and any side operation that the column may have such as pumparounds and side strippers. Any heat exchanger in the column should be modeled as a simple heater or cooler for overall column studies, and detailed heat-exchanger geometry should be added later when the study may require it. Internal column dimensions are not required for equilibrium column simulation, although they could be added as a side utility for flooding calculations once the column has been solved.

When building the column configuration, it is of special relevance to translate the number of actual column trays to model theoretical stages. Actual distillation columns never reach equilibrium at each tray, so the models need to take this effect into account. There are two options. One is to apply overall section efficiencies to the number of actual stages and create a model with the number of theoretical stages corresponding to the actual ones multiplied by the section efficiency. The other option is to build the model with the actual number of trays and apply tray efficiencies directly to the simulation model. Although the second option seems simpler from a model construction point of view, it has many disadvantages arising from the fact that the calculated tray liquid and vapor are no longer at equilibrium; this produces inconsistent temperature profiles. In addition, these tray efficiencies are experimental tuning parameters that will make any model predictions under conditions other than the reference conditions less useful.

It is possible to find typical column section efficiencies in the literature that can be used in building distillation models. The best option is to obtain them experimentally by finding the number of theoretical stages that makes the simulation results match the actual column performance with reasonable accuracy.

Finally, it is important to have the key operating conditions. Measurements and typical values are required for temperatures, pressures, internal flows, and stream compositions. The values obtained from such measurements vary from refinery to refinery, but the maximum available should be considered when building the model. The pressure is the only input value required for the column model to run. Any temperature, flow, or composition should be used to compare with the model results and validate the model before running any further study. It is also very important to assess the accuracy of such measurements because the instrumentation for many variables (i.e., internal and steam flows, tray temperatures) is not calibrated frequently.

Once the model is built, it is necessary to define several column specifications to fully specify the mathematical model. Specifications are defined by the degrees of freedom in the equations matrix built for each column. Their number will vary between different column configurations. For a simple column with a total condenser and a reboiler, the number of degrees of freedom is 2, corresponding to two possible specifications. If the column condenser is partial, then the number of specifications increases to three. Each additional draw from the column adds one more specification, and each pumparound adds 2 more degrees of freedom corresponding to two column specifications. The column user may then decide which variables will be fixed (specifications) to close the column degrees of freedom. There are many options, but most typically temperatures, flow rates or flow ratios, duties, component purities, and stream properties will be used. This selection must be made wisely and distributed across all of the column elements.

In addition to the tray-by-tray models, simpler section-by-section column models are also available. In these models, the performance of each section is calculated from a heat and material balance, which determines the liquid and vapor rates to and from the entire section. The fractionation between adjacent products is determined from the vapor/liquid traffic, the number of theoretical trays within a section, and the stripper performance. Special tuning factors are provided to closely match the product distillations measured from the refinery with those obtained by the model.

The main advantage of the tray-by-tray model is a good calculation of internal liquid and vapor rates and tray temperatures. However, the disadvantage is that it is not possible to fine-tune product composition to match measured data. Thus, we could say that both types of models (tray-by-tray and section-by-section) are complementary. In fact, it is possible to combine both models to facilitate the convergence of very complex units.

26.2.3.2.2 Reactor Models

Modeling reactor units requires chemical engineering fundamentals such as mass and energy balances and the definition of their reaction kinetics. Each reactor unit, FCC, catalytic reforming, hydrocracking, coking, etc., will need to have its own set of reactions between different product groups, defined according to the lumping methodology selected.

Once a suitable feed component group composition has been developed, the appropriate reactor kinetics are applied to calculate the new product composition on the basis of the same component group list plus some additional component groups not present in the feed, typically coke and light gases.

The main reactions that take place in refinery reactors include the following:

- *FCC:* Paraffin and naphthene cracking, aromatic dealkylation, boiling range reduction, and condensation and coke production.
- *Catalytic reformer:* Isomerization of paraffins and naphthenes, ring closure, ring expansion and contraction, dehydrogenation of naphthenes to aromatics, hydrocracking of paraffins to lighter paraffins, hydrodealkylation of aromatics, and condensation.
- *Hydrocracking:* Hydrodesulfurization (HDS), hydrodenitrogenation, aromatic saturation, ring opening and dealkylation, paraffin hydrocracking, and olefin saturation.
- *Thermal cracking units:* Radical chain pyrolysis.

This kinetic approach is complemented with the breakdown of reactor volume into several sections or slices that are numerically integrated for the whole reactor and that allow the model to calculate composition profiles along the bed as well as temperature or other property profiles, as shown in Figure 26.9. This is the most accurate way of modeling kinetic reactor models.

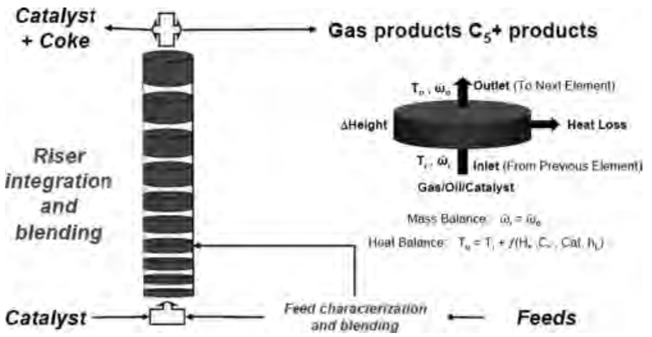


Figure 26.9—Reactor model calculations. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

Once the composition of the overall product has been calculated, it must be transformed into actual product streams, yields, and composition or characterization. A fractionation model is then required to divide the composition into the appropriate product yields and then convert from reaction component groups back into distillation curves, specific gravity, sulfur, etc. In fact, correlations are also needed to complete the model predictions in terms of product properties because of the necessary simplification of using a set of component groups and chemical reactions.

Because most of these reactors are catalytic, the extent of the reactions has to be determined by their characteristics (activity, selectivity, etc.) as well as any other reactor operating variable. All kinetic reactions defined in the reactor models need to be adjusted to reflect the behavior of a specific catalyst in a precise unit geometry. In some cases, there are catalyst databases available (commercially or created by refining companies) that allow for the selection of the catalyst within the model. Because having accurate and updated information for all catalysts is costly and time-consuming, most reactor models available make use of model calibration.

Model calibration consists of collecting a full set of experimental data (under test-run conditions) and introducing it into the model for reconciliation purposes. This way, feed flow rates and their characterization, all product flow rates, the composition for light gases, and the characterization of the rest of the products are fixed in the model. The same is applied to operating conditions such reactor temperatures, pressures, and hydrogen feed (in cases where it applies). The only variables that are free to calculate in the model are the kinetic adjustment factors, which will be calculated to ensure the products obtained with the model are close enough to the experimental ones.

The kinetics adjusted in this manner provide the best basis for model prediction for different feedstocks and operating conditions other than the ones used at the calibration point. It should be taken into account that the more these operating conditions vary, the larger the deviations between the model predictions and the actual reactor behavior will be.

Apart from the rigorous kinetic reactor models, there is another simple reactor model similar to the yield reactor models. In this kind of simple model, it is possible to define the product yields of all of the reactor products and define the properties of each product from the reactor. Models defined in this way are insensitive to changes in the operating conditions and feed characteristics.

To make the model predict different yields for different conditions, it is necessary to modify product yields and properties with correlations or "yield shift vectors." Both are experimentally determined and require significant data collection effort to be developed. These models are simple, but they can fail to provide predictions outside of the range of data over which they were obtained. Additionally, they cannot be applied to reactor units of the same type other than the one the model was developed for because correlations do not have an engineering foundation and there is no way to take into account the differences between the tuned reactor model (geometry, utilities used, catalyst variables, etc.) and the new one.

Once the refinery model has been built and validated with a minimal set of experimental data, it can be used to perform many different studies, starting with a unit design or revamp study, existing unit troubleshooting, or unit performance improvement including optimization.

26.2.4 Dynamic Model Building

Steady-state models provide a representation of a unit under stable conditions and do not account for accumulations or other restrictions due to equipment sizing. At steady state, any material going inside of a unit will be the output of the unit such that the material and energy balances are closed. In reality, before arriving at a steady-state condition, the unit will start to fill, and the size of the equipment and operating conditions will drive the control strategy.

As shown in Figure 26.10, there is a general four-stage progression from an initial steady-state simulation to a final dynamic model (percentages in the figure indicate typical time fraction of total time dedicated to build the model).

First of all, dynamic models require having the actual physical data about the unit operations inside of the process being modeled. Typically, for most processes this will include the following:

- *Valves:* Cv, characteristic curve, pressure drop, from valve datasheets.
- *Relief valves:* Type, setting pressures, from valve datasheets.
- *Pumps:* Head and efficiency curves, from pump test certificates.
- *Compressors:* Head and efficiency curves, flow limits.
- *Heat exchangers, heaters, and coolers:* Shell and tube volumes.
- *Air coolers:* Volume (of fluid tubes), number of fans, airflow per fan.
- *Vessels:* Volume, height, nozzles, level taps, from design datasheets.
- *Column:* Tray spacing and type, diameter, weir height and length from design datasheets.
- *Elevations:* From plant floor elevation sheet.
- *Controllers:* PV, OP, SP, range and tuning gains from distributed control system (DCS).

Steady-state models do not require the incorporation of all of the minor equipment and devices such as valves, pumps, filters, pipe segments, or bypasses. However, to replicate the plant dynamic behavior, it is necessary to introduce most of these items into the same steady-state model. Most data, such as those pertaining to volumes or controllers, are not used in the steady-state mode, but they are entered once to keep the entire data model in one file case because the steady-state case will be used as the starting point for the dynamic simulation.

Steady-state models need to be calibrated with the available process data. This is the most critical phase of the process because the model has to be manually tuned and calibrated to reflect the true conditions of the real plant. The user has to equilibrate the differences by changing boundary conditions by small increments: valve pressure drops and opening, efficiencies, heat losses, pressure drops, etc. Sometimes this task is not trivial, and frequently other hidden equipment or device problems are encountered when the model does not reproduce the plant data.

Once the model is calibrated, all of the heat transfer coefficients or flow resistance factors are calculated, and all pressure-flow relations are correctly configured, so that the steady-state model is ready to switch to dynamic mode.

Finally, the model can be switched to dynamics and allowed to stabilize: The integrator is started. The unit should then be stabilized and all of the controllers can be put in automatic mode. The model is then ready to be used for the operating changes and control studies [42].

If the dynamic model will be used for advanced process control (APC), the situation is even more complex, and one of the most time-consuming elements of an online project is the tuning of regulatory controls, modifying the DCS, implementing a robust connection to the DCS system, and maintaining all of the above [43].

26.3 USING REFINERY MODELS

Although process simulation is widely used in most of the groups inside of a refinery, there are significant differences in the type of application and in some cases even in the type of simulation tool applied. The following is a brief review on the approach followed by the different users when taking advantage of current simulation tools.

26.3.1 Planning and Scheduling

A plant's profitability is greatly influenced by its yield performance. Good performers economically optimize their planned yield performance and ensure that their operation is further optimized within the plant's capability by the on-shift operation engineers. A good monitoring process

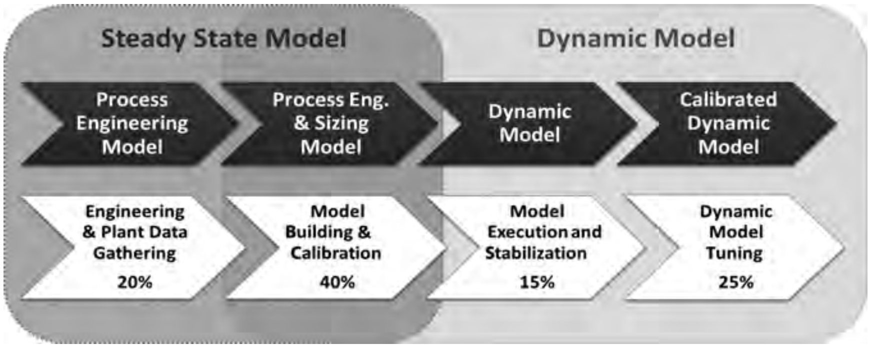


Figure 26.10—Steps to build a dynamic model.

is required to ensure that the tools accurately reflect the plant's capabilities and to help further optimize the process.

The different steps from planning production to managing operation are best explained by the time horizon, as shown in Figure 26.11. The planning process goes from long term to medium and short term. Software tools such as linear programming (for planning and scheduling), blending programs, and rigorous simulation are used to help with this complex task. The level of detail of the models used increases as the timeline shortens.

The purpose of the planning process is to effectively plan the future operation of a plant on the basis of economic driving forces and to further optimize the production within the actual operating plan and physical constraints.

The planning process covers multiple time periods, each with its own purpose and detail. The planning period is defined by the horizon required to make predictions. As described in Table 26.1, the best practices in planning [44] consist of several plans generated to forecast the long, medium, and short term.

The strategic plan sets the high-level guidelines that will determine the future direction of company operation. It takes into account external forces that may have an influence such as socioeconomical, political, technological, and legal factors. The strategic plan will take into account new product specifications, possible sources of new crudes that may become available, and the long-term feed and product price set development. In addition to the planning and optimization of existing facilities, the evaluation of potential new plant investments and possible changes in the refinery processing scheme required to comply with new product specifications and environmental legal requirements is required. The time scale for the strategic plan will typically range from 5 to 15 years.

A business plan covering the next 1–5 years is constructed from the strategic plan and covers more factors. Investment plans are typically more detailed during this period, as are the required changes to product specifications or environmental requirements.

The supply plan provides more details regarding the following year and can be split into multiple periods during the year. The plan covers detailed supply options, planned shutdowns, available feedstocks, actual product specification, etc. One of the outputs from the supply plan will be the expected cash flow for the refinery.

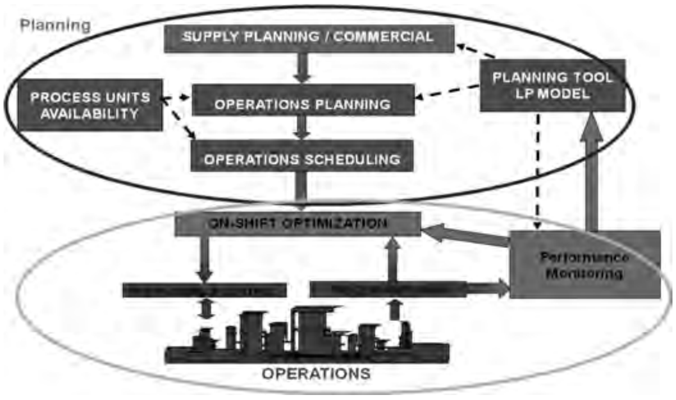


Figure 26.11—Timeline of a refinery from long term to short term. *Source:* Figure courtesy of KBC Advanced Technologies PLC [44].

TABLE 26.1—Typical Planning Periods

Plan	Typical Planning Period
Strategic	5+ years
Business	1–5 years
Supply	1–12 months
Operations	1–3 months
Production	2–4 days

Source: Data courtesy of KBC Advanced Technologies PLC [44].

The supply plan linear programming (LP) model will help rank the feedstock on the basis of the profitability for the facility and can help to evaluate possible mixtures of acceptable quality. The results will be communicated to the trading group for purchasing. The estimated time of arrival will fit into the operations plan, which will be adjusted, as necessary, with more precise dates of arrival.

Following the supply plan, the operations plan will assume the crude basket for the upcoming months on the basis of the information obtained from the trading organization. LP will find the most profitable operation for a given time period (typically 1–3 months for near-term planning) and is used to define the most profitable operating strategy and plan. The operations plan contains more details regarding the actions required to meet the relevant targets from the supply plan for the following planning period (typically 1–3 months).

The output of the operations plan is a comprehensive summary of the optimized future operation, which is translated into detailed instructions to be used by the operations team to implement the plan. The implementation includes further optimization of the plant operation, taking into account directions from the operating instructions. It focuses on realizing or exceeding the planned yield performance by taking into account the quality targets and actual plant capability.

The operating instructions will include the following:

- A detailed plan of operating blocks for each process unit on the basis of feed qualities or product types and quantities or both;
- Operating/control targets for the process units;
- A detailed blending plan including grades, quality targets, and quantities;
- A detailed feed and product movement plan; and
- Fuel selection.

The different processes mentioned above involve different departments, and a critical aspect of the correct functioning of a system is having good communication channels. The key to success is having the right people, tools, and a consistent methodology. Communication between the planning and scheduling functions and operations department is critical to the implementation of an optimized production plan.

The optimized near-future operation is defined in the operations plan described above. From this optimized plan, the scheduling process focuses on sequencing a series of operations such that it is feasible to meet a timetable of events within the logistical constraints. The scheduling process does not allow for a change in profit, regardless of whatever sequence is chosen. Schedulers devise a day-to-day plan to achieve the targets. Detailed scheduling is typically performed for 1 week up to 1 month.

One of the last steps in the production process, before transportation from the plant, is product blending. Scheduling blending operation (blend recipes and quality constraints) is optimized from the operations plan. An effective blending operation will minimize blend corrections and will therefore have a positive effect on reducing the required minimal operating inventory and hence working capital. On the other hand, poor blending operation can result in multiple blend corrections, crisis decision-making, and increased demurrage cost. Optimizing the blending operation within the scheduling process is therefore important to control a plant's overall operating costs.

The trading organization buys and sells refinery feeds and products based on the information from the operations planning. The arrival of feeds and liftings of products are summarized in a supply and liftings plan. Verification of the liftings plan with the scheduling activity of the plant is important to avoid suboptimal operation because of crisis decision-making (lost profitability) and demurrage cost as a result of unfeasible schedules.

It is important to have a scheduling tool available to represent the actual operation, including the process units and blending operations offsite. Time should be allowed for blending, tank settling, laboratory analysis, and product movement activities. Commercial scheduling tools that are based on LP models are increasingly replacing in-house spreadsheets.

The production plan focuses on the execution and further optimization of the operations plan. This process consists of practices for on-shift optimization and abnormal situation management as well as quality control and unit performance monitoring (UPM). By effectively implementing these practices, the plant can achieve the production plan, meet target production rates and product qualities, ensure reliable and safe operation, and optimize the process to increase profitability.

The following practices are involved in production plan management:

- *On-shift process optimization:* A good functioning on-shift team ensures that a plant can execute the production plan and capture and implement optimization opportunities that increase profitability, improve reliability, and maintain a safe working environment according to a given set of constraints and targets. Rigorous simulation tools and energy optimization models are important aids that help execute this function, although the most important factor is to have the work processes and the right organizational structure in place to allow personnel to optimize within specified boundaries.
- *Quality control:* Maintaining effective quality control on feeds, intermediates, and final products is a critical component to maintain a safe and profitable operation. The key aspects of this practice are
    - Ensure that the plant consistently meets product specifications.
    - Capture, analyze, and correct quality "near misses" for future operational improvement.
    - Ensure that this practice is not owned solely by laboratory and planning personnel but by the entire production team. One of the activities associated with this practice is to find strategies to minimize giveaways.
- *Energy conservation:* Effective and appropriate energy conservation measures adopted by any plant will enable the plant to minimize the energy portion of the overall operating costs without sacrificing overall profitability. This practice is an integral part of any plant operation and should be used in conjunction with the other process plant practices. Specific energy targets from the operating instruction can include
    - The prioritization of marginal fuel type (fuel oil, natural gas, gasified liquefied petroleum gas),
    - Power production/export, and
    - Maximization of turbo drivers or electrical motors for pumps and compressors.

  Other energy consumption targets such as the amount of stripping steam required for specific distillation towers will be provided by process engineers.

To summarize, Table 26.2 describes the different practices involved at different steps of the planning, scheduling, and production plan management processes from feedstock selection to the optimization of the operation. For each of these practices, there is a relevant software application that will be described later in this section. The main distinction regarding the software requirements is whether the tool is linear or nonlinear (rigorous simulation).

26.3.1.1 SOFTWARE APPLICATIONS FOR PLANNING ACTIVITIES

26.3.1.1.1 Linear Models

The overall optimization of a refinery or system of integrated refineries and petrochemical complexes is challenging because of many operating parameters and feed/product supply options. To help with this complex task, production planners make use of production plan optimization tools such as LP. The output of an LP model helps to provide directions and strategies to optimize facility operation.

TABLE 26.2—Software Applications Used in Different Phases of the Production Plan

Practice	Objectives	Software Application
Product demand and price forecasting	Price basis for evaluating initiatives	Crude assay management
Planning	Feedstock selection and optimal operation	LP run
Scheduling	Inventory control, plan production, and blending schedule	Scheduling run
Production optimization	Translation of operating plan into actions and further improvement	• Area target setting • Optimization
Model update	Ensure LP is up to date	• UPM • LP data generation

The LP model is a mathematical model of a process. The process can be that of a refinery, chemical plant, distribution network, or any situation with variables, constraints, and an objective function. The LP consists of a coefficient matrix representation of simultaneous equations with more unknowns than equations. Those unknowns may be fixed, bounded, or free.

For a complete and effective evaluation of feedstocks used to produce the highest margin product slate, LP tools model entire refinery operations. Planners use LP models to optimize crude purchases, other feedstock purchases, and anticipate operational resources to maximize refinery profitability. Operating capability and restrictions, feed and product prices, and supply and demand restrictions vary frequently. The LP model is updated regularly to reflect these changes and ensure effective optimization against up-to-date restrictions.

Trying to formulate refinery operation in a computer is a very complex task that requires hundreds of decision variables and thousands of constraints, as shown in Figure 26.12. The optimization of such a system is normally simplified using linear relationships, although current developments are increasingly adding nonlinearities to the system.

Three fundamental issues need to be addressed to produce a good LP model [45,46]: (1) structure of the LP model (2) quality of data, and (3) LP model surrounding processes. LP programs are used instead of rigorous nonlinear programs to handle sitewide or multisite optimizations because linear correlations reduce the complexity of the optimization process and guarantee convergence. However, LP models can be very complex; therefore, it is critical to design LP model structure to fit their needs. Overcomplexity is not desired and often does not improve accuracy. It is important to keep the balance between LP model accuracy and complexity. For example, strategic planning looks after improving long-term competitive advantage by covering investment/divestment opportunities, which can be addressed with simplified LP model structures.

The LP model contains relationships that reproduce plant operations. It is critical to populate these relationships with the proper parameters that correctly reflect the actual operation. It is best to generate these parameters using rigorous process simulators. The process simulators are tuned to reflect the actual plant operation. Multiple runs of the process simulator are used to generate data that describe the behavior of the process units in the LP model. This aspect of generating data to improve the accuracy of the LP will be covered later in this section.

The processes surrounding the LP model include obtaining the LP model input data. A significant amount of information is required that together forms the boundaries of the optimization process. These include a price set for all feeds and products, availability of feedstock (quantity and quality), limitations on product sales, operating costs, process unit limitations, product blend specifications, and the connectivity between the process units and all of the possible routes for every stream in the refinery. These parameters need to be updated on a regular basis

The input data/information required for the LP data generation is as follows:

- *Process model (distillation/conversion unit model):* This is the process simulation model used by unit engineers for unit monitoring. The process engineer should regularly calibrate the model as described in the UPM practice. This ensures that the same process unit operation bases are used by process engineers for unit monitoring and planning engineers for LP table generation.
- *LP table structure:* This is the design of the LP table, which includes all of the input parameters for the LP model. Best practice in process unit LP tables features feed-quality-dependent yields, product quality recursion, operating parameter optimization, and product cutpoint optimization. Best practice in crude assay tables features swing cuts for cutpoint optimization and actual fractionation qualities for product cuts.

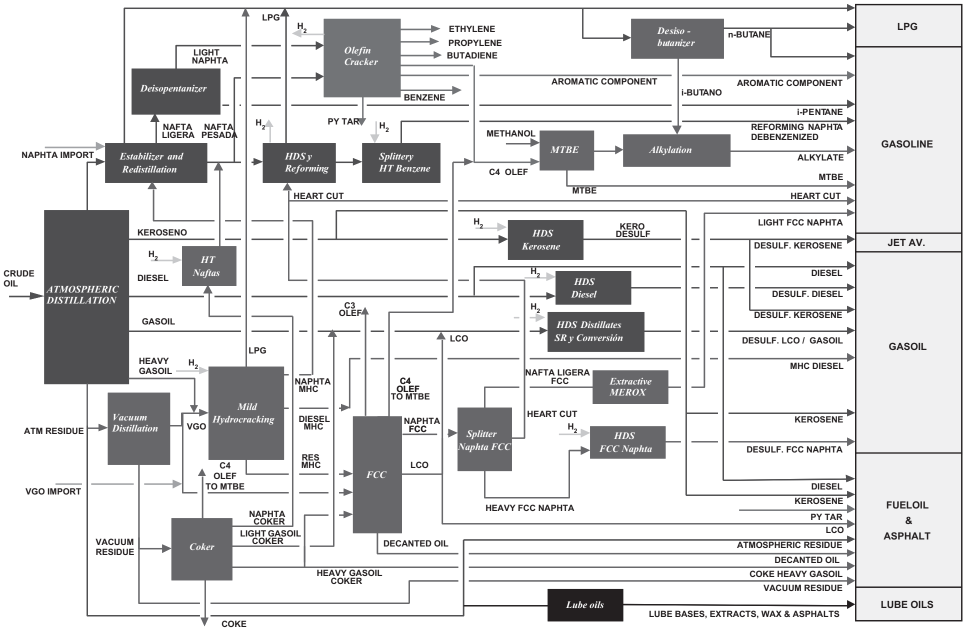


Figure 26.12—Complex nature of refinery operations.

- *Base operating conditions/feed qualities:* The base operating conditions and feed qualities are usually based on the plant data (reconciled) in the calibration case, although alternative base operating conditions may be defined on a case-by-case basis or with a delta-based vector obtained by rigorous modeling.
- *Operating range:* This is the typical operating experience envelope of the parameters used in the LP table (e.g., range of feed sulfur). This input should be obtained from a process engineer.
- *Process unit processing constraints:* This refers to operational limitations observed in the process unit (e.g., capacity constraints, total feed and product draw rates, FCC wet gas compressor capacity limit, reformer severity limit, reactor temperature limitations, etc.). All of these constraints should be configured to remain within the safe operating envelope for the process units concerned. This input should again be obtained from a process engineer.
- *Crude assays:* For assay data generation, raw crude assay information is available from laboratory analysis. This information is useful for LP and rigorous models.

The key to LP data generation is to produce a submodel for the LP that is up to date and behaves similar to the real operation. Having a good LP that matches plant operation under different scenarios allows for good decision-making with regard to which crudes to buy and will also provide the optimal operating parameters that will maximize profitability. The results of the LP run include feedstock selection, operating margin, and product balance for the refinery. This information will be sent to the refinery operations so that appropriate targets are set for the period. The effect of accurate LP for refinery economics may be decisive, as shown in Figure 26.13. Best practices include running refinery-wide rigorous models to further optimize the operation on the basis of operating constraints that are not contemplated in the LP.

Once the optimized production plan has been defined using the LP model for the operations plan (short-term future), the operation needs to be scheduled, taking into account logistics restrictions such as availability of storage, process units and product blenders capacities, jetty availability, etc.

The scheduling process may also become complex for sites with multiple feeds and products. Although some facilities use in-house constructed scheduling aids, commercially available scheduling tools have become more standard practice to ensure full utilization of plant capacities.

Most common refinery products are blended from multiple components using multiple quality and sometimes compositional constraints. Although the LP model and sometimes the scheduling tools provide guidance regarding the required blend compositions to produce in specification products, most facilities use additional tools for this purpose for each individual product blend. These tools are often based on spreadsheets using an optimization step to solve the best (economical) solution and sometimes include nonlinearities for some specific properties. It is common to have in-line product blenders with quality control to adjust the composition of specification products; however, these are not used for all products at all facilities.

An important practice is "backcasting" to check for lost opportunities; this compares the planned production with the actual production. Backcasting is used to validate the accuracy and capability of the LP. In addition to forecasting, backcasting is used to analyze the operation of a past period compared with the planned one using actual plant restrictions, price sets and feed, and product supply data. The outcome of this backcasted plan can be used to quantify lost opportunities (suboptimal operation) and provides a good indication of the capabilities and accuracy of the LP model. This backcasting process can be used to initiate LP model updates as described by the LP data generation application.

The LP model is also used to help to distribute the refinery products between different shareholders. Separate LP model runs for different shareholders are used, reflecting the respective operating plans and strategies, together with actual plant operating data for this purpose. To ensure the best outcomes and business decisions using the data from an LP model, regular updates of the refinery representation are essential.

26.3.1.1.2 Nonlinear Models

Nonlinear models are generally used to support and update LP models but also to optimize the operating plan on a daily basis to obtain the production plan, which is more detailed regarding the specific feedstocks processed in a refinery. This activity of updating the LP with rigorous

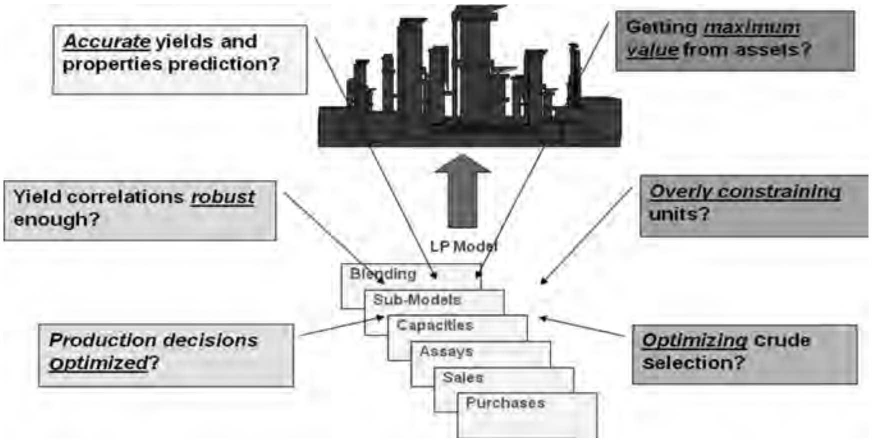


Figure 26.13—Effect of accurate LP on refinery economics. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

simulation is commonly described as LP data generation and is described below.

- *LP data generation (support to LP models):* LP models are not only used for forecasting crude selection to optimize the operation on a monthly basis but also to evaluate capital investments in the medium- to long-range time frame. To ensure the best outcomes and business decisions using the data from an LP model, regular updates of the refinery representation are essential. The LP data generation application is a key aspect to ensure that the refinery LP model is kept up to date, accurate, and robust to provide a firm foundation for accurate decisions in the supply plans and operating plans.

  Operating plans with different time horizons as well as crude selections are obtained with the use of LP tools, as mentioned previously. These tools require tables of information regarding refinery unit product yields and properties as well as operating requirements for each crude available.

  In the case of distillation columns, short-cut models are traditionally used to generate the required data for the refinery LP planning models. There is a benefit of using rigorous models, which in turn lead to more sound trends of LP predictions of column product properties because rigorously simulated products will contain a better representation of the tails of distillation curves, which contain components that may have a great effect on the prediction of product properties (e.g., freezing point, cloud point, etc.).

  In LP data generation applications, a calibrated rigorous simulation model is used to generate the predicted yields and properties for the different crudes and crude mixtures that will be potentially processed at the refinery. The generated table with yields and properties will be used by the LP. Further optimization by the LP will determine the most economically optimal crudes to process by the refinery as well as the unit's operating plan [47,48].

  A critical requirement for making good predictions of physical properties in the LP is having a good characterization of the fractionation imperfections, which are best described by the shape of the distillation curve tails. Figure 26.14 shows a comparison between a theoretical curve with perfect cuts—in which there is no overlap or heavier material going into the lighter product—and a fractionated cut taking into account the imperfections in the distillation and therefore the amount of product being interchanged between cuts.

  For the same example, Figure 26.15 shows a comparison among the actual values, the ones predicted by the simulated cuts with nonrigorous fractionation, and those used taking into account perfect fractionation to demonstrate the effect of the tails on the predicted properties.

  In addition to simulate distillation cuts overlapping, rigorous column models are used to generate swing cuts (narrow cuts between each of the major products), which are used in the LP to optimize the crude column cutpoints. Swing cuts are added to the crude assay tables along the stream representing the actual tower products (Figure 26.16). LP optimizes the distribution of these virtual cuts, either adding it to the lighter cut or to the heavier cut. This optimization is driven by preferred cut qualities and yields. Because swing cuts are not produced in the real column, their properties are determined by running a column model at two cutpoints and taking the difference [49].

  Of special importance is the use of kinetic reactor models in support of economic planning tools, especially LP modes. The reactor models in LP need to be simply represented because a planner needs to be able to optimize a full refinery (or several ones) in a very short time. Therefore, the kinetic approach described in Section 26.2.1 is not feasible even if the model is executed within a reasonable time of several seconds [50].

  The most widely used approach is to develop rigorous models, especially for the LP that is based on several operating modes (base points), and shift vectors to take into account the effect of operating variables on product yields or properties. All of these base yields and properties as well as the shift vectors are normally obtained from kinetic reactor models rather than from direct analysis of experimental data. Table 26.3 summarizes main feed qualities and operating parameters considered for LP reactor models.

  The main reason for using rigorous models to update the LP is that through the analysis of experimental data, it is not possible to quantify the effect of isolated feed variables (e.g., specific gravity or sulfur) because any crude change will produce differences in all feed characteristics and not simply a single characteristic. Making changes to one isolated variable at a time is the best practice for building LP. Additionally, obtaining multiple sets of experimental data is difficult (steady state, consistency, only under standard operating conditions, etc.) and very expensive [49].

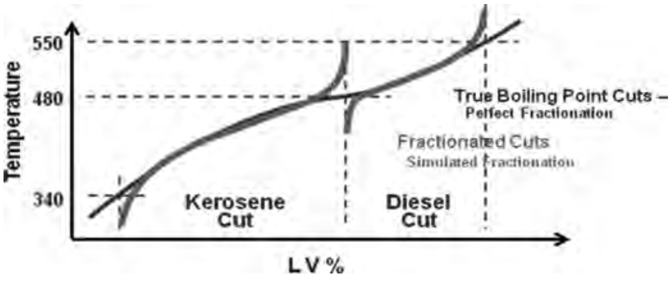


Figure 26.14—Kerosine and diesel fractionated cuts vs. ideal fractionation. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

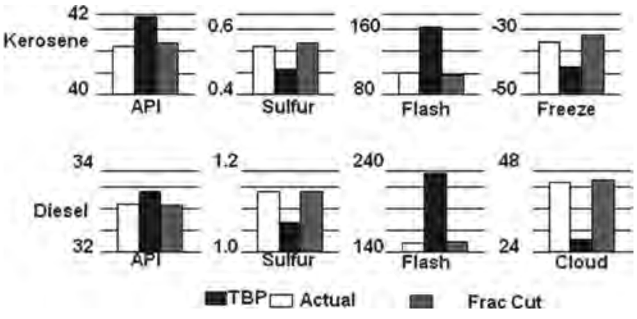


Figure 26.15—Property prediction differences from nonrigorous fractionation. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

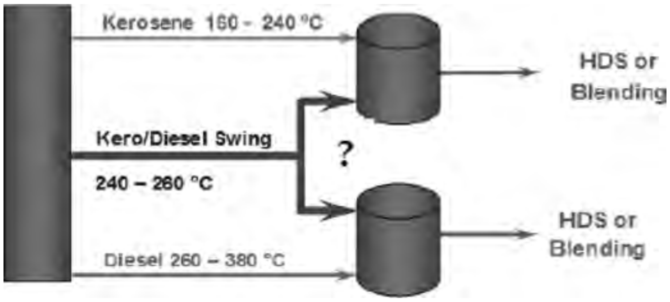


Figure 26.16—Representation of theoretical swing cuts in a rigorous model. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

TABLE 26.3—Important Feed Qualities and Operating Parameters for LP

Unit	Feed Qualities	Operating Variables
FCCU or RFCCU	Average Boiling Point Sulfur Nitrogen (basic) Specific Gravity Carbon Residue Nickel Vanadium	Preheat Temperature Riser Temperature VGO Flow Rate Resid Flow Rate Hydrotreated Feed Flow Rate Product Cut Points Catalyst Make Up Rate
Coker	Carbon Residue Sulfur Specific Gravity Average Boiling Point Nickel Vanadium	Drum Temperature Drum Pressure Combined Feed Ratio Product Cut Points
Hydrocracker	Average Boiling Point Sulfur Specific Gravity Nitrogen (basic) Bromine Number Carbon Residue Nickel Vanadium	Conversion Level N2 Slip (Unrec N2 in R-1 Efflu) Saturated Feed Flow Rate Unsaturated Feed Flow Rate Product Cut Points Catalyst Age
Hydrotreaters (Resid) (VGO) (Distillate) (Naphtha)	Sulfur Nitrogen (basic) Specific Gravity Carbon Residue Average Boiling Point Bromine Number Nickel Vanadium	Product Sulfur Level Saturated Feed Flow Rate Unsaturated Feed Flow Rate Product Cut Points Catalyst Age
Reformer (Fuels) (Chemical)	PNA for the Naphtha Components	RON Modes
Visbreaker	Sulfur Specific Gravity Carbon Residue Asphaltenes Viscosity Nickel Vanadium	Conversion Severity

Figure 26.17 illustrates the nonlinearities typical of an operation. The curve shows how product yield or properties change in a nonlinear fashion against changes in the feed properties or operating parameters. Thus, starting from a base scenario, the nonlinear changes in product yields and properties will be quantified in the rigorous simulation model as feed and operating conditions change. The results achieved will then be sent to the LP in the form of an LP table such that a linear model can predict more realistically.

- *UPM:* A UPM application is a system that collects plant data, performs some sort of reconciliation, and runs the model at given times to obtain predicted responses. For example, in the case of a distillation column, this application will provide trends for calculated variables such as distillation section efficiencies or flooding values. A process engineer can manually perform the process involved in UPM applications, but it is time-consuming and models are typically not maintained up to date, requiring more or less automated procedures for its successful implementation [51].

Kinetic reactor models can also be used to monitor units, mainly in fixed-bed units, where catalysis deactivation over run time is of key importance. Questions such as how long a catalyst will last or what the effect of any operating change over catalyst life is can be answered by a kinetic model more accurately than by a simple analysis of raw experimental data.

Experimental data variables (reactor average temperatures, product yields and quality) can be plotted versus catalyst age, but because of feed variations, they normally do not represent a clear trend that can be extrapolated. With the support of a kinetic model, operating variables such as those mentioned above are normalized to a unique feed type and conditions selected by the user, and the resulting “normalized” trends provide a clearer view of the unit performance [52,53].

The tools that are used to define the optimized production plan (LP model, rigorous process simulation models) must represent the actual operating capabilities of the plant. It is therefore critical that these models are verified frequently with respect to actual plant operation. UPM applications provide a feedback mechanism used to ensure that a plant is executing the optimized production plan.

Deviations between the model performance and actual plant operation may indicate that a plant’s performance has deteriorated or that the models need to be updated because of known changes to the plant operation or configuration. This performance management

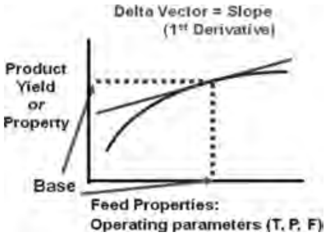


Figure 26.17—Representation of base case plus LP generated delta vectors. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

practice enables process engineers to capture these aspects and take appropriate actions.

Proper process UPM practices help ensure that a unit's health, utilization, and key performance indicators (KPIs) are adequately tracked and poor unit performance is resolved or taken into account until this performance can be rectified.

UPM will essentially compare the rigorous model against the LP submodel against the real operation [46,54]. Deviations will require troubleshooting. A good example is illustrated in the set of graphs of Figure 26.18. The LP model, the rigorous simulation model of the FCC, and the real plant data match well until a certain point, at which the LP and the rigorous model do not follow the actual operation (actual values). After investigation, the reason for the deviation is that the catalyst changed in the FCC and the models needed recalibration. Typically, if the unit performance is checked regularly following good UPM practice, the simulation model and the LP will behave similarly to the data used in the LP coming straight from the simulation model as described in the LP data generation application section.

The unit monitoring activities should be a mixture of online and offline calculations. In addition, selective monitoring results should be made "live" and translated/transmitted to the unit operators to assist them in executing the production plan.

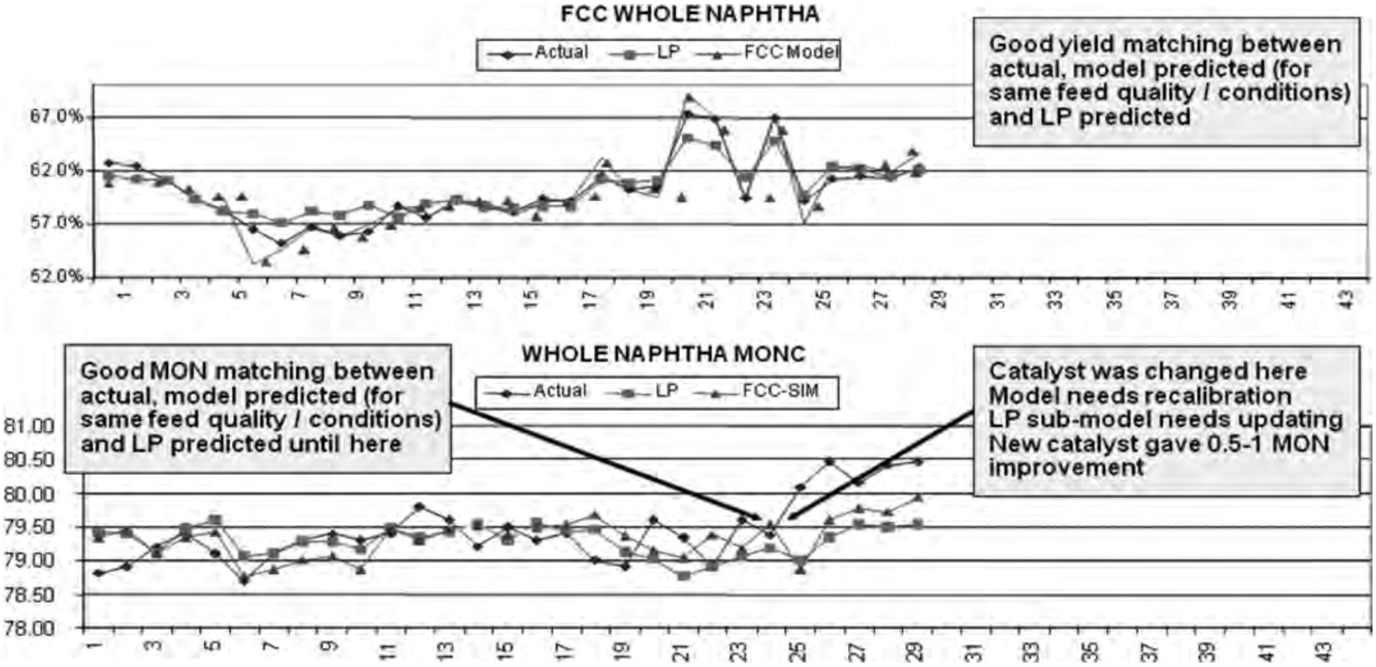
UPM is also about displaying key information to different levels in the organization because different departments will have different needs. Examples with their corresponding KPIs are shown in Figure 26.19 and may include operators; process engineering, production planning, and scheduling; and management.

To improve and sustain overall performance, the actual operation of the plant over a period of time (typically 1 month) should be validated against the original operations plan and against a "best possible" operation. The best possible operation is defined by an LP backcasting analysis. For LP backcasting, the LP model is used to reoptimize the operation of a past period using actual process plant operation and actual price set as input. This practice defines the most optimal operation using the actual plant restrictions and can be used to learn lessons for future production plan optimization. This practice can also be used to initiate updates to the LP model, as described earlier.

- *Area target setting:* Area target setting is used to provide further optimized operating instructions and control targets. This optimization uses rigorous models and is performed for continuous operation. Therefore, those parts of the plant with intermediate tankage to feed the units will be isolated from the rest of the units to perform the optimization (e.g., FCC and gas plant). The result will be an optimal operation in that area on the basis of the feed selected for a certain period. Improved targets will then be passed to the operators for input in the control rooms.

A very illustrative example of area target setting is described by López-Rodríguez [55] with respect to the Petronor refinery in Spain. This refinery is generally under continuous operation from crude feed to product blending such that the area selected for further optimization—once the initial control targets are set by the planning group—is the entire refinery. The refinery-wide model simulates the whole refinery using first principles. This model has multiple purposes, and the different processes involved in the maintenance and use are described in Figure 26.20.

Simulation models are used at different stages of the optimization process and are used by the different departments involved in the process. The following description will illustrate the involvement of different personnel inside of the company organization.



Good yield matching between actual, model predicted (for same feed quality / conditions) and LP predicted

Good MON matching between actual, model predicted (for same feed quality / conditions) and LP predicted until here

Catalyst was changed here
Model needs recalibration
LP sub-model needs updating
New catalyst gave 0.5-1 MON improvement

Figure 26.18—FCC UPM application shows deviation after catalyst change. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

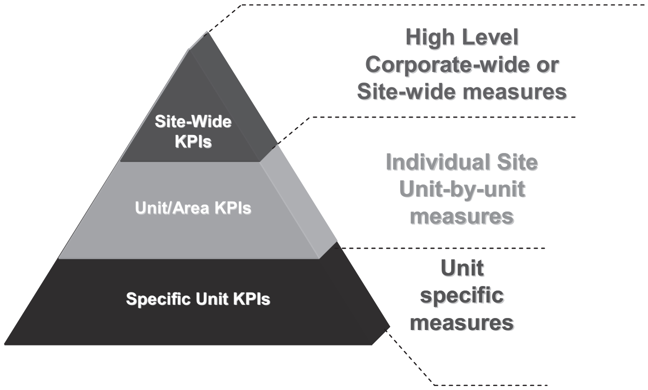


Figure 26.19—UPM users and KPIs. *Source:* Figure courtesy of KBC Advanced Technologies PLC.

- *Planning (headquarters):* The planning department uses daily market analysis to optimize the purchase of raw and intermediate materials. Raw feed accessible to the refinery is valued for different production schemes at market prices. Rigorous simulation models, which access the crude oil database, generate information (vectors and assays) for the LP tools that are used at this stage of the process. The planning headquarters (HQ) department selects crude oils with the help of the LP model and elaborates a detailed monthly production plan (MPP), aligned with current refinery status. Experience interpreting the results of the model and transferring them to the MPP is key to the success of the optimization process.

  The refinery-wide simulation model must be more precise and detailed than the LP for the refinery optimization. Having a global model in which the operating variables can be manipulated is essential to maximize the margins. It is also very important to use the same tool in the HQ and refinery planning groups.
- *Planning (refinery):* The planning department of the refinery receives the MPP from HQ. The plan contains an update of selected crudes, feed, and product stocks as well as the program of deliveries to the national and international markets. The refinery-wide model updates the scheduling software tool that is used to elaborate the refinery processing plan (RPP), which defines the basis of the operation by detailing how the crudes will be processed throughout the month. The RPP defines the feed to the units, raw material and product balances, schedule of product delivery and feed reception, evolution of crude stock and intermediate tankage, scheduling of ships, and crude processing.

  Therefore, the RPP defines the time periods during which the material contained in the ships and tanks will be processed based on manufacturing certain fuel product qualities. Each time period is then evaluated with the refinery-wide model, which contains input determined by the RPP. The objective of this evaluation is to define the basis of the production in the refinery (basis refinery production [BRP]), providing specific instructions regarding the operation of different units.

  This global model will contain a virtual picture of the refinery in a future time period defined by the RPP. Some of the key process variables that can be manipulated to optimize the operation during that interval of time may be crude mixture, atmospheric and vacuum distillation unit stream cutpoints, process unit throughput and severity, routing of streams to HDS units, and blending recipe optimization. Cutpoint optimization (e.g., naphtha/kero and heavy diesel/atmospheric gas oil) and product blending optimization are critical to minimize quality giveaway from specifications and may be translated into substantial economic benefits for the refinery.

  Although the simulation run produces very valuable information, in reality the day-to-day operation is more complex, and the model can diverge from reality

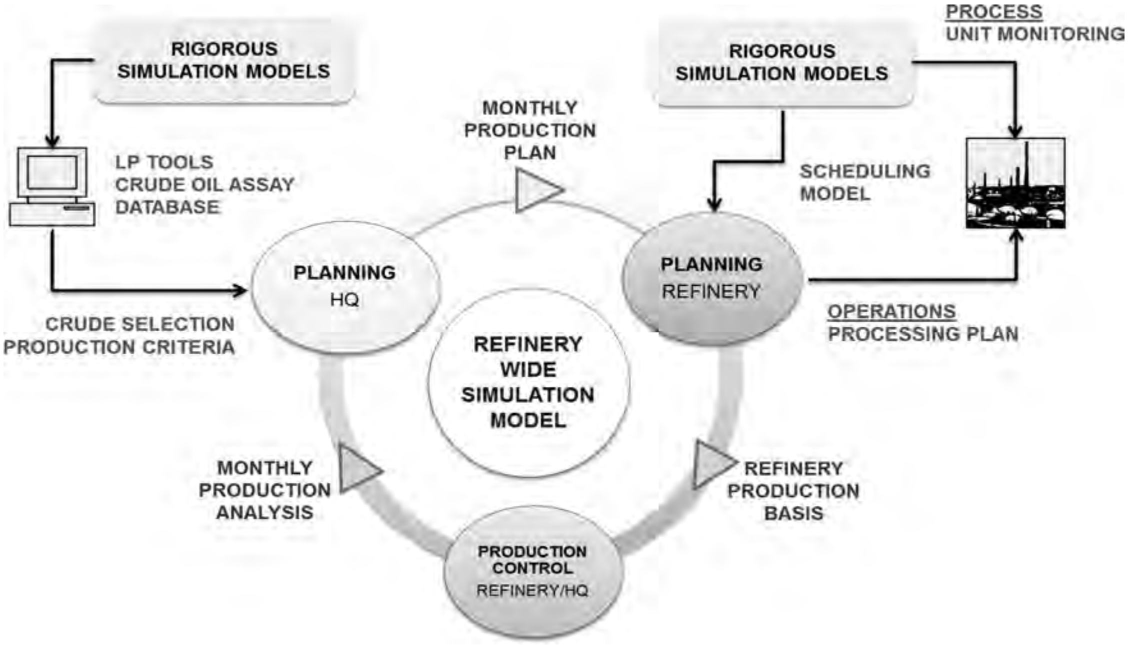


Figure 26.20—Refinery-wide optimization process.

because of incidences in the units or inaccurate data. Information provided by the model is contrasted with experience and analyzed daily during the production meetings, in which the operations department discusses and clarifies the BRP, which is then used as a reference until the analysis from the crudes processed is available from the laboratory. This information takes between 12 and 24 h after the tank is changed. Product blending is tuned by quality responsibles that work in shifts and use instructions from the production system, online NIR analysis, and laboratory data stored to guarantee final tank product specifications compliance. Given the fact that crude changes every 2–4 days, the immediate availability of information from the model facilitates the operation and increases the refinery margin.

- *Production control (refinery and HQ):* The daily control of yields, throughput, and operating conditions of the units is performed in the refinery to detect model deviations from reality. Those deviations are monitored and used to determine if the individual models need recalibration. In addition, the refinery planning department submits a monthly report on the production, in which the refinery-wide model is run with the past month data, the results are compared to the real production, and corrective action is taken for the future. The HQ planning department monthly analysis quantifies the differences between the MPP and the actual values in economic terms to be used as feedback for future plans.
- *Process engineering (refinery):* The process department is responsible for the up-to-date maintenance of the individual models. This department determines when the individual units need to be recalibrated. Common factors that require recalibration of the models are catalyst change, modifications to the unit configuration, or significant operational changes. The process department is also responsible for coordinating the test run that will provide the necessary data for the calibration of the unit models. Moreover, the individual models are used extensively by the process department for process monitoring and follow-up process problems by comparing the actual yields and product properties with those predicted by the model. The models are also used to optimize the individual units and detect bottlenecks or limitations given by certain operating conditions, which are important investment analysis tools because the changes in a unit can be quantified by looking into the refinery-wide model.

Finally, as commented previously, common tools and processes will enhance cooperation among the different groups involved in the refinery optimization.

26.3.2 Process Engineering

The simulation models used for process engineering applications as well as to support current refinery operations are mainly steady-state models. Although dynamic simulation is also available, it is mainly used for control applications and operator training purposes. This section only covers steady-state simulation and its application in process and production departments. Section 26.3.3 covers the applications of dynamic simulation.

Steady-state simulation is used to study process alternatives, equipment selection and design, and economic studies to justify capital expenditures. These same models are also used for existing units' operational improvement, debottlenecking, and troubleshooting studies. Refinery engineers can also develop tools on the basis of simulation models, such as unit monitoring applications that will allow them to track variables not accessible by direct measures, such as heat-exchanger fouling, distillation efficiency, or catalyst activity, as described in Section 26.3.3.2. Another important application of rigorous process models is to update different tools such as LP models, refinery-wide models, etc., that are used in production planning optimization.

The proper use of simulation models in the design process can significantly reduce upfront capital expenditures for grass-roots unit and refinery revamp projects. Making the correct decisions early in the design process has typically been shown to reduce costs by hundreds of thousands to millions of dollars.

Steady-state simulations used in refinery operational improvement, debottlenecking, and troubleshooting activities also provide an invaluable source of information for the plant engineer. The effect of such work is difficult to quantify because it depends on each problem addressed, but industry experience has shown that simulation-based projects greatly affect refinery operations.

The steady-state simulations that are used in design and troubleshooting are also the base models for unit monitoring applications. The unit engineer is able to develop a monitoring tool that allows plant personnel to follow variables of equipment performance that are not directly measurable, highlighting areas of deteriorating performance and allowing engineers to proactively deal with the growing constraints. Thus, process simulation constitutes a well-adapted method of developing basic knowledge regarding a given process, providing tools that can be applied to many different problems and their various stages.

By creating models with several key refinery units, including reactor models, and tracking the key refinery economic drivers (e.g., octane number, cloud point, pour point etc.) process engineers are able to evaluate the effect of their decisions beyond their specific unit, focusing on the critical economic drivers of the refinery and providing a valuable support to business operation planning. Thus, the process models are a common tool for the different groups involved in the refinery optimization, allowing them to speak the same language and to enhance cooperation.

26.3.2.1 SOFTWARE APPLICATIONS FOR PROCESS ENGINEERING

The use of rigorous models in process studies is a critical tool for refineries not only to understand plant data or to isolate certain variable effects but also to help in decision-making, which becomes increasingly difficult because of the limited margins of the refining industry. What follows are examples of refinery applications.

26.3.2.1.1 Engineering Design

The application of distillation models in designing new columns as well as in revamping existing ones has been widely used for years. From a simple study such as determining component profiles, feed location, or utility consumption, to a more complex study that evaluates the effect of any change in an existing column over other unit equipment, to the calculation of tray physical properties for column internal mechanical design, the possible applications of distillation models in design studies are unlimited [56].

Nevertheless, reactor models cannot be used to design new reactor units. Because reactor models require the calibration of kinetic factors to existing unit catalysts and unit geometries, it is not until the unit has been designed and these have been determined that the model can be applied. Basic information required would be catalyst and geometry, as described in the licensor process book. A model calibrated with process book information will allow the refinery to run many case studies for the unit operation and gain an understanding of the effect of many operating scenarios as well as their effect on the downstream separation units, but it is not applicable to the design phase.

26.3.2.1.2 Unit Troubleshooting

Unit troubleshooting with simulation models involves building a model once a unit is not operating as expected; after comparing the simulation results (theoretical performance) with actual data, the engineer must investigate the root cause of the problem. Sometimes the solution can be as easy as modifying the operating conditions (i.e., pressure) if the model is predicting column flooding under current conditions or to suspect tray damage if the section efficiency is much lower than usual. Heat integration issues and how they may affect column performance can also be investigated.

26.3.2.1.3 Operational Improvement and Debottlenecking

Simulation models can provide the best insight into column operation and reveal the effect of changing an operating variable such as the reflux ratio, stripping steam flow, pump-around profiles, etc., on the overall unit performance. These kinds of studies are not routinely performed in refineries, but they could lead to important operational improvements and in many occasions to changing operating procedures that may be outdated [57].

Distillation column models are often expanded to include in their scope the preheat train network, the operation of which is very deeply connected to the operation of the main distillation columns and lighter product separation. Heat-exchanger models need to predict heat-exchanger performance over a wide range of operating conditions (crudes to be processed, operating modes, etc.). The model can be basic and use the UA of each heat exchanger, or a more detailed model including the geometry of each heat exchanger (number of tubes, baffles, etc.). The UA models are simpler and faster to run, but U values change significantly with the flow rate and with the stream physical properties; moreover, the results of the model may not adequately represent the overall envelope of preheat train performance.

Models that take into account the detailed geometry of the heat exchanger are more accurate in representing the network behavior, but they are also more complex and feature very long execution times. Models including the preheat train are very useful when there is a capacity constraint on the furnace, and heat-exchanger network debottlenecking studies are required. Multiple operating conditions can be run in the model; therefore, the limiting conditions in a furnace can be calculated. Operating solutions such as split flows can be assessed for potential improvement [58].

These types of studies are relevant to performing a comprehensive energy review of a unit (especially high-energy-consuming crude and vacuum units) using pinch methodology, which features the possibility to modify heat-exchanger network architecture, as shown in Figure 26.21.

Finally, the application of reactor models for operational improvement, debottlenecking, and troubleshooting activities also provides many benefits to refineries. The unit optimization application adopts an operations perspective of the engineering studies conducted for operational improvement [59–61]. As an example, Figure 26.22 illustrates the different tasks involved in the calibration and use of a reformer reactor model.

26.3.2.1.4 Multiunit Refinery Models

A multiunit refinery model must include several major units such as FCC, hydrocracking, reforming, and isomerization models as well as main distillation columns such as crude and vacuum columns. These models can use the stream characterization approach according to boiling range, but they must also carry information regarding refinery

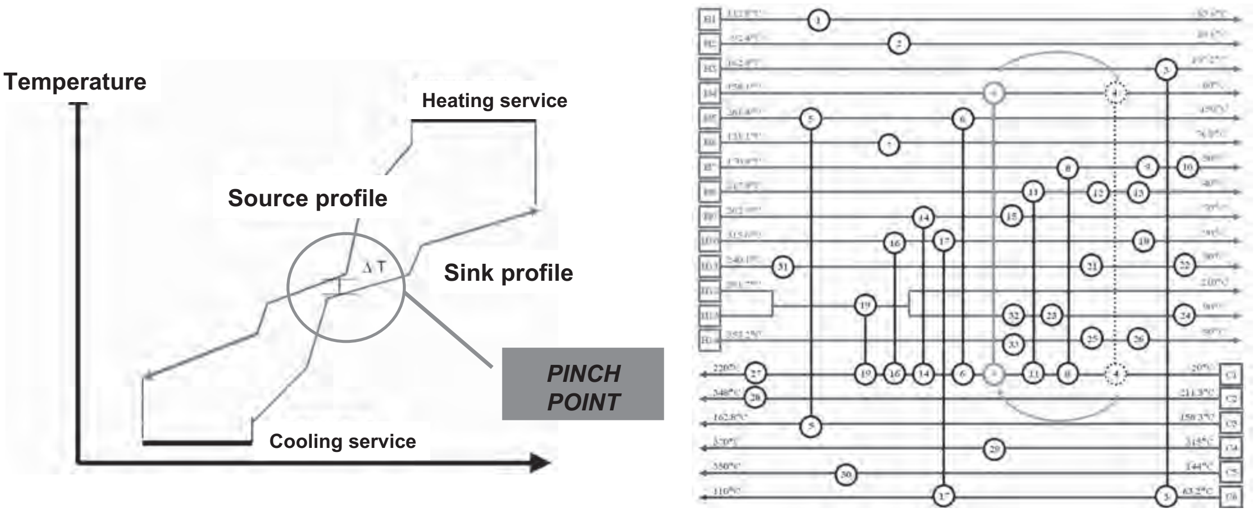


Figure 26.21—Pinch analysis for a heat-exchanger network.

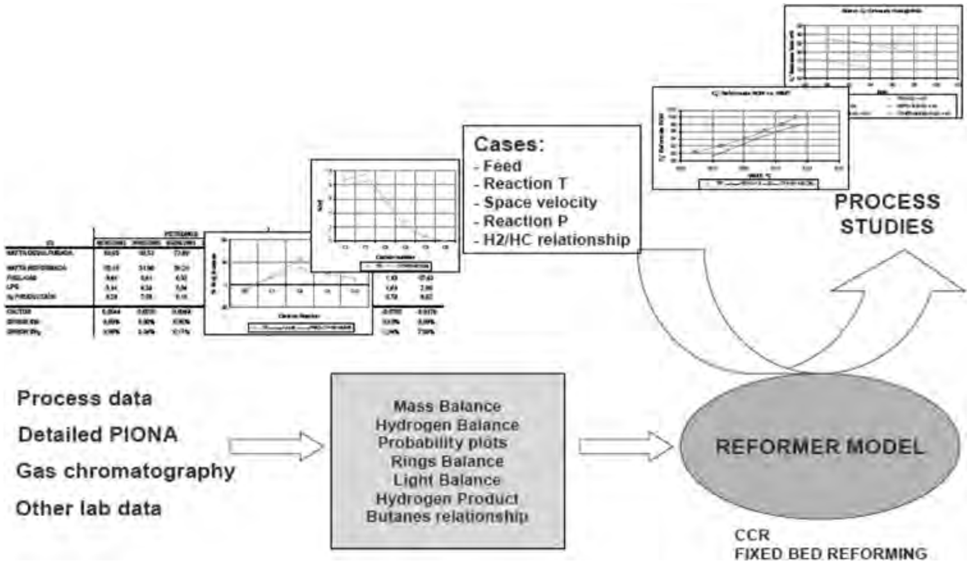


Figure 26.22—Development and application of a reformer reactor model.

properties (e.g., sulfur, nitrogen, PNA, concarbon, metals, etc.) to be used by the reactor model when developing the appropriate component composition of a given reactor.

These models are more difficult to adjust to actual refinery operating conditions, but they have the added benefits of capturing several unit operation behaviors; therefore, yield improvement or optimization is performed by taking into account their dependencies. A typical example of a multiunit refinery model with strong interactions is the FCC feed pretreater (mild hydrocracking) and FCC, in which the optimal operating conditions overall may be very different than the optimized conditions for each individual unit [62].

The naphtha complex, including a naphtha splitter, catalytic reforming, isomerization, olefin cracker, and their separation units, is another case of highly interconnected units that offer benefits when evaluated to improve one unique model [63].

Finally, models with all of the main units of a given refinery are of value in analyzing overall refinery interactions. Questions regarding the effect of a major potential change in the operating conditions in the overall refinery yields and properties can be best answered by a simulation model than any other way. Examples of these changes are new crudes, a different crude cutting scheme, or an additional unit to be evaluated [55], which was already discussed in Section 26.3.1.1.2.

26.3.2.1.5 Optimization

An optimization model can be completely offline, relying on the operations engineer to feed data to the model and to implement the model recommendations; online for data collection but offline for implementation of optimal set points; or fully online (called also “closed loop”), in which the model does everything without any human intervention. The intermediate option offers most of the benefits with less model implementation effort, but the refinery choice is normally based on the availability of technical personnel [64].

Thus, it is possible to consider the analysis of the commitment between the fractionation in a crude column (quality cuts) and the effect in the heat recovery of the preheat train of the unit feedstock (saving fuel in the furnace and the reduction of associated carbon dioxide emissions) [65]. The analysis of complex columns of this is simple for the few components involved and has a special role in the optimization of the margin of the propane-propylene superfractionator, improving the flow and purity of the propylene stream [66].

Using rigorous first-principles process models to optimize the operation of olefins plants has been successfully performed at various operating plants worldwide. These optimizers play an important role in maximizing the profitability of the plants. The optimization of closed-loop olefin plants is attractive, but in practice there are several problems to solve, such as modeling difficulties (including all furnaces, heat exchangers, distillation columns, compressors, pumps, etc.), predicting furnace run length (because predicting the furnace fouling rate is not easy), and implementing steady-state models in a dynamic environment (including finding steady-state conditions to adjust the model in a dynamic situation). Over the years, the different problems have been solved considering several approximations, including implementing a rigorous furnace optimizer but using simplified models for the recovery section (to capture >80% of the potential benefits) [67] and integrating the rigorous steady-state models with the dynamics among all of the individual controllers, providing an effective hybrid solution [68].

The problem with online optimization is that it is very expensive to implement and maintain and it has reliability problems and inherent inaccuracies that undermine the achievable benefits. In contrast, offline optimizers offer 90 % of the benefits of online optimizers at less than 10 % of the cost. Thus, an offline olefin plant optimizer as described in Figure 26.23 allows the user to optimize feedstock selection, cracking severity, and operating conditions according to the actual plant constraints and daily plant production [69,70].

To conclude this subsection, and as a complement to the success cases already discussed through the different applications, Table 26.4 summarizes several selected recent literature references for each of the main refinery process units. These selected examples illustrate recent approaches to refinery unit modeling.

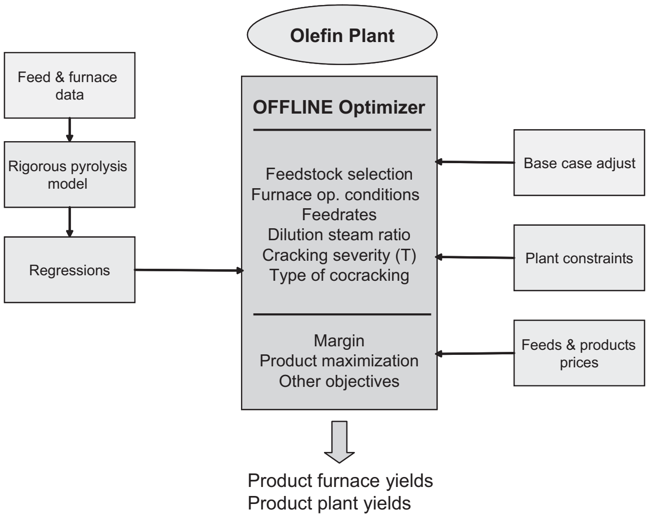


Figure 26.23—Olefin plant optimizer.

26.3.3 Process Control

The dynamic simulation of refinery processes based on first-principles models has also become a mature technology over the last few years. This technology is commonly used during design and revamps for testing control configurations, the development of operating procedures, and operator training. It can also be used in actual operating refinery units for control strategy troubleshooting and improvement as well as to accelerate the implementation of APC systems [104,105].

TABLE 26.4—Selected Examples of Applications of Refinery Unit Simulation Models

Unit	References
Pretreatment units	
Desalter	71,72
Preheat train	73,74
Distillation	
Atmospheric distillation	48,75,76
Vacuum distillation	77–79
Reactors	
Catalytic reformer	80–82
Hydrotreating	83–85
Hydrocracking	86–88
Fluid catalytic cracking	89–92
Delayed coking	93,94
Visbreaking	95,96
Other refinery units	
MTBE/ETBE	97–99
Lubricant production	100,101
Claus/hydrogen	102,103

MTBE = methyl tertiary butyl ether, ETBE = ethyl tertiary butyl ether.

Dynamic simulation requires steady-state models to be transformed into dynamics by specifying additional engineering details such as pressure/flow relationships across any unit operation, equipment dimensions, and control schemes.

26.3.3.1 DYNAMIC MODELS FOR PROCESS CONTROL

The applications of dynamic simulations are quite different than those of steady-state models and range across operational dynamic studies, safety and reliability, control studies, and operator training systems.

- *Process design:* In the process design area, dynamic simulation is used to evaluate operational stability to ensure the controllability of a future plant. Several typical disturbances should be run to check the plant response and determine the optimal designs from a controllability point of view. At the same time, dynamic models can also help in cutting capital costs by minimizing the overdesign of equipment.
- *Safety and reliability studies:* In the area of safety and reliability, dynamic simulation is mainly used for relief studies. It is necessary to ensure that relief systems are capable of handling all emergency relief scenarios with new process changes. The evaluation of the effect of possible pressure relief scenarios on flare system loading and identifying strategies to reduce relief loads are typical studies that are performed [106]. The determination of design and analysis of emergency shutdown systems with a cause-and-effect matrix is a special case of plant operational studies [107].
- *Process control and operation issues:* Dynamic simulation can be applied to develop a control strategy during process design activities or can be applied over an existing plant that needs to be evaluated. Dynamic simulation provides insight into the process by allowing the control engineer to perform the following:
  - Determine how disturbances propagate through a system;
  - Understand the relative sensitivity of process variables to process upsets;
  - Investigate process and control-loop interactions;
  - Determine the effect of equipment sizing or arrangement changes on disturbance rejection and overall operability;
  - Determine the effects of ambient conditions on process operation;
  - Compare the dynamic performance of alternative control strategies;
  - Perform control-loop tuning; and
  - Investigate startup, shutdown, and low-, mid-, and maximal throughput operation.

  A dynamic model that represents plant behavior correctly can be used to build a multivariable process control model in a very short time and move into a production system quicker, as shown in Figure 26.24. The multivariable controller requires knowledge of the transient responses of the process from known disturbances for their proper design and implementation. This

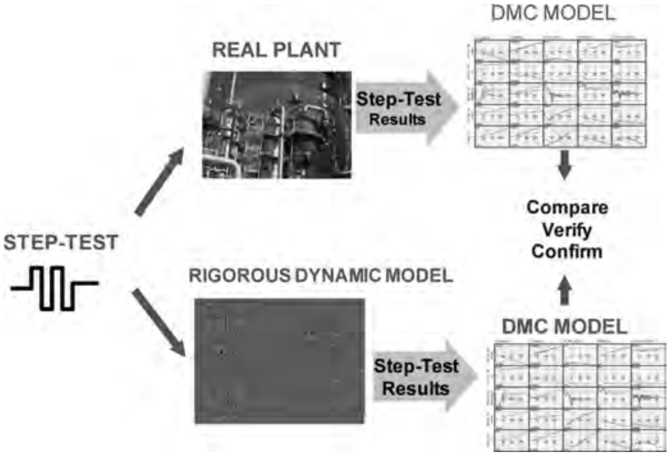


Figure 26.24—Dynamic matrix control model generation. *Source:* Figure used with permission from [110].

knowledge has usually been obtained from extensive plant testing, which is expensive and time-consuming. Using rigorous and validated dynamic models in addition to limited plant testing reduces the time and cost of the process identification step. Fine-tuning of the multivariable controller once it is operating is the final step in achieving the full benefits of a project [108–110].

A special case of control studies is in the benefits justification of the implementation of advanced control systems. Because most refinery reactor models are developed in the steady-state mode, these kinds of process models are used to analyze the benefits of APC systems, considering that it is necessary plant information (usually test-run data), after and before implementation to the controller.

Dynamic simulation can evaluate the benefits of adding an online analyzer, including its best location and the economical and operational advantages. For example, using HDS dynamic simulation, it is possible to study the possibility of adding an online sulfur analyzer to the feedstock of the unit. The model allows for the inclusion of this analyzer as a new variable in the multivariable controller and to check if an improvement in the control response would be achieved (Figure 26.25) in terms of the stabilization time and standard deviation [110].

It is important to mention that this HDS unit model is completely dynamic (reaction and recovery areas) because rigorous refinery reactor models are usually operated in steady-state mode.

Compressor studies are a key application of dynamic simulation because the operation of compressors below their minimal design capacity can result in compressor damage, offspecification products, and unanticipated plant downtime. To ensure the control and operability of this important process operation, dynamic simulation is used to test and validate the performance of compressor surge control systems during production changes, normal operation, and startup and shutdown. It is important to mention that this HDS unit model is completely dynamic (reaction and recovery areas) because rigorous refinery reactor models are usually in steady-state mode.

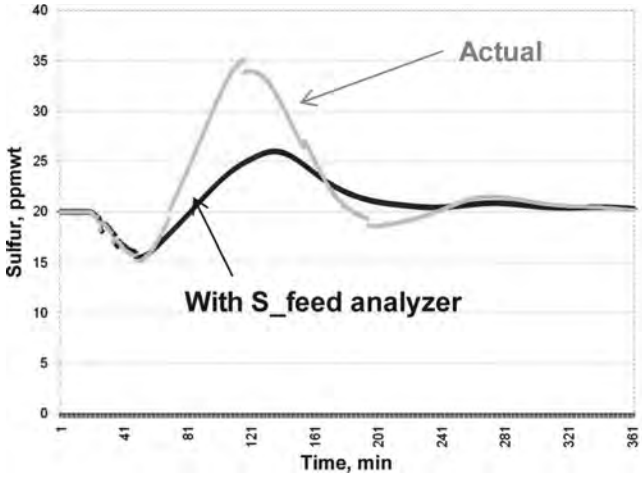


Figure 26.25—Control improvement with a feed sulfur analyzer. *Source:* Figure used with permission from [110].

- *Operator training simulators:* A natural extension of the plant control and operational studies is online operator training. Once the control configuration has been validated and is working as expected, the integrated DCS/dynamic model makes the perfect operator training station. Operators are able to practice, in a risk-free environment, startup, shutdown, and emergency action sequences using the actual control-room hardware. Operations trainers can be configured with an APC layer to mimic the actual operating system. Alternatively, this layer can be disabled, allowing operators to better understand the fundamental interactions of their process units [111].

26.4 FUTURE MODELING TRENDS

Because process simulation is such a widely implemented technology in today's refineries, different users have different perspectives about future trends regarding refinery model simulation. Some of the common ideas could be organized as follows:

- *Development of more robust models and open code:*
  - More simplicity in calibration of process unit models;
  - Better response to feed or catalyst changes or both, improving predictability;
  - Future product specifications will be reproduced; and
  - More open simulation environments (CAPE OPEN, third-party integration, etc.) that will allow integrating models from different providers.
- *Integration of models now specifically focused on particular applications such as planning, process and control:*
  - Planning models closer to reality of the plant, and
  - Nonlinear process models for control applications.
- *Development of new simulation techniques and new applications.*

These changes will occur in parallel with advances in mathematics, information systems, analytic techniques, and online applications.

26.4.1 More Robust and More Open Models

One of the main problems with the rigorous simulation of process units (in particular conversion reactors) resides in the difficulty to calibrate it. Model calibration relates to numerous factors, the most important of which are due to processing different feedstocks and different catalysts throughout the life of the unit. Therefore, the improvement in the predictive capability of the models involves having a database of unit factors linked to the different feedstocks and catalysts. To generate this database of calibration factors, it is necessary to have much information from the physical unit and from the pilot plant with different future feedstock and catalyst types (catalyst evaluation). This will expand the range of model validity, improving the model's predictive response.

Models will also need to be responsive to new product specifications so that they meet stringent environmental and quality restrictions. This will imply having more information regarding the chemistry of different streams, which will need to be analyzed on a more extended routine basis in refinery laboratories (properties such as benzene, sulfur, nitrogen, polyaromatics, etc.).

Therefore, models with complex kinetics will be developed to handle sulfur specifications. FCC models will not only use UOP characterization factor or the aromatic content to characterize the crackability of the feedstock but also the number of condensate cycles in aromatics to differentiate feedstocks, etc.

Commercial simulation packages are currently quite similar, although they often allow third-party extensions. Development seems to point in the direction of more open models. This is a continuation of CAPE OPEN, which will allow for the integration of any simulation model in any platform because all will have the same standards. The preceding discussion suggests that many advantages will be afforded to the user because they will allow for the best unit models implemented in the simulation interface of their choice.

Finally, data exchange using simple interfaces will allow users to send and receive data from spreadsheets to the simulation interface. Specifically, the most useful models are those that use Microsoft™ Excel or a .NET Excel emulation for input, output, and graphics. This area is very close to information systems but generally requires a good understanding of the models and its applications. Engineers like such models because they do not have to learn a new graphical user interface.

26.4.2 More Integrated Models

The development of new mathematical algorithms for solving massive equation systems is one of the challenges to cope with during the next few years. There are already new algorithms to resolve massive linear equation systems that avoid local optima [112]. Progress in the nonlinear area is expected along with changes in calculus systems and closer relationships with supercomputers in performing daily tasks.

Therefore, in the refinery of the future, it is expected that a closer link will be forged between rigorous and LP models for planning and scheduling, either to unify models or to automate the update of the LP. Nonetheless, the refinery's viability will be a function mainly of the execution time and convergence of the models.

26.4.3 Development of New Simulation Applications and Techniques

The following are some applications that currently need improvement. These applications may be critical for the future development of unit models.

- *Data mining:* The real-time data available from refineries present special challenges. They are usually corrupted by noise and are nonindependent; additionally, there is a large quantity of data. In that context, data mining is derived from traditional types of statistical analysis but is focused on processing large databases to find undetected patterns and associations. The first-level tools include several special linear statistical techniques such as partial least squares (PLS) and principal components analysis (PCA). When these are not sufficient, other tools will be applied to provide more general pattern recognition. Thus, within the statistical follow-up of units, these techniques will develop indicators that will allow for the detection of deviations from normal operation on the basis of managing large quantities of data from previous operations, with the purpose of detecting needs for preventive maintenance or to anticipate problems with operations in the units. In any case, these statistical models must be accompanied by a large dose of process understanding to obtain robust models, avoiding any erroneous conclusions.
- *Computational fluid dynamics (CFD) models:* An opportunity for the development of more rigorous models is in the area of fluid dynamics. Typically, process models are developed with a detailed treatment of physical properties, phase equilibria, and reaction kinetics but with simplified fluid dynamics, whereas CFD models treat fluid dynamics rigorously but with highly simplified or ignored chemistry. There is a great challenge in developing models that accurately treat chemical and physical phenomena.
- *Advances in dynamic simulation:* In the medium term, the technique will be extended to the study of reactors in conversion units. Thus, the application to operator training models will allow for the analysis of the normal operation of a unit, its startup, and emergency situations. It will also include the implementation of rigorous dynamic models for the optimization of online processes, supported by foreseeable advances in instrumentation and techniques for online analysis.
- *Molecular simulation:* Different currently used techniques (e.g., Monte Carlo, molecular dynamics, Gibbs ensemble simulations, etc.) will allow for the analysis of complex systems in regions that cannot be tackled with current techniques. Thus, molecular simulation will be the experimental counterpoint for determining the limiting properties of compounds (such as critical properties, viscosity, etc.).

REFERENCES

[1] Rose, A., and Williams, T.J., "Punch Card Devices for Distillation Calculations," *Ind. Eng. Chem.*, Vol. 42, 1950, pp. 2494–2497.

[2] Göebel, H., "Process Simulation: A Walk through Its Development in Time," paper presented at the *Aspentech User Group Meeting*, Amsterdam, The Netherlands, 2005.

[3] Svrcek, W.Y., and Satyro, M.A., "Process Simulation—From Large Computers and Small Solutions to Small Computers and Large Solutions," *Chem. Prod. Process Model.*, Vol. 1, Article 5, 2006, pp. 1–46.

[4] Ahmad, A.L., Low, E.M., and Abd Shukor, S.R., "Safety Improvement and Operational Enhancement via Dynamic Process Simulator: A Review," *Chem. Prod. Process Model.*, Vol. 5, Article 25, 2010, pp. 1–25.

[5] Zitney, S.E., Brüll, L., Lang, L., and Zeller, R., "Plantwide Dynamic Simulation on Supercomputers: Modeling a

Bayer Distillation Process," *AIChE Symp. Ser*., Vol. 91, 1995, pp. 313–316.

[6] Ondrey, G., "Simulation and Modeling Spread Their Wings," *Chem. Eng*., Vol. 112, 2005, pp. 27–31.

[7] Riazi, M.R., *Characterization and Properties of Petroleum Fractions*, ASTM International, West Conshohocken, PA, 2005, pp. 87–151.

[8] Watt, M.R., and Roussis, S.G., "Crude Assay," in *Practical Advances in Petroleum Processing, Vol. 1*, C.S. Hu and P.R. Robinson, Eds., Springer, New York, 2006, pp. 103–116.

[9] Speight, J.G., *Handbook of Petroleum Analysis*, John Wiley & Sons, New York, 2001.

[10] Peña-Díez, J.L., "Improving Refinery Planning through Better Crude Quality Control," in *Practical Advances in Petroleum Processing, Vol. 2*, C.S. Hu and P.R. Robinson, Eds., Springer, New York, 2006, pp. 393–407.

[11] Daubert, T.E., and Danner, R.P., Eds., *API Technical Data Book—Petroleum Refining*, 6th ed., American Petroleum Institute, Washington, DC, 1997.

[12] Riazi, M.R., and Daubert, T.E., "Simplify Property Predictions," *Hydrocarbon Process*., Vol. 59, 1980, pp. 115–116.

[13] Riazi, M.R., and Daubert, T.E., "Characterization Parameters for Petroleum Fractions," *Ind. Eng. Chem. Res*., Vol. 26, 1987, pp. 755–759 (corrections p. 1268).

[14] Whitson, C.H., "Characterizing Hydrocarbon Plus Fractions," *Soc. Petrol. Eng. J*., August, 1983, pp. 683–694.

[15] Riazi, M.R., "A Distribution Model for C7+ Fractions Characterization of Petroleum Fluids," *Ind. Eng. Chem. Res*., Vol. 36, 1997, pp. 4299–4307.

[16] Riazi, M.R., and Al-Sahhaf, T., "Physical Properties of n-Alkanes and n-Alkyl Hydrocarbons: Application to Petroleum Mixtures," *Ind. Eng. Chem. Res*., Vol. 34, 1995, pp. 4145–4148.

[17] Marano, J.J., and Holder, G.D., "General Equation for Correlating the Thermophysical Properties of n-Paraffins, n-Olefins, and Other Homologous Series. 2. Asymptotic Behavior Correlations for PVT Properties," *Ind. Eng. Chem. Res*., Vol. 36, 1997, pp. 1895–1907.

[18] Peng, B., *Molecular Modeling of Petroleum Processes*, Ph.D. Thesis, University of Manchester Institute of Technology, Manchester, UK, 1999.

[19] Saine Aye, M.M., and Zhang, N., "A Novel Methodology in Transforming Bulk Properties of Refining Streams into Molecular Information," *Chem. Eng. Sci*., Vol. 60, 2005, pp. 6702–6717.

[20] Vakili-Nezhaad, G.R., Modarress, H., and Mansoori, G.A., "Thermodynamic Modeling and Experimental Studies of Dearomatization Process from a Complex Petroleum Fraction," *Sep. Sci. Technol*., Vol. 35, 2000, pp. 743–754.

[21] Espada, J.J., Coto, B., and Peña, J.L., "Compositional and Structural Analysis of Lubricating Oil Feedstock Obtained from a Light Crude Oil," *Energy Fuels*, Vol. 23, 2009, pp. 888–893.

[22] Katzer, J.R., Ramage, M.P., and Sapre, A.V., "Petroleum Refining: Poised for Profound Changes," *Chem. Eng. Prog*., July, 2000, pp. 41–51.

[23] Blanding, F.H., "Reaction Rates in Catalytic Cracking of Petroleum," *Ind. Eng. Chem*., Vol. 45, 1953, pp. 1186–1197.

[24] Frye, C.G., and Mosby, J.F., "Kinetics of Hydrodesulfurization," *Chem. Eng. Prog*., Vol. 63, 1967, pp. 66–70.

[25] Sapre, A.V., "Kinetic Modeling at Mobil: A Historical Perspective," in *Chemical Reactions in Complex Mixtures*, A.V. Sapre and F.J. Krambeck, Eds., Van Nostrand Reinhold, New York, 1991.

[26] Quann, R.J., and Jaffe, S.B., "Structure-Oriented Lumping: Describing the Chemistry of Complex Hydrocarbon Mixtures," *Ind. Eng. Chem. Res*., Vol. 31, 1992, pp. 2483–2497.

[27] Jaffe, S.B., Freund, H., and Olmstead, W.N., "Extension of Structure-Oriented Lumping to Vacuum Residua," *Ind. Eng. Chem. Res*., Vol. 44, 2005, pp. 9840–9852.

[28] Powell, R.T., and Yu, C.-Y., "Refinery Reaction Modelling Trends," *Hydrocarbon Engineering*, January, 2004, pp. 21–26.

[29] Rhodes, C.L., "The Process Simulation Revolution: Thermophysical Property Needs and Concerns," *J. Chem. Eng. Data*, Vol. 41, 1996, pp. 947–950.

[30] Gani, R., and Pistikopoulos, E.N., "Property Modelling and Simulation for Product and Process Design," *Fluid Phase Equil*., Vol. 194–197, 2002, pp. 43–59.

[31] Satyro, A.M., "Thermodynamics and the Simulation Engineer," *Chem. Prod. Process Model*., Vol. 3, Article 24, 2008, pp. 1–41.

[32] "DIPPR: Design Institute for Physical Properties, Research Group of AIChE," http://www.aiche.org/DIPPR/about/ (accessed December 20, 2011).

[33] "DDB: Dortmund Data Bank, Research Group of University of Dortmund," http://www.dortmunddatabank.com/en/ddbst/index.php (accessed December 20, 2011).

[34] Carlsen, E.C., "Don't Gamble with Physical Properties for Simulations," *Chemical Engineering Progress*, October, 1996, pp. 35–46.

[35] Liu, Y., and Watanasiri, S., "Successfully Simulate Electrolyte Systems," *Chemical Engineering Progress*, October, 1999, pp. 25–42.

[36] Coto, B., Van Grieken, R., Peña, J.L., and Espada, J.J., "A Generalized Model to Predict the Liquid–Liquid Equilibrium in the Systems Furfural + Lubricating Oils," *Chem. Eng. Sci*., Vol. 61, 2006, pp. 8028–8039.

[37] Agarwal, R., Li, Y.K., Santollani, O., Satyro, M.A., and Vieler, A., "Uncovering the Realities of Simulation, Part I," *Chem. Eng. Prog*., Vol. 97, 2001, pp. 42–52.

[38] Agarwal, R., Li, Y.K., Santollani, O., Satyro, M.A., and Vieler, A., "Uncovering the Realities of Simulation, Part II," *Chem. Eng. Prog*., Vol. 97, 2001, pp. 64–72.

[39] Kister, H.Z., "Can We Believe the Simulation Results?" *Chem. Eng. Prog*., Vol. 100, 2002, pp. 52–58.

[40] Seider, W.D., Seader, J.D., and Lewin, D.R., *Process Design Principles: Synthesis, Analysis and Evaluation*, 1st ed., John Wiley & Sons, New York, 1999.

[41] Kaes, G.L., *Refinery Process Modeling: A Practical Guide to Steady State Modeling of Petroleum Processes*, 1st ed., Kaes Enterprises, Puyallup, WA, 2000.

[42] González, R., and Ferrer, J.M., "Analyzing the Value of First-Principles Dynamic Simulation," *Hydrocarbon Processing*, September, 2006, pp. 69–75.

[43] Robinson, P.R., and Cima, D., "Advanced Process Control," in *Practical Advances in Petroleum Processing, Vol. 2*, C.S. Hu and P.R. Robinson, Eds., Springer, New York, 2006, pp. 247–255.

[44] KBC, *Operational Excellence Standard: The Key to Safe, Reliable and Profitable Production*. Revised Internal Document. Revised January 10, 2007, KBC, Walton on Thames, UK, 2007.

[45] Anderson, M., *Linear Programs, Their Applications and the Need for a Development of Accurate Asset Representations*, KBC, Walton on Thames, UK, 2003.

[46] Tucker, M.A., "LP Modeling—Past, Present and Future," *NPRA 2001 Annual Meeting*, March 18–20, 2001, New Orleans, LA.

[47] Morales, A., and Guerra, M.J., "Process Simulation for Planning," *Hydrocarbon Engineering*, November, 2006.

[48] Miller, J., and Forrest, J., "Modeling Crude Unit Product Overlap for Better Linear Program Modeling," *World Refining*, December 1, 2001.

[49] Aldag, A., and Chukman, G., "The Rigorous Model," *Hydrocarbon Engineering*, November, 2007.

[50] Turpin, L.E., "Catalytic Reforming: Real-Time Planning and Optimisation," *Petroleum Technology Quarterly*, Q3, 1997.

[51] Hawkins, A., Budny, S., Pongo, J., and Oettli, M., "A Modern Architecture for Unit Monitoring and Performance Improvement," *NPRA 1999 Computer Conference*, November 14–17, 1999, Kansas City, MO.

[52] Hu, H.C., Powell, R.T., Yomoji, N., and Ohshima, D., *How to Use a Steady State Simulator to Monitor Commercial Hydrotreater Performance*, KBC, Walton on Thames, UK, 2002.

[53] Powell, R., "Model Behaviour. The Benefits of Using Process Models in Refineries," *Hydrocarbon Engineering*, November, 2006.

[54] Llanes, J.M., Miranda, M., and Mullick, S., "Use Modeling to Fine-Tune Cracking Operations," *Hydrocarbon Processing*, September, 2008, pp. 123–132.

[55] López-Rodríguez, A., Jiménez-Asenjo, P., Arteagabeítia, A., Martínez-Cámara, J.M., and Aguilar, C., "Rigorous Refinery-Wide Optimization: A Case Study for Petronor," paper presented at the *19th World Petroleum Congress*, June 29–July 3, 2008, Madrid, Spain.

[56] Golden, S.W., Villalanti, D.C., and Martin, G.R., "Feed Characterization and Deepcut Vacuum Columns: Simulation and Design," *AIChE Spring National Meeting*, March 20–24, 1994, Houston, TX.

[57] Sundaram, S., "Simulation in Operation," *Process Engineering*, October, 2005, pp. 11–13.

[58] Tamminen, E., "Maximization of Projected Crude Capacity with Rigorous Integrated Preheat Train Aspen Hysys Model," paper presented at the *Aspentech User Group Meeting*, Amsterdam, The Netherlands, 2005.

[59] Sayles, S., Bailor, J., and Ohmes, R., "ULSD Problems and Solutions," *Petroleum Technology Quarterly*, Q3, 2004.

[60] Miranda, M., "FCC Optimization & Monitoring with Refsys FCC Simulator Model," paper presented at the *Aspentech User Group Meeting*, Frankfurt, Germany, 2007.

[61] López-Rodríguez, A., Guerra, M.J., and Vázquez, R., "Analysis of Aspen Conversion Models: A Comparison with Industrial Plant Data," paper presented at the *Aspentech User Group Meeting*, Frankfurt, Germany, 2007.

[62] Lee, R., Leunenberger, E., and Powell, R., "Optimizing the Cat Feed Hydrotreater/FCCU Complex with Detailed Simulation Tools," *World Refining*, July, 2001, pp. 32–39.

[63] García, A., Vázquez, R., Suárez, M.L., and López-Rodríguez, A., *Global Model of Naphtha Complex at a Repsol Refinery: Feed Distribution Optimization*, Repsol Internal Report, Repsol, Madrid, Spain, 2008.

[64] Wagner, S., McLeod, R., and Al-Ghazzawi, A., "Using Process Models to Justify Real Time Optimization Implementation," paper presented at *AspenWorld 2004*, Orlando, FL, 2004.

[65] Basak, K., Abhilash, K.S., Ganguly, S., and Saraf, D.N., "On-Line Optimization of a Crude Distillation Unit with Constraints on Product Properties," *Ind. Eng. Chem. Res.*, Vol. 41, No. 6, 2002, pp. 1557–1568.

[66] Yugo, M., De Manueles, A., López-Rodríguez, A., Ferrer, J.M., and Manzulli, M., *Propane-Propylene Splitter Optimization*, Repsol Internal Report, Repsol, Madrid, Spain, 2010.

[67] Shindo, H., Lau, K., Kaneko, R. and Ayala, J.S., "Furnace Optimizer in a Naphtha Cracker," paper presented at the *AIChE Annual Meeting*, New Orleans, LA, 2004.

[68] Alzein, Z., and Nath, R., "Ethylene Plant Optimization," *Petroleum Technology Quarterly*, Q1, 2005.

[69] Le Geyt, D.C., "Improving Olefins Plant Performance," *Petroleum Technology Quarterly*, Q1, 2005.

[70] López-Rodríguez, A., and Vázquez, R., *Off-Line Olefin Plant Optimization*, Repsol Internal Report, Repsol, Madrid, Spain, 2009.

[71] OLI Systems, Inc., "Desalter Simulation," in *Electrolyte Modeling Basics—Process Simulation* OLI Systems, Inc., 2007, p. 96, http://support.olisystems.com/Documents/Manuals/EMB-Process.pdf (accessed, December 20, 2011), 2007.

[72] Mahdi, K., Gheshlaghi, R., Zahedi, G., and Lohi, A., "Characterization and Modeling of a Crude Oil Desalting Plant by a Statistically Designed Approach," *Petrol. Sci. Eng.*, Vol. 61, 2008, pp. 116–123.

[73] Ishiyama, E.M., Wilson, D.I., Paterson, W.R., Heins, A.V., and Spinelli, L., "The Importance of Scheduling and Desalter Control of Preheat Trains of Crude Distillation Units: A Case Study," *Proceedings of International Conference on Heat Exchanger Fouling and Cleaning VIII*, June 14–19, 2009, Schladming, Austria.

[74] Akpa, J.G., Dagde, K.K., and Okoroma, J.U., "Transient Analysis of Heat Exchanger Networks in the Crude Distillation Unit of Port-Harcourt Refinery," *J. Emerg. Trends Eng. Appl. Sci.*, Vol. 2, No. 5, 2008, pp. 810–816.

[75] Kaes, G.L., "Some Practical Aspects Of Modeling Crude Oil Distillation," http://www.cadfamily.com/online-help/VMGSIM5_web/Oil_Characterization/Some_Practical_Aspects_Of_Modeling_Crude_Oil_Distillation.htm (accessed December 20, 2011).

[76] Alattas, A.M., Grossmann, I.E., and Palou-Rivera, I., "Integration of Nonlinear Crude Distillation Unit Models in Refinery Planning Optimization," *Ind. Eng. Chem. Res.*, Vol. 50, 2011, pp. 6860–6870.

[77] More, R.K., Bularasa, V.K., and Uppaluri, R., "Optimization of Crude Distillation System Using Aspen Plus: Effect of Binary Feed Selection on Grass-Root Design," *Chem. Eng. Res. Des.*, Vol. 88, 2010, pp. 121–134.

[78] Anitha, K., Shuwana, T., and Kumar, V.R., "Simulation of Atmospheric and Vacuum Crude Units Using Aspen Plus," *Petrol. Sci. Technol.*, Vol. 29, 2011, pp. 1885–1894.

[79] Mittal, V., Zhang, J., Yang, X., and Xu, Q., "E3 Analysis for Crude and Vacuum Distillation System," *Chem. Eng. Technol.*, Vol. 34, 2011, pp. 1854–1863.

[80] Sotelo, R., and Froment, G.F., "Fundamental Kinetic Modeling of Catalytic Reforming," *Ind. Eng. Chem. Res.*, Vol. 48, 2009, pp. 1107–1119.

[81] Pashikanti, K., and Liu, Y.A., "Predictive Modeling of Large-Scale Integrated Refinery Reaction and Fractionation System from Plant Data, Part 3: Continuous Catalyst Regeneration (CCR) Reforming Process," *Energy Fuels*, Vol. 25, 2011, pp. 5320–5344.

[82] Rodriguez, M.A., and Ancheyta, J., "Detailed Description of Kinetic and Reactor Modeling for Naphtha Catalytic Reforming," *Fuel*, Vol. 90, 2011, pp. 3492–3508.

[83] Mederos, F.S., and Ancheyta, J., "Mathematical Modeling and Simulation of Hydrotreating Reactors: Concurrent Versus Countercurrent Operations," *Appl. Catal. A*, Vol. 332, 2007, pp. 8–21.

[84] Lopez-Garcia, C., Hudebine, D., Schweitzer, J.-M., Verstraete, J.J., and Ferre, D., "In-Depth Modeling of Gas Oil Hydrotreating: From Feedstock Reconstruction to Reactor Stability Analysis," *Catal. Today*, Vol. 150, 2010, pp. 279–299.

[85] Jarullah, A.T., Mujtaba, I.Q., and Wood, A.S., "Kinetic Parameter Estimation and Simulation of Trickle-Bed Reactor for Hydrodesulfurization of Crude Oil," *Chem. Eng. Sci.*, Vol. 66, 2010, pp. 859–871.

[86] Kumar, H., and Froment, G.F., "Mechanistic Kinetic Modeling of the Hydrocracking of Complex Feedstocks, Such as Vacuum Gas Oils," *Ind. Eng. Chem. Res.*, Vol. 46, 2007, pp. 5881–5897.

[87] Chang, A.F., and Liu, Y.A., "Predictive Modeling of Large-Scale Integrated Refinery Reaction and Fractionation System from Plant Data, Part 1: Hydrocracking Processes," *Energy Fuels*, Vol. 25, 2011, pp. 5264–5297.

[88] Elizalde, I., and Ancheyta, J., "On the Detailed Solution and Application of the Continuous Kinetic Lumping Modeling to Hydrocracking of Heavy Oils," *Fuel*, Vol. 90, 2011, pp. 3542–3550.

[89] Froment, G.F., "Single Event Kinetic Modeling of Complex Catalytic Processes," *Catal. Rev. Sci. Eng.*, Vol. 47, 2005, pp. 83–124.

[90] Gupta, R.K., Kumar, V., and Srivastava, V.K., "Modeling of Fluid Catalytic Cracking Riser Reactor: A Review," *Int. J. Chem. Reactor Eng.*, Vol. 8, 2010.

[91] Pashikanti, K., and Liu, Y.A., "Predictive Modeling of Large-Scale Integrated Refinery Reaction and Fractionation System from Plant Data, Part 2: Fluid Catalytic Cracking (FCC) Process," *Energy Fuels*, Vol. 25, 2011, pp. 5298–5319.

[92] Ancheyta, J., *Modeling and Simulation of Catalytic Reactors for Petroleum Refining*, Wiley, New York, 2011.

[93] Bozzano, G., and Dente, M., "A Mechanistic Approach to Delayed Coking Modelling," *Computer Aided Chemical Engineering*, Vol. 20, 2005, pp. 529–534.

[94] Zhou, X.-L., Chen, S.-Z., and Li, C.-L., "A Predictive Kinetic Model for Delayed Coking," *Petrol. Sci. Technol.*, Vol. 25, 2007, pp. 1539–1548.

[95] Bozzano, G., Dente, M., and Carlucci, F., "The Effect of Naphthenic Components in the Visbreaking Modeling," *Comp. Chem. Eng.*, Vol. 29, 2005, pp. 1439–1446.

[96] Reza, S., Mohaddecy, S., and Sadighi, S., "Simulation and Kinetic Modeling of Vacuum Residue Soaker-Visbreaking," *Petrol. Coal*, Vol. 53, 2011, pp. 26–34.

[97] López-Rodríguez, A., and Peña, C.V., "Modeling of a MTBE Industrial Unit with Reactive Distillation," *Aspentech User Conference*, October, 1997, Boston, MA.

[98] Higler, A.P., Taylor, R., and Krishna, R., "Nonequilibrium Modelling of Reactive Distillation: Multiple Steady States in MTBE Synthesis," *Chem. Eng. Sci.*, Vol. 54, 1999, pp. 1389–1395.

[99] Jhon, Y.H., and Lee, T.H., "Dynamic Simulation for Reactive Distillation with ETBE Synthesis," *Separ. Purif. Technol.*, Vol. 31, 2003, pp. 301–317.

[100] Espada, J.J., Coto, B., Van Grieken, R., and Moreno, J.M., "Simulation of Pilot-Plant Extraction Experiments to Reduce the Aromatic Content from Lubricating Oils," *Chem. Eng. Process*., Vol. 47, 2008, pp. 1404–1409.

[101] Mokhlif, N.D., and Al-Kayiem, H.H., "Modeling of the Waxing-Dewaxing Process in Scraped Surface Exchangers," *J. Appl. Sci*., Vol. 11, 2011, pp. 1594–1599.

[102] Zagoruiko, A.N., and Matros, Y.S., "Mathematical Modelling of Claus Reactors Undergoing Sulfur Condensation and Evaporation," *Chem. Eng. J*., Vol. 87, 2002, pp. 73–88.

[103] Zamaniyana, A., Behroozsarandb, A., and Ebrahimia, H., "Modeling and Simulation of Large Scale Hydrogen Production," *J. Nat. Gas Sci. Eng*., Vol. 2, 2010, pp. 293–301.

[104] Dissinger, G.R., "Studying Simulation: A Case for Dynamic Simulation As an Important Factor in the Design and Operation of a Plant," *Hydrocarbon Eng*., Vol. 13, 2008, pp. 113–118.

[105] Stephenson, G., Henderson, P., and Schindler, H., "Profit More from Process Simulation," *Chem. Process*., Vol. 72, 2009, pp. 23–26.

[106] Gruber, D., Leipnitz, D.-U., Sethuraman, P., Alos, M.A., Nougues, J.A., and Brodkorb, M., "Are There Alternatives to an Expensive Overhaul of a Bottlenecked Flare System?", *Petrol. Technol. Quart*., Vol. 15, 2010, pp. 93–95.

[107] Contreras, J., and Ferrer, J.M., "Dynamic Simulation: A Case Study," *Hydrocarbon Engineering*, Vol. 10, 2005, pp. 103–108.

[108] Pannocchia, G., Gallinelli, L., Brambilla, A., Marchetti, G., and Trivella, F., "Rigorous Simulation and Model Predictive Control of a Crude Distillation Unit," paper presented at the *International Symposium on Advanced Control of Chemical Processes* (ADCHEM 2006), April, 2006, Gramado, Brazil.

[109] Alsop, N., and Ferrer, J.M., "Step-Test Free APC Implementation Using Hysys," paper presented at the *Ethylene Producers Conference*, AIChE Spring National Meeting, 2006, Orlando, FL.

[110] Manzulli, M., Ferrer, J.M., Yugo, M., De Manueles, A., Alonso, F., Santos, M., García, M.A., and López-Rodríguez, A., "Repsol Uses HDS Simulation to Meet New EU Sulphur Specs," *Oil & Gas J*., Vol. 108, 2010, pp. 80–89.

[111] Coronel, R., "Why Hammers Can't Screw," *Chem. Eng. Mag*., Vol. 838, 2011, pp. 50–51.

[112] Dougherty, A., and Grupa, M., "Using PIMS/PIMS-AO for Refinery Green House Gas Modeling," paper presented at the *Aspentech User Conference*, May 3–5, 2010, Boston, MA.

27

Maintenance Simulation and Optimization in Refineries and Process Plants

Miguel Bagajewicz[1]

27.1 INTRODUCTION

Appropriate maintenance actions are of paramount importance from a safety and economic point of view. Once safety levels have been achieved through appropriate maintenance, the question is how much additional preventive maintenance is economically advisable.

A typical refinery experiences approximately 10 days of downtime per year due to equipment failures resulting in an estimated economic loss of \$20,000–\$30,000 per hour [1]. Maintenance is defined as all actions appropriate for retaining an item/part/equipment in, or restoring it to, a given condition [2]. The annual cost of maintenance (corrective and preventive) as a fraction of total operating budget can go up to 40–50 % for the mining industry [3] and 20–30 % for the chemical industry [1]. The typical size of a plant maintenance group in a manufacturing organization varied from 5 to 10 % of the total operating force [2]. It is estimated that over \$300 billion are spent on plant maintenance and operations by U.S. industry each year, and that approximately 80 % of this is spent to correct the chronic failure of machines, systems, and human errors. The elimination of these chronic failures through effective maintenance can reduce the cost between 40 and 60 % [2].

Maintenance is defined as all actions appropriate for retaining an item/part/equipment in, or restoring it to, a given condition [2]. The perception about maintenance has shifted from being a "necessary evil" to being an effective tool to improve processing efficiency and ultimately larger profit. The trend is part of the new approach to processing named smart plants [4,5], which advances the concept that such plants anticipate problems instead of reacting to them.

Modern practices and management philosophy of maintenance can be found in various textbooks (e.g., the *Maintenance Engineering Handbook* [6]). In addition, there are many computerized maintenance management systems (CMMS) software packages devoted to help in the management/organization of the maintenance activities (over 360 software packages are listed in the website www.plant-maintenance.com). Despite this abundance, the optimization of decision variables in maintenance planning (such as preventive maintenance frequency or level of availability of labor and spare parts), referred to as the maintenance optimization problem, is usually neither discussed in detail in textbooks nor it is included as a feature in the aforementioned software packages. Thus, for the most part, these packages are excellent databases that help track repair orders and maintain appropriate bookkeeping but are not capable of optimizing maintenance decision making.

Over the past 4 decades, several modern maintenance management theories such as reliability-centered maintenance (RCM) and total productivity maintenance (TPM) have gained widespread popularity in the industry. These modern maintenance theories are systematic and have demonstrated that a remarkable improvement in plant performance and productivity over the traditional approach, the main goal of which is simply to correct equipment failures [7], can be achieved.

In this chapter we do not review all of these techniques in detail (another chapter focuses on the different types of maintenance and other important practices); rather, we focus on determining what is the effect of the decision variables (preventive maintenance frequency, task prioritization, parts inventory levels, labor available, among others) on safety and production economics using simulation and on determining the level of preventive and corrective maintenance that is optimal for a plant.

None of the aforementioned preventive maintenance (PM) planning models consider constraints on resources available in process plants, which include labor resources and material (spare parts) resources. Limitation on manpower is usually the most critical constraint affecting the ability to perform scheduled PM tasks on time. For example, the maintenance work force, which usually is limited, cannot perform scheduled PM tasks for some equipment at the scheduled PM time because of the intervening repair of other failed equipment. Such dynamic situations cannot be handled by deterministic maintenance planning models or are not considered in published maintenance planning models that use Monte Carlo simulation tools. Resource constraint is more realized in the scheduling phase, so it is usually ignored in the planning phase. In fact, there are only a few papers that considered resource constraint, and they are all concerned with maintenance scheduling, namely the research papers of Gopalakrishnan et al. [8], Ahire et al. [9], and Yao et al. [10].

To ameliorate all of the aforementioned shortcomings, a new methodology that is based on the use of Monte Carlo simulations and incorporates all of the contributing factors to evaluate the effectiveness of maintenance policies was recently introduced [11]. This technique was later expanded further and merged with a genetic algorithm for its optimization by Nguyen and Bagajewicz (see Chapters 18 and 19 in [12]).

---

[1] University of Oklahoma, Norman, OK, USA

We now discuss the merits and shortcomings of the most popular models.

In general, a maintenance model needs to include the following:

- *A maintenance policy*: The most common maintenance policy is the standard periodic PM, enhanced sometimes by age-dependent features, sequential strategies, different replacement policies, opportunistic maintenance practices, and or predictive maintenance, etc. [13].
- *A set of decision variables*: The most common ones are the periodic PM time or PM frequency (in periodic PM policy) for each piece of equipment or groups of equipment, labor workforce size, and the inventory level of parts.
- *The objective*: Objectives can include minimizing cost, maximizing profit, or maximizing reliability for safety purposes. To assess safety, hazard and operability analysis (HAZOP) and failure modes and effects analysis (FEMA), which is reviewed in another chapter and is an important component in modern maintenance programs such as RCM, can be used. Cost reductions come from savings obtained by reducing losses, labor costs, inventory costs, etc. Because all of these issues are intertwined and apply to several pieces of equipment simultaneously, the analysis cannot be made on an equipment-by-equipment basis, but rather considering the system of equipment as a whole.
- *The constraints:* Constraints include limitations on labor, budget, storage of spare parts, etc.

Any model needs to consider the breakdown or corrective maintenance as well as the preventive and predictive maintenance schedules. Because labor is usually limited, prioritization rules (i.e., how much corrective maintenance is postponed to accommodate preventive maintenance) need to be considered. There is a third maintenance policy, predictive maintenance, which is also considered [6].

PM is in turn divided into two types: time-driven PM and condition-driven PM [7]. Condition-driven PM is basically the same as predictive maintenance. Because there is a very limited number of decision variables involved for these kinds of maintenance policies, they are usually not subjects for maintenance optimization research. Various versions of time-driven PM policy have been proposed and were summarized in a review paper by Wang [14]. For a single piece of equipment, they are age-dependent PM, periodic PM, PM that is based on failure limit (reliability reaches a threshold value), and unequal interval sequential PM (usually at shorter and shorter intervals). Finally, for multiunit systems with dependence between units, group maintenance or opportunistic maintenance policies can be used [14].

27.2 EVALUATION USING MONTE CARLO SIMULATION

In this technique, repeated sampling of the equipment failure and subsequent evaluation of the cost of maintenance activities as well as the economic losses associated with the failed states are performed. The average of all of these sample-driven instances is computed, and the process is repeated until it converges to a finite value.

The sampling procedures to simulate equipment status within a finite time horizon in accordance with a maintenance policy used by Nguyen et al. [15] are:

- Failure times of all equipment are sampled using the reliability function (failure rate) of equipment.
- At failure times of the equipment, the type of failure modes that caused the equipment failure is sampled in accordance with the probability of occurrence.
- The cost of corrective maintenance, the repair time, and the economic losses are determined based on the type of failure mode identified.
- PM requests for equipment are generated in accordance with the predetermined PM schedule (predetermined PM policy).
- The planning time horizon is divided into time intervals of weeks.
- In each week:
  - All of the corrective (breakdown) maintenance (CM) requests (when equipment failed) and all of the scheduled PM requests are identified.
  - CM and PM requests for equipment with the highest priority are fulfilled, and CM and PM requests of equipment with lower priority are continued until the available resource is used up (labor and material resources are considered). The reader is directed to the article by Nguyen et al. [11] and the work of Nguyen and Bagajewicz [12 (chapters 17–19), 15] for more details.
  - If a CM or PM request is not fulfilled, it has to be delayed to the next week. Delayed CM requests are scheduled to be fulfilled early the next week or when the needed parts for repairing the equipment are available.
  - If a CM action on equipment was performed before the scheduled PM request for that equipment for a predetermined period, that PM request will be ignored.
  - If the CM action for equipment has been delayed more than a predetermined period (current value is 21 days), the priority level of that equipment will be upgraded one level.
- When a maintenance action is performed on a single piece of equipment at time t, that equipment is assumed to be as good as brand new and failure events for that piece of equipment will be resampled (updated) starting from time t.
- The next week is considered, and the calculation is repeated. The procedure continues until the end of the planning time horizon is reached.

27.2.1 Sampling

To perform the sampling, the equipment failure data are needed. These can be obtained through historical values in the plant or from literature. Different distributions are available (Exponential, Weibull, Normal and logarithmic, among others). Nguyen et al. [11] used the exponential distribution. In addition, conditional probabilities need to be considered for the cases where the probabilities of certain failure are dependent on the occurrence of other failures. Equipment reliability data such as MTBF are obtained from reliable sources such as *Guidelines for Process Equipment Reliability Data with Data Tables* from the AIChE Center for Chemical Process Safety [16].

27.2.2 Costs and Economic Losses

Many approaches use maintenance cost rate (cost per unit time) and do not consider economic losses. Nguyen et al. [11]

use the total costs plus economic losses incurring within the planning time horizon, which is to be minimized. The cost term is computed as follows:

$$Cost = PM\ cost + CM\ cost + Labor\ cost + Inventory\ cost \tag{27.1}$$

where *PM cost* and *CM cost* are the costs associated with PM and CM activities, respectively. Two types of losses are considered:

1. Economic loss associated with failed (or malfunctioned) equipment that has not been repaired (e.g., a fouled heat exchanger can continue operating but at reduced heat transfer rate)
2. Economic loss due to unavailability of equipment during repair time (applied to equipment that does not have a backup).

The economic losses are obtained from the reduction of production throughput or even shutdown, the deterioration of product quality, the consequences of accidents, etc.

27.2.3 Safety Issues

Some equipment failure leads to accidents, as noted above, which results in economic loss, but some could also lead to personnel injuries. As tempting as it is to associate personnel injuries with the associated economic losses, human injury prevention is handled in a different way. Nguyen et al. [11] suggest a constraint that limits the likelihood of events leading to human injury and death and infer the appropriate tradeoff from the Pareto optimal curve, but they did not explore it any further.

27.2.4 Maintenance Rules and Scheduling

Several different organizational rules can be adopted and encoded in a Monte Carlo simulation. Nguyen et al. [11] considered PM performed at regular intervals and assumed negligible time between the identification of the failure and the decision-making, among other smaller assumptions. They assumed that a classification of severity of failure leads to different priorities (such as emergency, urgent, pressing, and affordable repairs) and assumed a certain prioritization to distribute repair tasks and certain changes in priority when equipment remains unrepaired for too long. They used tables connecting levels of failures to consequences (following Tischuk [17]) to assign priorities.

Finally, Nguyen et al. [11] used the PM frequency as a fraction of the mean time between failures (MTBF) of each piece of equipment (i.e., *PM time interval* = $a \times$ *MTBF*, where the fraction a is optimized for each piece of equipment) and discussed different policies regarding which parts are to be kept in inventory.

27.2.5 Input Data

To perform a simulation, the following data for each piece of equipment are needed:

- Reliability data such as the MTBF
- Information on the failure modes and the associated probability of occurrence for each type of failure mode
- The time and the associated material cost of performing CM (for each type of failure mode) and PM
- The economic loss associated with each type of failure mode
- The inventory cost rate for each type of spare part
- Other input data are the waiting time for an emergency-ordered spare part to arrive, the labor rate paid, the available labor hours per employee per week (default value = 40), the ranking (for repair), and the classification (interfering or noninterfering) of the equipment.

27.3 MONTE CARLO SIMULATION RESULTS

Nguyen et al. [11] solved a medium-size plant taken from literature (the Tennessee Eastman problem [18]) shown in Figure 27.1.

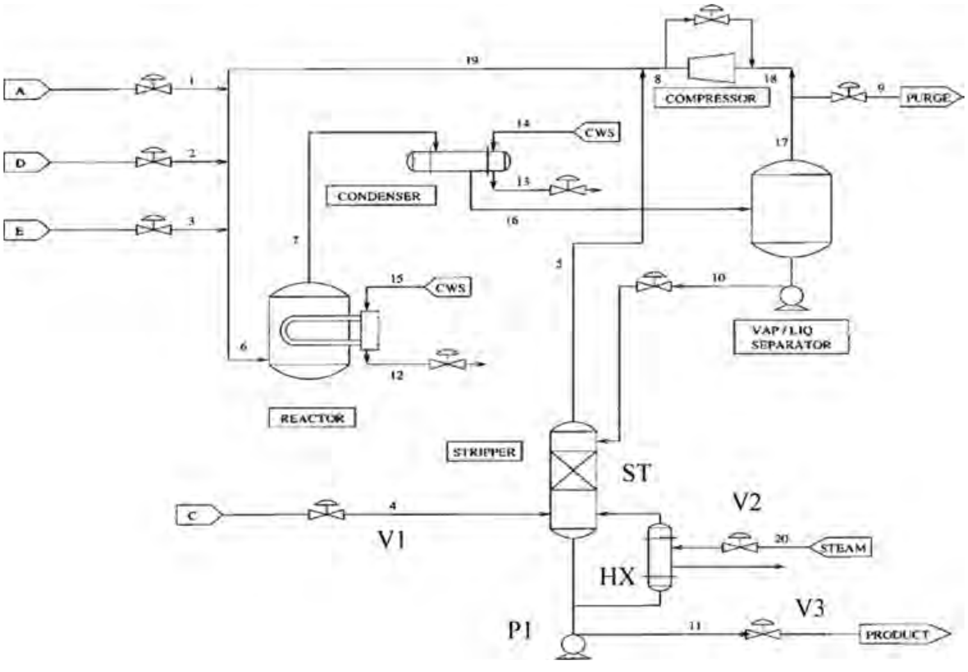


Figure 27.1—Tennessee Eastman process flow diagram.

Figure 27.2 shows the simulation results (cost + losses) obtained using PM with no resource limitations assuming that only CM is used, there are 10 maintenance personnel (more than enough for a plant with 19 pieces of equipment; hence, labor resources are always available), and spare parts are always available. The probability distribution of costs obtained is shown in Figure 27.3. This distribution is useful because it may identify extreme events (large cost + loss) and low probability that one may want to avoid if a risk analysis is desired to be made. Finally, Figure 27.4 shows the effect of introducing labor limitations and identifying the minimum cost when three workers are used. Nguyen et al. also looked into the effect of having all spare parts available, some available, or no spare parts in inventory. We refer the reader to the original article for further detail, such as the effect of the planning horizon, other PM policies, and analysis (computing time, etc). Nguyen and Bagajewicz [15] (see also Bagajewicz [12], Chapters 17–19) present a more detailed model for this plant and show that a genetic algorithm (GA) can predict the same results that are obtained by inspection in Figure 27.4.

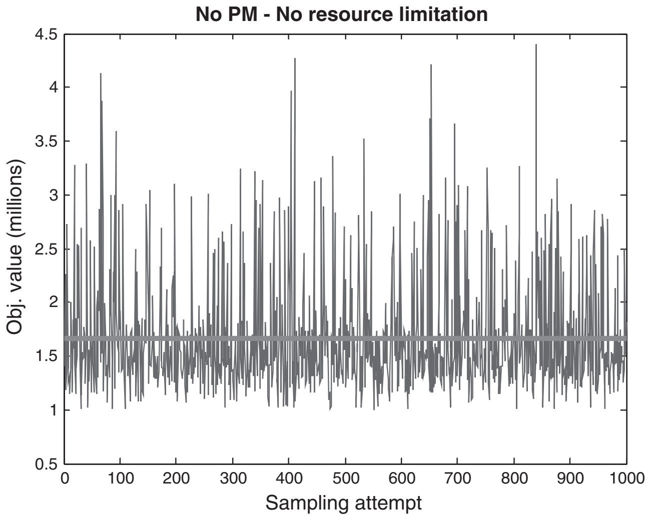


Figure 27.2—Objective value at various sampling attempts, no PM–no resource limitation.

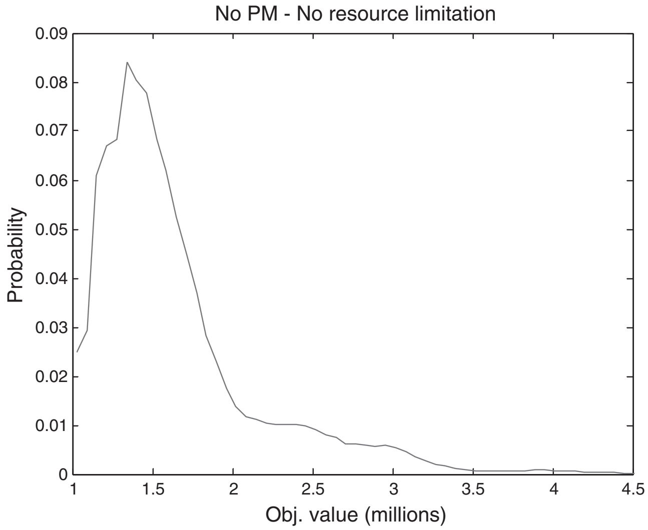


Figure 27.3—Probability distribution of the objective value, no PM–no resource limitation.

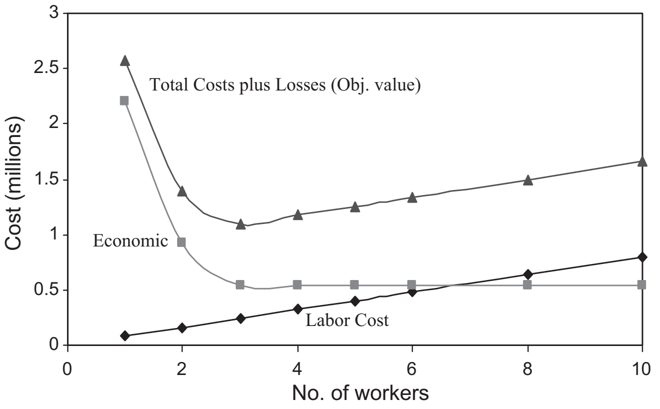


Figure 27.4—Effect of labor availability on maintenance cost and performance, no PM.

27.4 MAINTENANCE OPTIMIZATION

Maintenance optimization has been studied extensively, and many maintenance models have been published. Many models were discussed and summarized in the excellent textbook by Wang and Pham [19] and various review papers [14,20]. Most of the optimization models are deterministic models that use simplified assumptions. Typical simplified assumptions are negligible maintenance time or repair time, the unit has an increasing failure rate, and "as-good-as-new" (perfect) maintenance. The decision variables depend on the PM policy (e.g., the time interval length needs to be optimized in periodic PM).

The most common optimization criterion is minimum cost and the constraints are the requirements on system reliability measures, including availability and average uptime or downtime. For systems such as nuclear power plants or power generation systems in which reliability is much more important than cost, the optimization criteria are the highest reliability measures at a given maintenance budget.

In addition, GAs are used to solve complicated maintenance optimization models that simultaneously consider many decision variables (e.g., optimal PM time intervals, spare parts inventory levels, labor workforce size, resources allocation, and replacement strategy) or solve realistic maintenance models that do not use simplified assumptions. Finally GAs were used by Savic et al. [21], Tan and Kramer [1], Sarker and Haque [22], Marseguerra and Zio [23], Marseguerra et al. [24,25], Podgorelec et al. [26], Saranga [27], Shum and Gong [28], and Ilgin and Tunali [29]. On the other hand, Monte Carlo simulations are usually used to estimate some outputs that are a result of very complex relationships, such as reliability. Finally, Tan and Kramer [1] as well as Nguyen and Bagajewicz ([12] Chapters 18 and 19, [15]) used Monte Carlo simulations and GAs.

27.5 GENETIC ALGORITHMS

In brief, a GA is based on mimicking the principles of genetics, natural selection, and evolution; it allows a population composed of many individuals to evolve under specified selection rules to a state that maximizes the "fitness" (i.e., minimizes the cost function) [30]. The algorithm includes a population, a set of rules for "mating" to produce offsprings, a set of rules to produce "mutations," and a procedure for survival of individuals so that the population is kept at the same size. The algorithmic procedure and detailed description of the well-known GA method can be found in various textbooks such as Haupt and Haupt's book [30].

The advantage of using Monte Carlo simulation/GA is that the Monte Carlo simulation approach is quite general and versatile for analyzing complex maintenance policies in which many decision variables are sought or realistic situations (e.g. resource limitation) are considered and it is computationally tractable for large systems [1,11,15], whereas a GA (or other stochastic search methods) is the only choice for a nondeterministic model.

Okogbaa and Peng [31] proposed a method for PM analysis under transient response. They developed analytical maintenance models based on a renewal theory. The resulting model consists of differential and integral equations and was solved numerically. Some of the setbacks of this methodology include numerical inaccuracies and computation errors. It is also very complicated and cannot be easily modified for different plants as in the case of a simulation.

Tan and Kramer [1] optimized the opportunistic maintenance policy using a combination of Monte Carlo simulation and a GA. A Monte Carlo simulation was used to evaluate the cost rate, which is the total maintenance cost plus lost production costs divided by the time simulated. The GA was then used to minimize a stochastically evaluated cost rate objective function. Solving maintenance optimization models already published in previous works, they compared their optimization approach with other techniques such as an analytical approach and concluded favorably for the Monte Carlo simulation/GA combination. Thus, Tan and Kramer [1]:

- Optimize the "opportunistic maintenance policy"—a realistic PM policy for chemical processes that usually have dependency among units
- Focus on the optimization algorithm, not the maintenance model
- Did not include realistic issues such as spare parts management and resource limitations.

Spare parts management or inventory policy is an important issue in maintenance optimization because the availability of spare parts can decide whether a requested maintenance activity can be conducted or not. Review of models for optimizing a spare parts inventory level can be found in Kennedy et al. [32]. The models usually focus on the spare parts inventory optimization problem itself, and only a few papers addressed the simultaneous optimization of maintenance policy and spare parts inventory; two such papers are described next. Shum and Gong [28] developed an analytical model and used GA to simultaneously optimize the maintenance frequency, part replacement frequency, and the purchasing quantity. Ilgin and Tunali [29] presented a simulation approach integrated with GA-based optimization for finding the optimal inventory level and periodic PM intervals.

Nguyen and Bagajewicz [11] considered the "standard" periodic PM policy for each piece of equipment (Chapter 18), mostly because it is suitable for managing labor resources and it is commonly used in the industry. They assume independence among units and address resource limitations and spare parts inventory policy, which were not considered together before, and extended the model to consider complex policies for labor assignment, more detailed spare parts inventory rules, and other failure distribution in addition to the exponential. Finally, they added imperfect maintenance (i.e., the fact that repairs are not "as good as new," but some deterioration in reliability takes place [14].) They use a set of rules about breakdown/CM prioritization and spare parts inventory policy as part of the Monte Carlo simulation tool. The decision variables in the maintenance model are

- The PM time schedule for each piece of equipment involves two parameters: the time to perform the first PM (called the PM starting time) and the PM time interval. The PM starting time and PM time interval are expressed as a fraction of MTBF (e.g., *PM time interval* = $a \times MTBF$), where the fraction a is to be optimized (for each piece of equipment).
- Inventory level for each spare part.
- Number of maintenance employees in each group.

27.6 GENETIC ALGORITHM OPTIMIZATION RESULTS FOR AN FCC PLANT

As a large-scale problem, the fluid catalytic cracking (FCC) unit in a refinery is now considered. A large West Coast refinery volunteered equipment and volume specifications for its FCC unit. This unit, which processes roughly 50,000 bbl/day of feed, is composed of 61 pumps (31 primary, 30 spare), 2 compressors, 4 heaters, 87 heat exchangers, 15 vessels, 1 catalytic reactor and its associated catalyst regenerator, and 12 columns and strippers. The main process equipment (process vessels, the catalytic reactor and its associated catalyst regenerator, and columns and strippers) and the valves are not included in this study. The reasons are

- The failure of main process equipment is very rare; the failure rate is from 10^{-4} to 10^{-2} (failures/year) (from data listed in [33])
- Practically, the main process equipment is preventively maintained only at turnaround (i.e., when an entire processing unit or the refinery is shut down for overhaul). Thus, only rotating equipment (pumps and compressors), heaters, and exchangers are included in this study. These types of equipment are indeed the ones subjected to a PM program in refineries.

The MTBFs and the mean time to repair of the equipment considered in this study are listed in Table 27.1. These values are estimated (corresponding to the operating condition in a refinery) based on the values provided by Mannan [33]. The mean time to perform PM is estimated.

The following assumptions were made in estimating the economic losses:

- The economic loss of product is assumed to be $10/bbl. This results in an economic loss of $500,000/day if the process unit is fully shut down.
- For the pumps in the process:
    - Spare pumps always work. If a spared pump fails, the spare instantaneously comes online.
    - If a spare is insufficient to maintain a stream at its normal operating rate, the economic loss is proportional to the loss in throughput.

TABLE 27.1—List of Equipment of the FCC Unit

Units	Quantity	MTBF (days)	Time needed for CM (h)	Time needed for PM (h)	Priority
Pumps	61	694	6–8	4	1, 4, 5
Compressors	2	381	30	8	1
Heaters	4	1344	25–36	8	2
Heat Exchangers	87	1344	25–36	8	1, 2, 3, 4

With these assumptions, the economic loss corresponding to the failure of pumps with a spare is essentially zero (it takes a nominal value of $10/day in the model).

- For the heat exchangers and heaters in the process:
  - Failed exchangers transfer heat, but at a reduced rate (20–30 % heat transfer loss).
  - Any exchanger located in series with other exchangers may be bypassed while being serviced without interrupting the process.
  - Economic loss is proportional to the portion of the heat-duty lost because of the failure.
- For the compressors:
  - If the component fails, the process goes offline.
  - The result is a maximal economic loss per day ($500,000/day).

TABLE 27.2—Sample of Economic Data in the FCC Example

Equipment	Failure Mode	Failure Mode Description	Probability of Occurrence	CM cost ($/CM action)	Economic Loss, Type 1 ($/day)	Economic Loss, Type 2 ($/day)	Inventory Cost ($/part/year)
Pump	1	Seals failure	0.4	6,900	10	10	98
	2	Leak	0.05	6,900	10	10	88
	3	Motor failure	0.05	6,900	10	10	79
	4	Couplings	0.05	6,900	10	10	101
	5	Bearings	0.05	6,900	10	10	91
	6	Corrosion	0.2	6,900	10	10	0
	7	Wear/tear	0.2	6,900	10	10	0
Compressor	1	Lubrication breakdown	0.15	37,400	200,000	500,000	1927
	2	Seal failure	0.2	37,400	200,000	500,000	1730
	3	Excessive vibration	0.15	37,400	200,000	500,000	1554
	4	Fatigue/rupture	0.2	37,400	200,000	500,000	1927
	5	Corrosion	0.15	37,400	200,000	500,000	1730
	6	Erosion/wear	0.15	37,400	200,000	500,000	1554
Heater	1	Fouling	0.5	69,000	50,000	100,000	930
	2	Fatigue/crack	0.1	69,000	50,000	100,000	831
	3	Tube rupture	0.1	69,000	50,000	100,000	747
	4	Corrosion	0.2	69,000	50,000	100,000	1002
	5	Others	0.1	69,000	50,000	100,000	897
Process heat exchanger	1	Fouling	0.5	12,600	14,940	49,800	465
	2	Fatigue/crack	0.1	12,600	14,940	49,800	416
	3	Tube rupture	0.1	12,600	14,940	49,800	374
	4	Corrosion	0.2	12,600	14,940	49,800	501
	5	Others	0.1	12,600	14,940	49,800	449
Heat exchanger	1	Fouling	0.5	6,700	1,500	3,000	310
	2	Fatigue/crack	0.1	6,700	1,500	3,000	277
	3	Tube rupture	0.1	6,700	1,500	3,000	249
	4	Corrosion	0.2	6,700	1,500	3,000	334
	5	Others	0.1	6,700	1,500	3,000	299

A sample of economic data is given in Table 27.2, which shows the cost of CM, the economic loss due to the unrepaired failure of equipment (type 1), the economic loss due to unavailability of equipment during the repair time (type 2), and the probability of occurrence for each type of failure modes for some equipment.

To save computational time, only 100 simulation runs are used to evaluate the total cost plus loss of a candidate PM policy (i.e., a chromosome). The objective value is the total costs plus losses for a 10-year span. The solutions (optimal and near-optimal) obtained by GA are re-evaluated by using a higher number of simulations (1000) to confirm the optimality of the solutions (it is the difference in objective values of the obtained solutions that matters, not their absolute values). Note that because GA does not guarantee global optimality, the term "optimal" is meant to be the best possible obtained by GA. The computational time is 6 h and 20 min. Figure 27.5 depicts the convergence of the GA.

Table 27.3 depicts the results. The inventory level for a group of equipment is calculated as the average inventory level of all types of spare parts serving that group of equipment. The inventory level for a specific spare part is in turn calculated as the number of stored items divided by the number of pieces of equipment it services (assuming one spare–one equipment relationship). For a specific group of equipment, the inventory levels for each type of spare part are optimized separately (they are generally different from one another, but the difference is small) but only the average inventory level is reported. The results show that, in general, a reasonable inventory level of 50 % is recommended.

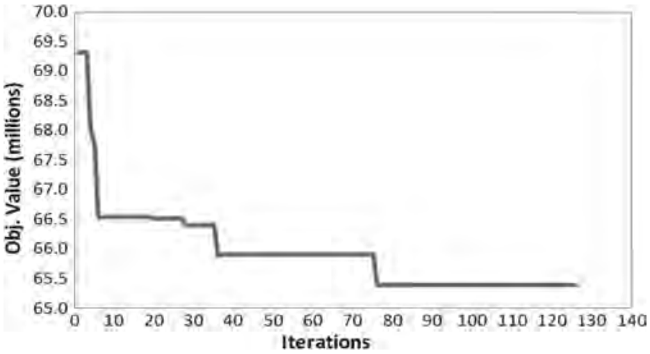


Figure 27.5—Optimal objective value by GA, FCC unit.

The results show that PM is used for all types of equipment under consideration in this FCC unit, but too frequent of PM is not recommended (the PM frequency is generally in the magnitude of fractions or multiples of the MTBF). There are two explanations for this:

1. For equipment with a spare copy online such as pumps, their PM does not interfere with production (favorable condition to perform PM), but the economic loss incurred by their failures is also small (the reduction in loss, which is the benefit or the incentive to perform PM, is small). Moderate PM frequencies (0.9, 0.1, and 0.35) are used for this type of equipment.
2. For equipment without a spare copy such as heat exchangers and compressors, it is assumed that their PM interferes with production (the extent of interference is quantified by the economic loss incurred during the maintenance time of the equipment). As Nguyen et al. [11] pointed out, there are two competing effects of PM on economic loss for this type of equipment: as PM frequency increases (doing PM more often), the economic loss may decrease because PM reduces failure-induced downtime, but the economic loss may also increase because PM increases PM-induced downtime. It may be beneficial to apply PM for this kind of equipment, but the PM should not be done so frequently. The result shows that, for exchangers with a minor effect of PM activities on production (groups

TABLE 27.3—Optimal Maintenance Policy by GA Optimization for FCC Unit

Equipment Group	Description	Group Size	PM Starting Time	PM Frequency	Inventory Level*	Range of Economic Loss Type 2 (thousands/day)
1	Pumps	14	1.3	0.9	0.29	0.01
2	Pumps	14	0.5	0.1	0.43	0.01
3	Pumps	3	1	0.35	0.8	10–73
4	Compressors	2	1.3	1.6	0.63	500
5	Heaters	4	1.3	1.05	0.5	100
6	Exchangers	13	1.1	0.85	0.54	7–9
7	Exchangers	12	0.5	0.9	0.47	15–33
8	Exchangers	6	0.7	1.05	0.39	45–58
9	Exchangers	6	1	1.3	0.33	115–450
10	Exchangers	13	0.6	1.2	0.56	5–7
11	Exchangers	9	0.8	0.7	0.3	8–15
12	Exchangers	10	0.7	0.9	0.47	3
13	Exchangers	9	0.7	1.6	0.56	22
14	Exchangers	9	1	1.2	0.37	3

TABLE 27.4—Optimal Labor Workforce Size

Labor Group	Equipment Covered	Number of Employees
1	Rotating equipment (pumps, compressors)	2
2	Heaters, heat exchangers	5
Total		7

TABLE 27.5—Contribution of Different Terms in the Objective Function

Solutions	PM Cost (%)	CM Cost (%)	Labor Cost (%)	Inventory Cost (%)	Total Economic Loss (%)	Objective Value (millions)	Average Inventory Level	Labor Size
Best	0.26	5.54	4.28	0.85	89.07	65.39	0.47	7
Second best	0.19	5.50	4.13	0.89	89.30	67.82	0.50	7
Third best	0.16	5.65	4.65	0.74	88.79	68.74	0.44	8

6, 7, 10, 11, 12, and 14), PM is used with moderate frequencies (from 0.7 to 1.2). For main process equipment (compressors, heaters, and exchangers groups 8, 9, and 13) for which the PM activities cause significant PM-induced downtime and economic loss, PM is generally not recommended (PM frequency ranges from 1.05 to 1.6) because the gain (reducing failures-related cost and lost) is shadowed by the undesirable side effect of PM (economic loss increases).

The optimal labor workforce size is shown in Table 27.4.

The contribution of different terms in the objective value for some solutions found by GA (the top chromosomes in the final population) is given in Table 27.5.

The reported average inventory level is the mean value of inventory levels for all groups of equipment. The inventory cost of the top five solutions ranges from \$500,000 to \$610,000 (the optimal inventory cost is 558,000). The economic loss ranges from \$58.25 million (best solution) to \$61.62 million (fifth-best solution). It can be seen from Table 27.5 that the total economic loss accounts for a large part (roughly 90 %) in the objective function. Thus, to reduce the total costs plus losses, it is necessary to reduce economic losses by maintaining sufficient resources (labor and spare parts) for punctuality of maintenance actions. The obtained optimal number of employees (7) is larger than the actual number in the actual FCC plant used in this example (5), and the optimal inventory level may also be larger than the standard level in industrial practice in which minimal inventory level is desired. The PM policy (PM frequency) and the size of resources of the optimal solution are comparable to those of the next two top solutions, but the optimal solution either better allocates labor resources (as compared with the second-best solution for which the sizes of the two labor groups are 4 and 3) or has a larger spare parts inventory (as compared with the third best).

27.7 CONCLUSIONS

There are several maintenance policies and methods that have been used, and over 300 software programs available, most of which are large databases incapable of major decision-making. In this chapter, we presented a new Monte Carlo simulation-based maintenance [11] that is capable of capturing all of the intricacies of putting together labor availability, spare parts policy for each part, PM frequency, aging, costs, and losses. We also show that GAs can be used to obtain optimal allocation of resources and PM schedules.

REFERENCES

[1] Tan, J.S., and Kramer, M.A., "A General Framework For Preventive Maintenance Optimization in Chemical Process Operations," *Comput. Chem. Eng.*, Vol. 21, 1997, pp. 1451–1469.

[2] Dhillon, B.S., *Engineering Maintenance*, CRC Press, Boca Raton, FL, 2002.

[3] Murthy, D.N.P, Atrens, A., and Eccleston, J.A., "Strategic Maintenance Management," *J. Qual. Mainten. Eng.*, Vol. 8, 2002, pp. 287–305.

[4] Christofides, P.D., Davis, J.F., El-Farra, N.H., Clark, D., Harris, K.D., and Gipson, J.N., "Smart Plant Operations: Vision, Progress and Challenges," *AIChE J.*, Vol. 53, 2007, pp. 654–668.

[5] Humphrey, J.L., Seibert, A.F., Lewis, J.C., and Farone, J.P., "Smart Manufacturing Plants: Advances and Priorities," presented at the *AIChE Annual Meeting*, November 18, 2008, Philadelphia, PA.

[6] Mobley, R.K., and Higgins L.R., *Maintenance Engineering Handbook*, McGraw-Hill, New York, 2002.

[7] Gopalakrishnan, M., Ahire, S.L., and Miller, D.M., "Maximizing the Effectiveness of a Preventive Maintenance System: An Adaptive Modeling Approach," *Manage. Sci.*, Vol. 43, 1997, pp. 827–840.

[8] Smith, A.M., and Hinchcliffe, G.R., *RCM Gateway to World Class Maintenance*, Elsevier: New York, 2004.

[9] Ahire, S., Greenwood G., Gupta, A., and Terwilliger, M., "Workforce-Constrained Preventive Maintenance Scheduling Using Evolution Strategies," *Decision Sci.*, Vol. 31, 2000, pp. 833–858.

[10] Yao, X., Fernández-Gaucherand, E., Fu, M.C., and Marcus, S.I., "Optimal Preventive Maintenance Scheduling in Semiconductor Manufacturing," *IEEE Trans. Semicond. Manuf.*, Vol. 17, 2004, pp. 345–356.

[11] Nguyen, D.Q., Brammer, C., and Bagajewicz, M., "New Tool for the Evaluation of the Scheduling of Preventive Maintenance for Chemical Process Plants," *Ind. Eng. Chem. Res.*, Vol. 47, 2008, pp. 1910–1924.

[12] Bagajewicz, M., *Smart Process Plants*, McGraw Hill, New York, 2009.

[13] Wang, H., and Pham, H., "Optimal Age-Dependent Preventive Maintenance Policies with Imperfect Maintenance," *Int. J. Reliability Quality Safety Eng.*, Vol. 3, 1996, pp. 119–135.

[14] Wang, H., "A Survey of Maintenance Policies of Deteriorating Systems," *Eur. J. Oper. Res.*, Vol. 139, 2002, pp. 469–489.

[15] Nguyen, T., Quang, D., and Bagajewicz, M., "Optimization of Preventive Maintenance in Chemical Process Plants," *Ind. Eng. Chem. Res.*, Vol. 49, 2010, pp. 4329–4339.

[16] Center for Chemical Process Safety, *Guidelines for Process Equipment Reliability Data with Data Tables*, AIChE, New York, 1989.

[17] Tischuk, J.L., *The Application of Risk Based Approaches to Inspection Planning*, Tischuk Enterprises (UK), Ltd., Aberdeen, United Kingdom, 2002.

[18] Ricker, N.L., and Lee, J.H., "Nonlinear Modeling and State Estimation for the Tennessee Eastman Challenge Process," *Comput. Chem. Eng.*, Vol. 19, 1995, pp. 983–1005.

[19] Wang, H., and Pham, H., *Reliability and Optimal Maintenance*, Springer Series in Reliability Engineering, Springer-Verlag, London, United Kingdom, 2006.

[20] Garg, A., and Deshmukh, S.G., "Maintenance Management: Literature Review and Directions," *J. Qual. Mainten. Eng.*, Vol. 12, 2006, pp. 205–238.

[21] Savic, D.A., Walters, G.A., and Knezevic, J., "Optimal Opportunistic Maintenance Policy Using Genetic Algorithms, 1: Formulation," *J. Qual. Mainten. Eng.*, Vol. 1, 1995, pp. 34–49.

[22] Sarker, R., and Haque, A., "Optimization of Maintenance and Spare Provisioning Policy Using Simulation," *Appl. Mathem. Model.*, Vol. 24, 2000, pp. 751–760.

[23] Marseguerra, M., and Zio, E., "Optimizing Maintenance and Repair Policies via a Combination of Genetic Algorithms and Monte Carlo Simulation," *Reliability Eng. Syst. Safety*, Vol. 68, 2000, pp. 69–83.

[24] Marseguerra, M., Zio, E., and Podofillini, L., "Condition-Based Maintenance Optimization by Means of Genetic Algorithms and Monte Carlo Simulation," *Reliability Eng. Syst. Safety*, Vol. 77, 2002, pp. 151–165.

[25] Marseguerra, M., Zio, E., and Podofillini, L., "Multiobjective Spare Part Allocation by Means of Genetic Algorithms and Monte Carlo Simulation," *Reliability Eng. Syst. Safety*, Vol. 87, 2005, pp. 325–335.

[26] Podgorelec, V., Kokol, P., and Kunej, A., *Nuclear Power Plant Preventive Maintenance Planning Using Genetic Algorithms*, Lecture Notes in Computer Science Book Series, Springer-Verlag, Berlin, Vol. 1821, 2002, pp. 611–616.

[27] Saranga, H., "Opportunistic Maintenance Using Genetic Algorithms," *J. Qual. Mainten. Eng.*, Vol. 10, 2004, pp. 66–74.

[28] Shum, Y.S., and Gong, D.C., "The Application of Genetic Algorithm in the Development of Preventive Maintenance Analytic Model," *Int. J. Adv. Manufact. Technol.*, Vol. 32, 2006, pp. 169–183.

[29] Ilgin, M.A., and Tunali S., "Joint Optimization of Spare Parts Inventory and Maintenance Policies Using Genetic Algorithms," *Int. J. Adv. Manufact. Technol.*, Vol. 34, 2007, pp. 594–604.

[30] Haupt, R.L., and Haupt, S.E., *Practical Genetic Algorithms*, 2nd ed., Wiley-Interscience, Hoboken, NJ, 2004.

[31] Okogbaa, O.G., and Peng X., "A Methodology for Preventive Maintenance Analysis under Transient Response," In: *Proceedings of the Annual Reliability and Maintainability Symposium*, January 22-25, 1996, pp. 335–340.

[32] Kennedy, W.J., Patterson, J.W., and Fredendall, L.D., "An Overview of Recent Literature on Spare Parts Inventories," *Int. J. Product. Econ.*, Vol. 76, 2002, pp. 201–215.

[33] Mannan, S., Ed., *Lees' Loss Prevention in the Process Industries*, 3rd ed., Elsevier Butterworth-Heinemann, Oxford, United Kingdom, 2005.

28

Roles of Computers in Petroleum Refineries

Cheng Seong Khor[1] and Ali Elkamel[2]

28.1 INTRODUCTION

The world experienced a "crude awakening" more than 3 years ago when oil prices began to surpass one barrier after another within a short span of time. From approximately \$50 (U.S.)/bbl then to more than \$120 (U.S.)/bbl now (at the point of writing this chapter), this worldwide phenomenon has had an impact on almost every facet of our life. Rising crude oil price and global energy concern have revived great interests in the oil and gas industry, including the overall optimization of petroleum refinery operations. However, the economic environment of the refining industry is typically one of low margins with intense competition; hence, the refinery of the future is one that is able to operate in a globally competitive energy market. This situation calls for a continuous improvement in operation efficiency by reducing costs through strategies derived based on an understanding of the world energy market as well as superiority in information and technology. With regards to the latter, the application of information technology (IT) and information systems (IS) in process engineering via computer-aided systems for process operations has been crucial in providing technical process services and support in navigating a tight operating range yet ensuring enough room for operation flexibility and resiliency in refineries.

The major functions of IT-supported computer-aided process operation systems in refineries include the following [1]:

- To optimize supply decisions on crude oil feedstock, intermediate products, and residues;
- To assist in determining the control and operating parameters (mainly the setpoints of throughputs, temperatures, pressures, ratios, and transition regimes) that are optimal (technically and economically) for the production expected from the process units in terms of quantity (volume and yields) and quality;
- To contribute to the analysis of the possible discrepancies in expected performance, including the availability of process units and their actual performance, to identify the probable causes and to recommend remedial actions;
- To perform regular surveillance of the operating parameters to
  - Identify the bottlenecks restricting process unit capacity and thus, identify potential for debottlenecking opportunities;
  - Be ready to supply data to the short-term scheduling and long-term planning services, hence be able to execute the required plant improvement projects, which have been commercially justified; and
  - Identify opportunities for increasing operational efficiency (e.g., by reducing energy consumption);
- To ensure that the relevant technical parameters of the refinery short-term databases and plant simulation models are continuously updated; and
- To maintain a repository of the refinery's knowledge, expertise, and best practices on the processes already installed or those that are potentially attractive for implementation in the existing sites, which mainly includes distillation, conventional or deep conversion, hydrogenation, desulfurization, octane enhancement, and production of specialty products (notably lubricants, solvents, and bitumen [i.e., asphalt]). Other aspects of refinery operations of interest concern utility management and site-wide energy intensity as well as environmental protection considerations on effluent treatment technology and emissions reduction. An illustration of this function is the role of computerized systems in providing structured communication networks using written and computerized support materials (mainly process manuals and analytical and diagnostic tools) to enable accessing and sharing know-how, information, and experience pertaining to refinery operations because most of the major integrated oil and gas companies have their own research and development (R&D) centers and are inventors of or license holders for the processes operated in their refineries.

Integration of process operations in refineries (and process plants in general) has been stimulated by global competition, focus on customer needs, cost pressures, societal expectations, and rapid technological changes and has been facilitated by tremendous performance advances in computing technology. Pompéi [1] further advocates that in recent decades, the development and advancement in computerized systems have influenced refinery operations and organizational structures the most, rather than the technologies that are more directly related to the refining processes themselves.

28.1.1 *Aims of the Chapter*

IT, with its associated spin-off of IS, is developing very rapidly, as readers will be well aware of from their experience with personal computers, electronic mail, and the Internet. The same speed of development is apparent in the applications of IT to the field of process plant engineering. For this reason, there would be little value in devoting this article to a detailed review of the technology currently available because that would quickly become obsolete. Hence, the principal objective of this work is to examine how IT has contributed

---

[1] Chemical Engineering Department, Universiti Teknologi PETRONAS, Malaysia

[2] Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

to the improvement in operation, safety, and ultimately the profitability (or margins) of the petroleum refining industry. The emphasis will therefore be on the related concepts and benefits brought about by computer-based applications in the following areas of refinery operations:

- *Process automation:* Automated safety systems and sequential automation systems;
- *Process control:* Data reconciliation and parameter estimation, fault detection, fault diagnosis, advanced process control, and real-time online optimization;
- *Technical management systems:* Planning and scheduling, process simulation, product quality, maintenance, inspection, including the use of IT for document management; and
- The systems-based applications for utilization as decision-making tools in various technical and economic (technoeconomic) performance measurements, evaluations, and analyses.

The term "computerized systems" in this chapter always implies a computer program running in the background that possesses an algorithm, which attempts to model and emulate and thus automate an engineering task that used to be performed solely by a human. Aspects of IT not specific to the refining industry such as payroll, budgeting, and accounting systems are elaborated here insofar as they interface with production management systems.

In this chapter, the authors adopt a discussion framework that is largely based on and influenced by the excellent work of Valleur [2,3] of Technip (the French engineering and construction company) in the book edited by Favennec [4] of the French Institute of Petroleum (IFP). The general structure of each section in the chapter begins with the roles of computerized systems on a particular area of refinery operations, followed by the associated benefits and challenges from technical and economic points of view. Excellent references on computer-aided process operations of refineries with coverage beyond the scope of this article can be found in the following (cited in order of recency): Valleur [2,3], Pompéi [1], Reklaitis and Koppel [5], and Bodington [6]. The latter is a representative text on computer-aided planning, scheduling, and control in process plants, which for many years (at least before the publication of the Technip–IFP book edited by Favennec [4]) has been the source of a nonmathematical, qualitative expository on the subject.

The extensive breadth that spans the coverage of computer-aided process operations has entailed a sheer amount of development and documentation of new knowledge and information pertaining to industrial practices and academic research. As such, the authors wish to assert that this chapter is certainly not intended to be a complete review—the citations are only examples of a much richer literature, even for the problems described here, and there are also many more applications than those presented.

28.1.2 Current Developments and Trends on Roles of Computers in Refineries

The major recent developments and trends in the implementation of computerized systems in refineries include the following [1–3]:

- The technical and financial constraints limiting the use of computer hardware are diminishing as computing equipment becomes more powerful and less expensive.
- Storage capacities are increasing and the modes for information retrieval are improving, allowing common information management systems to be used throughout the refinery as well as the entire supply chain and value chain network of the industry.
- Communication capacities have experienced an immense upsurge that eliminates constraints in the transmission of texts, images, and sound, and that provides for the remote control of certain facilities—in this respect, the Internet has opened up a multitude of new possibilities.
- Standard electronic data processing tools, particularly personal computers and the associated processing systems, are becoming commonplace, thus obviating the reliance on earlier monolithic proprietary systems.
- More and more standard application software is available, especially web-enabled applications.
- Constant progress in computer programming tools has enabled customized software to be developed within the expected time frame and cost.
- Raw data in digital form from the operating field are increasingly available—whereas previously only connected to the distributed control system (DCS), computerized systems are now used in domains that range from signal processing to enterprise-wide systems covering (almost) the entire spectrum of refinery operations.
- Systems to aid operational management and decision-making are progressively more sophisticated, giving refiners more time to devote to the real issue of economic optimization. The impact of these developments in refinery control rooms can be considered as analogous to those in aeronautical cockpits, in which the role of the operators has changed from supervising the process to supervising a machine that supervises the process.
- Those once-disparate applications have now continuously become increasingly integrated, particularly those related to planning, scheduling, control, maintenance, and operations so as to produce a homogeneous control system with the objective of optimizing margins, as part of the concerted efforts for supply chain management and optimization.

The real difficulties that are now encountered, and that are likely to persist in the future, in implementing computerized systems in refineries are more often than not related to natural resistance to change, to reorganization, and to the ability to cope with the complexities generated.

28.2 SYSTEMS AND STRATEGIES FOR COMPUTER-AIDED PROCESS OPERATIONS IN REFINERIES

A wide range of computerized systems, strategies, and tools (including instrumentation) have become increasingly available to help refinery engineers with the construction of their desired and intended applications, as depicted in Figure 28.1, with the major elements highlighted as follows:

- Instrumentation such as sensors, analyzers, and actuators, which are delivering digital information at an enhanced rate—the challenge now concerns how far to "overinstrument" for automation and for reconciliation of process data.
- Programmable logic controllers (PLCs), DCS, and personal computers, real-time servers, which are becoming less and less expensive to buy and to maintain;

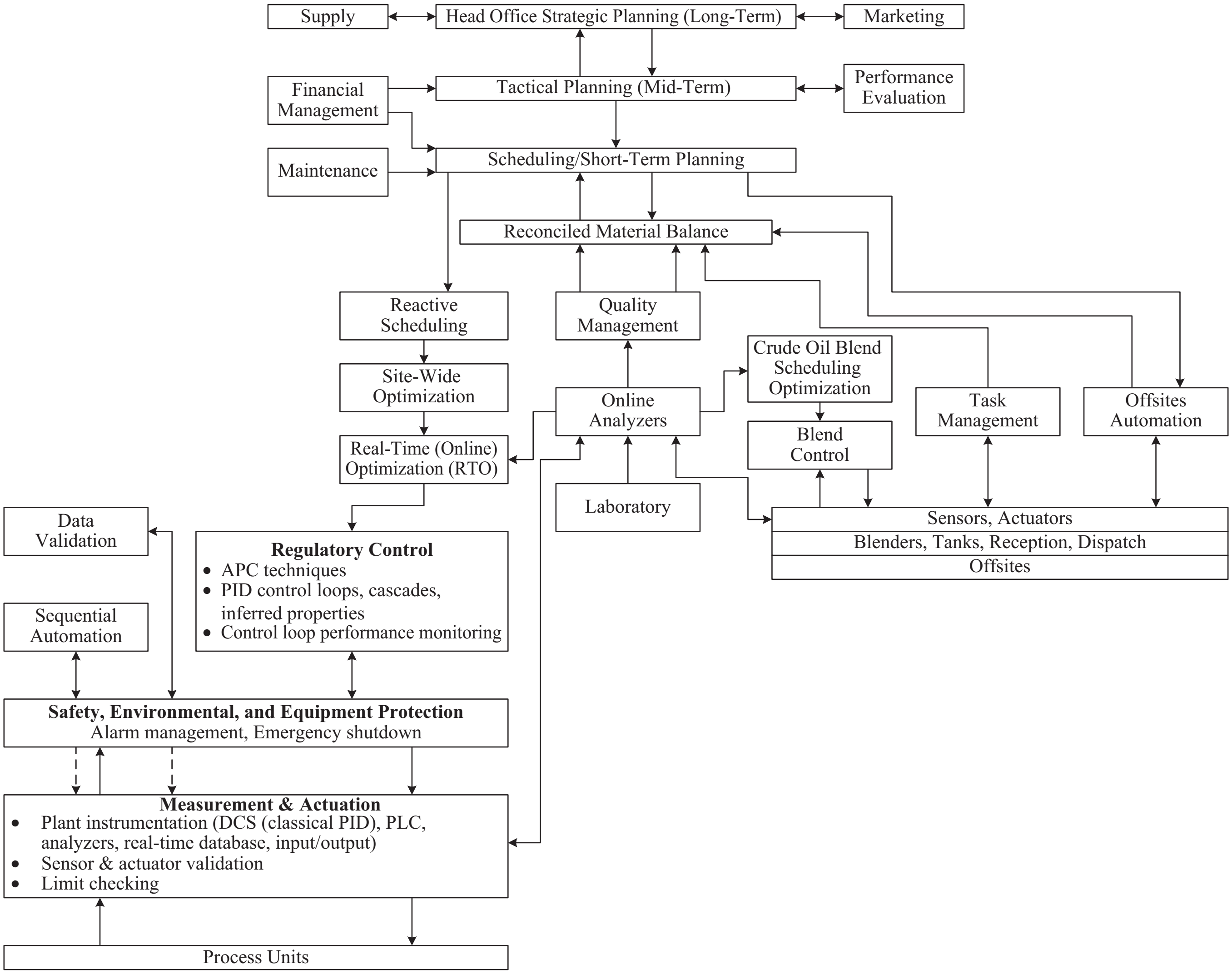


Figure 28.1—Overall configuration of computer-aided decision support systems in a typical refinery. *Source:* Figure based on [3].

moreover, they are progressively more available with capacities in excess of requirements.

- New online analysis technology such as near-infrared spectroscopy (NIR).
- High-performance tools for storing and accessing data.
- Electronic technologies (e-technologies), which capitalize on the power afforded by the Internet.
- Increasingly rapid and reliable means of communication, covering the transmission of the initial input data up to integration with the head office.
- Software developments that are continually reducing the need for specialist proprietary systems.
- New powerful software development concepts and techniques such as constraint (logic) programming and fuzzy logic.

28.2.1 Process Automation in Refineries

The implementation of computerized systems for the purpose of automation of processes in refineries broadly involves two types of applications [3]:

1. Automated safety systems, which are capable of operating either automatically or when activated by the operator. The principal characteristics are the reliability and irreversibility of the operation once started.
2. Sequential automated systems, which are used for operations that are neither dangerous nor highly repetitive. Customized DCS subsystems and PLCs are primary examples of these types of applications.

28.2.1.1 AUTOMATED SAFETY SYSTEMS

The initial functions of sequential control by PLCs have been extended to include safety when successive reorganizations of work functions in control rooms put crisis management in question. Procedures for shutting down unit operations, which could be activated by pushing an emergency button in the control room, have therefore been included in the programs of the PLCs. For emergency use, these automated procedures are duplicated in the DCS and are synchronized on operator activation so that all anomalies in the operation of the sequential procedures can be detected, allowing the operator to take over the controls if necessary. The DCS also provides automatic switching to back up controllers and online testing of sensing elements.

This approach to sequential control has proved to be particularly effective because it allows consistency of the control instructions and process data such as temperature and pressure profiles over a consistent time horizon. The most common examples of this type of operator-controlled automatic security system include furnace shutdown, furnace steam blowdown, partial shutdown of a certain section of a unit, recirculation, and general emergency shutdown. In the most critical cases such as emergency shutdowns, the PLCs are made redundant at the different levels of the central processing system and at the input and output points. The redundant PLCs are valuable tools for this type of application because they offer very high operational availability. In this regard, by capitalizing on the experience of operating nuclear plants and offshore oil facilities, refineries have been able to reach a higher level of safety than in the past with respect to emergency shutdown procedures [3].

28.2.1.2 AUTOMATED SEQUENTIAL SYSTEMS

The first applications to undertake the functions of sequential control have been mainly concerned with the replacement of traditional relay equipment. Such implementations have offered the flexibility of accommodating modifications in operating strategy as well as changes in input and output materials. Common applications include the switching of molecular sieves, filters, and absorbers and the local supervision of analyzer housing. These implementations have been extended to most repetitive operational procedures, which include automatic purges, emergency pump switching, bypassing of process sections, and furnace stack cleaning. With the installation of the necessary instrumentation, it is possible to dispense with the permanent presence of an operator by automation of the procedures using a PLC or a DCS. In refineries with the highest level of automation, it is not unusual to have more than 100 PLCs undertaking most sequential operations. The objectives for doing so are to minimize the need for personnel on the units, to ensure the total repeatability of operational procedures, and to provide the console operators with effective tools for use in the event of a crisis.

In conclusion, the systematic use of programmed automatic systems in refineries is taking place in a general context of increasingly automated operations and improved safety [3].

28.2.2 Process Control Systems

The discipline of process control has made remarkable advances in the last 3 decades or so with the advent of computer control of complex processes, such as those implemented widely and successfully in a refinery. Low-level control actions involving regulatory control of opening and closing valves, which used to be performed by human operators, are now routinely executed in a computer-aided automated environment. Needless to say, the benefits to the refining industry have been enormous, with considerable sustained progress as demonstrated by the computerized systems of DCS and multivariable process control (MPC).

Two major types of control systems are implemented in refineries:

1. Preventive systems are intended to anticipate incidents and intervene by exception. Thus, the systems free the operators from the need for continual surveillance of problems, including plugging, fouling, choking, and foaming, in addition to abnormal developments that involve complex parameters (e.g., severity of a visbreaking unit), rotating machineries, control valves, and burners (flare).
2. Systems for assistance in crisis management enable the following functions: automatic emergency shutdowns and safety alerts; automatic steam curtain partitioning in the case of a fire, and emergency management in general.

28.2.2.1 CONTROL SYSTEMS ARCHITECTURE

Most refineries adopt a combination of standard proportional-integral-derivative (PID) controllers and linear multivariable process control (LMPC) to solve dynamic regulation problems. The PID–LMPC configuration has been deemed adequate, thus significantly reducing the incentive for further developments over the years and instead turning the attention to ensuring its optimal use for maximal performance of the installed applications

The following observations generally describe the major trends of process control implementations in refineries [7]:

- LMPC will continue to be the workhorse of process control in oil refineries and will be used to control the largest and most important process units.
- For certain small systems that are highly nonlinear and not well understood, which are two characteristics not well handled by LMPC, the availability of user-friendly software and affordable hardware will result in the use of MPC technology, notably for systems involving high-purity distillation columns and reactors with extensive fluid viscosity.
- On the other hand, MPCs will be used more for the purpose of driving the process units toward their actual limits, in which the units are bound to exhibit stronger nonlinear behavior that consequently will also expose the limitations of existing technology.
- In addition, there exist hybrid systems involving continuous and discrete decision variables that cannot be handled using current commercial packages but that have fuelled intense research efforts in academia, as evidenced by the work of Morari and coworkers (for example, see reference 8) and by Marquardt and coworkers (for example, see references 9 and 10). These hybrid systems will become more important in the future because of the increased integration of process units, as characterized by continuous variables, with the refinery offsites, in which yes–no types of discrete decisions abound [7].

28.2.2.2 REFINERY PROCESS DATA RECONCILIATION AND PARAMETER ESTIMATION

Process measurements taken from a process via DCS, sensors, or any other methods of data collection in a refinery typically do not reveal the complete and correct information about the process state. This situation is attributable to two reasons: (1) the limited number of process quantities accessible to measurement instruments, and (2) unavoidable measurement errors caused by imperfect instrumentation and signal processing, some of which are difficult to detect. Thus, computer-aided techniques of data reconciliation provide a means of upgrading the quality of this process data by adjusting process measurements with random errors to satisfy material and energy balance constraints and by estimating unmeasured process quantities on the basis of a steady-state process model. This is achieved through establishing relationships among different variables, which are based on available redundant information, by using independent measuring devices and laws of conservation of material, energy, and momentum, which relate one measurement to another through the topology of the integrated processes in a refinery [11–13].

Refineries typically require some form of data reconciliation of their aggregated and real-time process data to verify custody transfer and field flowmeters, field analyzers, and laboratory instruments, including the automatic tank gauging systems. In general, the reconciled process data are used for the following purposes:

- To specify the current status of the plant model to monitor the effectiveness and efficiency of the manufacturing process and to benchmark its performance against other plants consuming and producing similar feedstock and product stock, and
- To estimate the model parameters for plant model matching.

28.2.2.3 COMPUTER-AIDED REFINERY FAULT DETECTION AND FAULT DIAGNOSIS SYSTEMS

Fault detection and diagnosis is a highly important problem in refineries and in the general realm of process engineering. It is the central component of abnormal event management (AEM) that deals with the timely detection, diagnosis, and correction of abnormal conditions of faults in a process. Early detection and diagnosis of process faults while the refinery is still operating in a controllable region can help to avoid abnormal event progression and therefore reduce productivity losses. Because the downstream oil and gas industry suffers an estimated loss of billions of dollars every year, AEM has been rated as the major problem to be addressed in refineries.

In this regard, there has been much interest in the concept of total process control [14] with the realization that automation of decision-making requires the addition of an exception-handling decision layer because of limitations that exist in developing accurate models. This necessitates tasks that include identification of occurrence of events outside of normal operation, diagnosis of the root cause, and culminating with the synthesis and implementation of corrective actions. The use of computerized artificial intelligence tools such as expert systems and neural networks, separately or in an integrated fashion, for monitoring and diagnosis has been a commonplace feature in refinery systems. For reviews on developments in fault detection and diagnosis, the interested reader is referred to the excellent survey by Venkatasubramanian et al. [15,16]. Fault diagnosis clearly shares with other process operations the realization that with powerful knowledge representation schemes on computerized systems, one could possibly capture the expertise of operators and control engineers with years of experience. Figure 28.2 illustrates an integration framework of process operational tasks of control with the operator.

28.2.3 Advanced Process Control Applications

The applications of advanced process control (APC) in refineries are concerned with real-time multivariable control on the basis of models of the process units. With the support of excellent instrumentation (and sufficient degrees of freedom), the main objectives of APC in refineries have brought forth enormous benefits as follows, particularly through the applications of model predictive control:

- Increased ease in management of process units due to greater stability of operating conditions in the face of changes in the operating environment (e.g., changes in feedstock quality and variable atmospheric conditions);
- Increased process capability due to reduction in process variabilities;
- Maximized throughput (i.e., higher feed rate as a result of pushing multiple process constraints to higher levels);
- Increased yield of high-value products;
- Increased energy and general operating efficiency through reduced consumption of utilities and chemicals;
- Reduced production losses; and
- Reduced fluctuations in quality and the associated product quality giveaways.

Furthermore, in most refinery revamp projects, APC is responsible for a major part of the quantifiable benefits; therefore, it is a priority in executing such projects.

A popular APC software system widely used in refineries is Honeywell’s Robust Multivariable Predictive Control Technology (RMPCT). The periodical *Hydrocarbon Processing* annually publishes the *Advanced Process Control & Information Systems Handbook*, which contains information on currently operating APC systems (or that have been in operation).

28.2.4 Real-Time Optimization

Despite its many advantages (as elucidated in the previous section), a possible objection to APC is that even erroneous setpoints are simply implemented quickly when a most difficult part of refinery operations is ensuring that correct setpoints are established in the automated controls. Thus, real-time optimization (RTO) systems (also known as online optimization) are used for determining the optimal values for the setpoints sent to the APC by executing online calculation.

At present, there are relatively few commercial applications for RTO (see Table 28.1) because the models must be able to generate solutions within minutes, and on top of that, they must be continually and automatically updated with data on the economic and technical conditions of the process units, which require a high-quality infrastructure to collect and verify the data entered into the models. For this reason, some packages such as Aspen Plus (version 11 and later) couple a process simulator with RTO capabilities. Because the models used for the optimization must be able to integrate all of the system’s constraints and use the degrees of freedom available, the optimization models are particularly complex with over hundreds of thousands of equations, with some possibly nonconvex, and millions of variables, all requiring a simultaneous solution strategy.

The standard approach to rigorous RTO typically involves the following procedure: (1) periodic execution of an algorithm that gathers data from steady-state operation, (2) reconciliation of these data, (3) adaptation of some model parameters so that the model results match the reconciled data, (4) calculation of the optimal targets for the process, and the final effect of (5) modification of

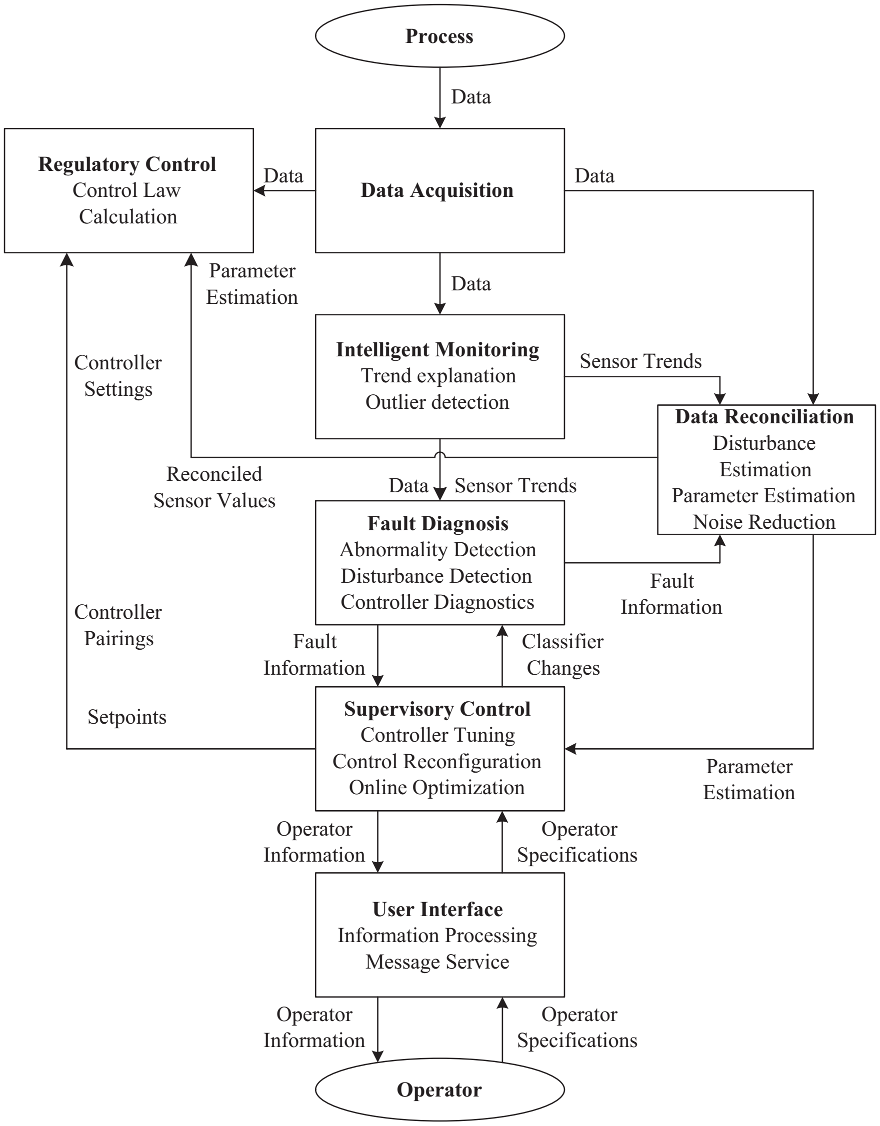


Figure 28.2—A knowledge-based integration framework for continuous operations that integrates the lower-level process operational tasks encompassing data acquisition, regulatory control, intelligent monitoring, data reconciliation, fault diagnosis, supervisory control, and communication with the operator [15,16].

the process setpoints as necessary [6,7]. Recent developments in some refineries are witnessing the implementation of simultaneous optimization of multiple units in real-time mode, with the ultimate goal of attaining an online commercial optimization of the total refining process.

28.2.4.1 RTO SOFTWARE PACKAGES

Powerful nonlinear optimization algorithms are crucial for successful RTO applications to industrial optimization problems [17]. RTO software packages are (typically) equation-oriented systems that make use of large-scale sequential quadratic programming (SQP) concepts. An example is SimSci-Esscor's ROMeo [18], which provides the following features to its users:

- Enables plant engineers and management to model process units and optimize operations on a plantwide basis;
- Uses a combination of real-time plant data and current economic objectives to precisely replicate plant operations;
- Calculates the optimal process setpoints for the plant control systems on the basis of a rigorous model of the operating facility;
- Assists in determining the location and cause of operating constraints and problems; and
- Unlike older optimization technology, it uses one model for process simulation, data reconciliation, and optimization—this single-model concept and state-of-the-art graphical plug-and-play environment minimizes the costs of model building, implementation, and maintenance.

28.2.4.2 CHALLENGES TO RTO IMPLEMENTATION IN REFINERIES

Despite good results reported in many respectable industrial and academic publications, RTO still lacks a general

TABLE 28.1—Commercial RTO Software [17,19]

Software with RTO	Developer/Vendor	Remarks
Aspen RTO	Aspen Technology	Resulted from merging of DMO and RT-Opt
Aspen Plus (Release 11), DMC-Plus	Aspen Technology	—
ROMeo (Rigorous On-line Modeling with Equation Based Optimization)	SimSci-Esscor (an operating unit of Invensys Process Systems)	—
Aspen RT-Opt	Aspen Technology	• Equation-based closed-loop optimization • Originally developed by Dow Chemicals for application in multitrain ethylene plants
DMO (Dynamic Matrix Optimization)	SUNCOR	First DMO application took place in 1988 for a hydrocracker in Sunoco's Sarnia Refinery in Canada, incorporating dynamic matrix control (DMC) technology of Cutler and Ramaker [20,21].
Opera	Shell	Released in 1986 for implementation in ethylene plants.
NOVA Optimization and Modeling System	Honeywell	Originally developed by Dynamic Optimization Technology (DOT), Inc.

commercial acceptance because several practical limitations significantly degrade the potential benefits in addition to uncertainties in the reported economics data of the process units. The practical limitations are primarily due to insufficiently detailed feed characterization, imprecise and poorly detailed models, and nonexistence of true steady state in reasonably disturbed plants. This situation applies particularly to the petroleum refining industry, but it can be expected that the gradual solution to these problems, including the implementation of efficient nonlinear programming (NLP) algorithms for parameter estimation, will see the successful application of the RTO technology, as evidenced from developments in the gas-based petrochemical industry [7,22].

28.2.5 Refinery Offsite Automation

The areas covered by this application extend throughout the refinery and include its interfaces with the outside world that are made up of: (1) tank farms for crude oil, intermediate products, and finished products; (2) tankage at the loading and discharging terminals; (3) pumps; (4) blenders; and (5) reception and loading facilities for rail, road, barges, vessels, and pipelines. For a long time ignored, offsite management is now accorded priority attention because of the increasing quality constraints on the finished products. At a time when substantial effort was expanded on the optimization of the refinery units, it was paradoxical that suboptimal operation, for example in the failure to control the quality giveaways, was accepted because of the lack of offsite controls. Thus, the main objective of computerized automated offsite systems is to optimize and reduce the high costs of this part of the refinery operations in addition to enhancing overall safety and flexibility, with the expected benefits as follows:

- Elimination of operator errors that have resulted in line contamination, undetected leaks, tank overflows, and other problems;
- Increased speed of reaction to changes in operating conditions; and
- Increased rapidity of blending with a reduction in the need for reblending operations [2].

28.2.6 Refinery Planning and Scheduling

The planning and scheduling of refinery operations is responsible for establishing the detailed manufacturing programs of a plant at various time scales. The plans and schedules must enable the operational departments to define the timing of the specific activities to produce the volumes of the essential products that are required for the company's objectives to meet the demands of the core outlets of the supply and marketing departments for national and international retail sales [1,22]. This production must be ensured while minimizing the associated volumes of byproducts, which are generally sold uneconomically. Thus, computer-aided planning and scheduling systems play a very important function in refineries because of the potential realization of huge margins, large cost savings, and improved feeds to the process units. However, it is notoriously challenging and complicated to model refinery operations because they involve units operating in batch and continuous modes with multiple grades of crude oil and refined products. These models impart additional flexibility to the problem by allowing the modeling of discrete and continuous types of decisions and constraints [23].

The refinery planning and scheduling activities can be divided into the following three categories as shown in Figure 28.3 [24–26]:

1. *Front-end scheduling of crude oil movement and blend scheduling optimization:* Involves handling of the crude arrivals, encompassing (1) crude oil unloading from the marine vessels, (2) crude oil transfer to the storage tanks, (3) blending of the different crude feedstock, and (4) charging schedule for each crude oil mixture for processing in the crude distillation units (CDUs).
2. *Hydraulics planning and scheduling of refinery production:* Encompasses operations of the process units and inventories among the units to properly control the intermediate inventories. These involve reaction and fractionation processes, in which the former sections alter the molecular structure of hydrocarbons mainly to improve the octane number whereas the latter sections separate the reactor effluent into streams of particular properties and values.

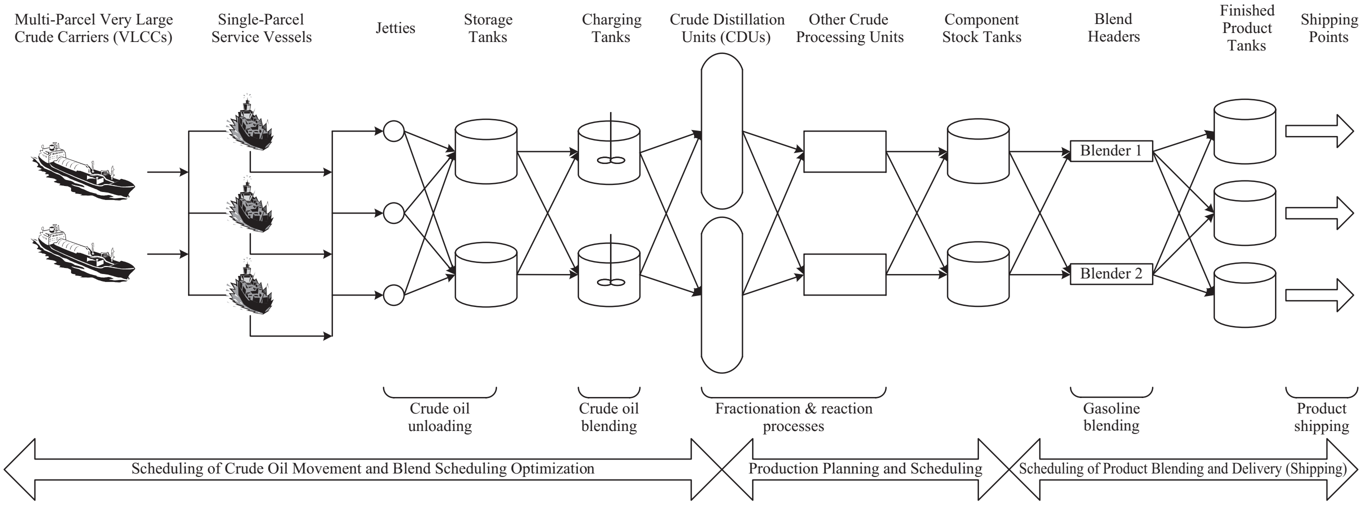


Figure 28.3—The full spectrum of planning and scheduling activities of refinery operations.

3. *Scheduling of product blending and distribution:* Concerns the blending, storage, and lifting of final products for delivery (or dispatch) and shipping while ensuring inventory control.

28.2.6.1 BENEFITS OF COMPUTERIZED REFINERY PLANNING AND SCHEDULING SYSTEMS

The successful role of the centralized planning unit and the local scheduling department largely determines the commercial success of the refineries. This clearly underlines the enormous importance of having highly reliable computerized planning and scheduling systems in automatically computing feasible schedules [1]. To guarantee the consistent implementation of the scheduling programs, a short-term refinery scheduling database is often used, which conventionally runs on linear programming (LP) models that are continuously updated with all of the necessary data. The data mainly include the minimal and maximal throughputs, yield structures, and marginal operating costs, including the ranges of validity. The establishment and maintenance of this database is a substantial task that has been greatly facilitated by the full integration of the database with the overall refinery IS.

28.2.6.2 CURRENT STATUS OF COMPUTERIZED REFINERY PLANNING AND SCHEDULING

The following recent developments have generated renewed interests in computerized decision-making tools for the optimization of refinery planning and scheduling:

- Refiners are encountering more and more scheduling problems because of the increasing number of constraints that reduce their degrees of freedom, such as more stringent product specifications, environmental constraints, and tankage limitations;
- Operations of refinery processing schemes and the number of different types of crudes processed are becoming increasingly complex; and
- Response times are becoming increasingly shorter—processing refineries in particular must respond very quickly to dynamic market demands.

At the same time, technical advances have given rise to new possibilities of reaping greater benefits from improvements in planning and scheduling activities as follows:

- The problems can now be formulated more easily and by using more powerful state-of-the-art modeling techniques such as logic-based constraint programming, artificial-intelligence-based expert systems, and hybrids involving mixed-integer optimization [27].
- Increased computing and computational power due to a meteoric rise in the availability of more powerful computer hardware as well as the advancement in efficient and robust planning and scheduling algorithms [28–30].
- The availability of data on company networks provides immediate access to the necessary information, particularly by using the resources made available by the Internet and web-based technologies available in refineries.

This has enabled complex planning and scheduling problems, with solutions involving discrete decisions that require the evaluation of many possible feasible schedules and combinations (hence, giving rise to a combinatorial optimization problem), to be handled now with acceptable computational time and effort. The techniques of object-oriented programming and graphical interfaces have been largely instrumental in enabling the practical use of these resource- and data-intensive systems. The joint use of artificial-intelligence-based cognitive techniques (e.g., expert systems and neural networks) and the latest clever mathematical algorithms, which has been made possible by high-performance computer hardware (as previously mentioned), has demonstrated great potential for the practical use of such planning and scheduling systems [31]. In light of the above, computerized systems are bound to substantially replace the function of many of the spreadsheet-based tools currently used in the planning and scheduling departments of complex refineries, particularly those that handle the processing of multiple crudes, which involve decision-making to the following multiperiod problems: (1) sequence of crude runs and crude blending rules, (2) allocation of storage and charging tanks, (3) operating conditions of the process units, (4) sequence of product movements, and (5) blend formulations for finished products to be shipped.

28.2.6.3 CHALLENGES TO IMPLEMENTATION OF COMPUTERIZED PLANNING AND SCHEDULING SYSTEMS IN REFINERIES

Planning and scheduling applications are at the core of a refinery's IS and therefore require a substantial quantity of data that chiefly include tank levels at any time, operating conditions of process units, product qualities, component qualities, main equipment availabilities, marketing requirements, forecast deliveries from outside of the refinery, and forecast lifting requirements. To efficiently gather this amount of information requires a reliable communications network and a plantwide side database; hence, there exists room for major improvements in the current planning and scheduling systems of most refineries.

Planning and scheduling functions are presently adopted as decision support systems, but such systems do not always possess the capability of optimizing the entire refinery's overall operations. For example, in practice, the crude oil movements and blend scheduling programs at the front end of refineries are typically separated from the computer programs used for the planning and scheduling of product blending and delivery. For the latter problem, the uncertainties arising from fluctuating product demands and other changing parameters of the market often render the schedules to be obsolete very quickly. Thus, for such problems the scheduling programs are mainly used for studies on tankage or for product optimization. For the former problem, the next section provides a more in-depth discussion in view of its growing significance.

28.2.6.4 OPTIMIZATION OF CRUDE OIL BLEND SCHEDULING

Millions of dollars can be saved if the critical operation of scheduling crude oil blends charged to the CDUs is executed in an optimal manner because crude oil costs account for nearly 80 % of a refinery's turnover [13]. With declining supplies and increasing prices of premium crude oils, one of the main challenges facing refineries is how to best exploit the greater margins of the low-cost crude oils to increase profits by using varying blends of premium crudes with low-cost crudes. However, there is a penalty in using low-cost crudes because of their high content of the undesirable components of sulfur, aromatics, high residues, and others, which is bound to cause processing and product quality problems in the CDUs and the downstream units. Hence, a key strategy to the refiners is to identify and process the optimal blend(s) of low-cost and premium crude oils in an effort to minimize the operational problems yet maximize profit margins. However, the crude scheduler's functions and tasks in a refinery have become increasingly complex in recent years. They must continuously observe the crude oil movements and the operational status of the plant and match them to fluctuating market demands. The crude schedulers typically react to the crude arrivals by assigning destination tank(s) for each crude, blending crudes as needed to meet the targets for yields and qualities of the fractionated products from the CDUs, and by subsequently determining the charging rate to each CDU. However, in most cases, under intense time pressure and low inventory flexibility, the schedulers rely largely on their experience and will be inclined to select the first feasible solution computed by a spreadsheet-based model (or some other available tools), thus forsaking the tremendous opportunities for economic and operability improvements that potentially exist. Clearly, crude scheduling is a largely manual task with minimal rigorous optimization involved simply because it is almost impossible for the human scheduler to identify "optimal" crude blends to process in each CDU [32–34].

There is clearly value in exploiting a reliable automated scheduling system for crude oil blend optimization in an oil refinery. The potential economic and operational benefits to a refinery for using a computerized crude oil blend scheduling optimization procedure include improved options of crude blends, increased utilization and throughput, economic use of less expensive crude feedstock, capture of high-quality crude oil barrels, reduction of yield and quality giveaways, improved control and predictability of downstream production, and reduced demurrage costs [33].

28.2.6.5 RECENT ADVANCES AND CURRENT DEVELOPMENTS IN COMPUTERIZED REFINERY PLANNING AND SCHEDULING

The way forward in refinery planning and scheduling is to expand the planning process to include larger systems involving a group of refineries instead of just a single site [35–37]. Another current development is the inclusion of some discrete scheduling decisions in the planning process pertaining to decisions dealing with binary 0–1 variables, in which complication arises because of a difference in the time scales of the two activities of planning and scheduling [31,38]. For instance, this form of integration is necessary in multiperiod planning when certain decisions are exclusively related to the operating modes of process units. Finally, another important development is the overall integration and coordination of planning, scheduling, and control, which has been touted often as the holy grail of process operations. The interested reader is referred to recent work along this effort [39–43]. For further reference, the following provides representative publications in the three major activities of refinery operations:

- Front-end crude oil scheduling [33,44–51],
- Production planning and scheduling [52–57], and
- Product blending and distribution scheduling [24,55,58–60].

Table 28.2 provides a partial list of commercially available industrial system applications software packages for the simulation and optimization of planning and scheduling of refinery operations.

28.2.7 Tools for Process Modeling, Simulation, and Optimization in Design and Retrofitting of Refinery Processes

28.2.7.1 STEADY-STATE PROCESS SIMULATION

Commercial process simulators are available to enable refinery engineers to perform detailed material and energy balances for debottlenecking studies on unit operations for plant revamp and rejuvenation exercises. Notable examples include steady-state simulators such as Aspen Technology's Aspen Plus, Honeywell's UniSim, Virtual Materials Group's VMGSim [79], and PETRONAS's iCON; SimSci-Esscor's PRO/II (of Invensys Process Systems) and KBC's Petro-SIM are dedicated simulation programs for refinery and petrochemical processes. Specialized tools are also commercially available for accomplishing realistic modeling and simulation of certain process units requiring detailed diagnostic

TABLE 28.2—Industrial Systems Applications Software for Planning and Scheduling of Refinery Operations

Software/Tool	Vendor/ University/ Researcher	Major Features	Technique	Reference
aspenONE Planning and Scheduling for Refining and Marketing	Aspen Technology			
aspenOne consists of the following components:				
• Aspen PIMS (Process Industry Modeling System)		• Facilitates enterprise-wide linear and nonlinear planning, allowing for multiplant and multiperiod requirements based on optimizing feedstock selection, product slates, plant design, and operational execution plans. • Interfaces to rigorous process simulator models.	Sequential linear programming (SLP)	61, 62
• Aspen XT		Supports and enables more accurate scheduling and optimization of refinery activities through a single solution for crude receipts, crude and feedstock scheduling, process operations, unit operations, product blending, and product shipping.	• simulation • LP • expert systems	63
• Aspen MBO (Multi-Blend Optimization)		• For offline blend scheduling and optimization of gasoline, distillates, fuel oils, and other refinery products. • Generates optimal recipes for individual blends or aggregate blends into time partitions. • Develops optimal schedules for short- or long-term campaigns, or both, using an event-based, multiperiod, and multiblending modeling system. • Automatic generation and simultaneous solution of entire blending process model that considers complex nonlinear blending correlations, tank constraints, discrete volume and recipe constraints, and all relevant events such as blends, product shipments, intermediate receipts, and tank-to-tank transfers.	Mixed-integer nonlinear programming (MINLP)	64
Refinery and Petrochemical Modeling System (RPMS)	Honeywell Process Solutions (the software was originally developed by Bonner & Moore)	• Powerful graphical user interface (GUI)—highly effective and intuitive interface for working with the LP model. • Contains model navigation window with graphical objects; the latter contain information on charge yields, feeds, products, results, etc. • "Data Factory" and "Report Factory" facilities provide integrated application for input of static and variable data and for generating standard reports in Excel. • Enables multiperiod modeling considering different capacity availabilities and seasonal quality specifications via intermediate storages. • Enables multiplant modeling for integrating multiple refineries (including petrochemical plants) in single production and supply model, with sharing of raw materials, product pools, and transportation and distribution logistics. • Handles nonlinearities via automatic recursion techniques.	LP	65

OmniSuite	Haverly Systems (HIS)	• For supply-chain management of integrated planning and scheduling encompassing crude supply, refining, product blending, and product distribution.
		• A unified package with major modules consisting of
		  • OMNI model management system,
		  • GRTMPS optimization planning system,
		  • H/SCHED scheduling system, and
		  • H/CAMS (Haverly Crude Assay Management System).
		• Main features of GRTMPS:
		  • Enables formulation of multiperiod, multirefinery, and multilocation models;
		  • Enables specification for recipe blending;
		  • Applicable for transportation, inventory, and investment planning problems;
		  • Features distributive recursion and delta-base structures; and
		  • Applicable as standalone planning application.
			LP	66–69

TABLE 28.2—Industrial Systems Applications Software for Planning and Scheduling of Refinery Operations (Continued)

Software/Tool	Vendor/ University/ Researcher	Major Features	Technique	Reference
MIMI (Manager for Interactive Modeling Interfaces)	Aspen Technology (software is formerly owned by Chesapeake Decision Sciences, Inc.)	• Includes a family of supply-chain solutions. • Modeling system approach is a combination of modeling language and matrix generator with a strong database orientation.	SLP	70
PETRO LP	Invensys Production Management	• Refinery-wide LP refinery planning system. • Originally developed by ChevronTexaco in 1970s and widely used in their refineries. • Implements distributive recursion, an LP approach that enables construction of realistic refinery-wide models.	LP	71
PLATOFORM	ExxonMobil	• For the computational treatment of optimization problems arising in the production planning and sales of petroleum products at ExxonMobil. • Encompasses applications that are not limited only to refinery planning and scheduling but also include the following: single refinery and chemical plant model, regional models for the coordination of several refineries or chemical plants, product distribution through intermediate facilities, distribution facility investment, drilling rig scheduling, portfolio investment, blocked operations scheduling, truck fleet sizing, and vessel scheduling.	LP	72, 73
GEMMS	Shell Global Solutions International (SGSI)	Integrated with SimSci's PROMOTE–PRO/II simulator to ensure process models are tuned to observed plant performance.	LP	74
RefSim	SGSI	High-level decision-making tool focusing on production planning and blending operations (with minimal operational details).	LP	75
ProPlan and ProSched	Ingenious, Inc.	• Integrated with crude assay database. • Web-enabled (can be installed in different locations and can be executed via Internet). • Generate reports on return on investment (ROI), net present value (NPV), and internal rate of return (IRR) for ease of financial assessments.	• Optimization • Genetic algorithms	76, 77

RefOpt	Centre for Process Integration, University of Manchester (formerly UMIST—University of Manchester Institute of Science and Technology)	• Performs simulation and optimization of refinery processes and operations.
		• Useful for overall refinery operation planning.
		• Determines appropriate flow distribution and operating conditions for various unit operations.
		• Maximizes overall refinery profit by accounting for
		  • Major aspects associated with plantwide operations (e.g., selection of feeds and products, distribution of intermediate products, connections between different processes and allocations of utilities), and
		  • Operating details (e.g., temperatures, pressures) within each process.
		• Also useful for analysis and design of hydrogen distribution systems in refineries. Sets targets for minimum overall hydrogen supply required by a refinery by maximizing recovery between various consumers. Purification options can also be considered. Generates automated hydrogen network design with user having full control over network complexities and constraints.
			• LP
			• Nonlinear optimization
				78

studies, for example, in modeling of conversion units such as catalytic reformers, catalytic crackers, and hydrocrackers that requires the incorporation of the kinetics of the reaction zones.

In addition, for certain applications, simulators have been directly integrated with available plant optimization routines on a continuous real-time basis, in which current process information from a simulator is used to update the process model. For instance, Aspen Technology has reported undertaking reactor modeling for optimizing hydrogen production via rigorous kinetic modeling to obtain a good understanding of process operation under different hydrogen feed conditions. The reactor models are linked to Aspen PIMS and by automatically updating the latter; the models are capable of enhancing detailed planning and scheduling activities as well as economic evaluation [80].

To improve its value to refiners, the real challenge in the use of these supporting tools lies in ensuring realistic simulation results that can be translated into practical plant operation language for implementation, leading to improvement quantifiable in terms of dollars and cents. Current developments have witnessed automatic linkage of simulators with real-time database and linear-programming-based optimization tools, which not only allow access to information on selected process stages and their comparison with simulator output but also more accurate long-term planning and target-setting.

28.2.7.2 DYNAMIC PROCESS SIMULATION

Significant research over the past 20 years has produced several highly developed software packages that are designed for plantwide dynamic simulation with ready adoption by refineries. Examples of these equation-based modeling environment software include SPEEDUP [81], DIVA [82], gPROMS [83], and ABACUSS [84]. These packages facilitate large-scale dynamic system simulation by isolating the engineer from numerical algorithms, code generation, and debugging, thereby leaving the engineer free to concentrate on model formulation and application. The productivity gains afforded by this modeling support largely determine the feasibility of dynamic-simulation-based activities in a refinery such as those encountered in parametric sensitivity studies, safety interlock design verification, control system design, and start-up–changeover–shutdown studies [85,86].

28.2.7.3 OPERATOR TRAINING SIMULATORS

The reorganization of control rooms and the considerable increase in the level and reliability of automation installed have meant that panel operators are exposed to operational incidents much less frequently than in the past. The increased scope of automation requires a different approach and much longer periods of training. In the event of a plant failure or failure of the automatic systems, the panel operators must use their superior level of training to guarantee the safety of the refinery. Refinery training simulators, which are based on dynamic simulation, have become an essential tool in delivering this form of training with the dual objectives of

1. Training new operators, particularly panel operators, who are stationed in the control rooms; and
2. Maintaining and regularly updating the knowledge and skill of the operators to react to exceptional circumstances.

This is very much similar to the role of flight simulators for aircrew training.

Using dynamic simulation models ensures the representation of realistic operating conditions, especially in enabling the simulation of the period of transient time after either an incident or a change in operations. The latest simulators possess the ability to produce several possible scenarios and to assess how the operators react in real time. It is a common feature that training simulators incorporate operator consoles that are identical to those in the control rooms and are linked to the DCS so that they can access the initial state of the process variables. The comprehensive use of training simulators in refineries is an indication of competence in operational safety and can simultaneously ensure a level of safety assurance.

28.3 INSTRUMENTATION FOR AUTOMATION AND COMPUTERIZED SYSTEMS IN REFINERIES

The quality of a refinery's operational and management systems depends to a large extent on the quality of its instrumentation. It is worth mentioning that many automation projects have failed because the basic principles governing this facility have been neglected. The tools developed for automation and computerized systems in refineries are often identical, and they collectively realize the multiple applications of decision support systems used in a refinery.

28.3.1 Online Analyzers

The degree to which online analyzers are used for various management and control applications, which could extend from just a few to more than a few hundred, is a representative indication of the extent computer-based technology has permeated a refinery setup (with the exception of hydrocarbon detectors, the use of which is related to safety). Online analyzers are most commonly found in refineries to be in APC schemes for maintaining key critical controlled variables for determining characteristics such as research octane number (RON) and motor octane number (MON) (by the Cooperative Fuel Research [CFR] engine), Reid vapor pressure (RVP), relative density, and ASTM distillation. Its use serves to reduce excessive inferential calculations that are computationally expensive and highly dependent on the accuracy of thermodynamic property data used. Furthermore, online analyzers eliminate the need to rely on laboratory data, which could take a few hours for the feedback to reach control schemes.

It is fortunate that the reliability and ease of maintenance of online analyzers have improved in recent years such that today, they can be used for autodiagnosis and calibration, most frequently with digital DCS. New qualitative analytical technologies, such as NIR and inferential analysis, have reduced the investment cost and simplified the installation of online analyzers, although the former remains a significant burden [2,87].

28.3.1.1 ONLINE ANALYZERS FOR SAFETY ASSURANCE

Online analyzers are used to detect breaches of environmental threshold limits, particularly in terms of hydrocarbon content. This use is especially important for highly automated refineries with reduced number of personnel for which reliable information on the exact location of an alarm is essential. The installation of detectors in matrix networks ensures that an entire refinery area has been covered in addition to installations at fixed points in critical areas. Basic information from the detectors provides the crisis management subsystems with the prediction of the release of potentially explosive or toxic gases into the atmosphere. This knowledge of the nature and location of the reported leak makes it possible to calculate future concentration and location of the gas plume (from the meteorological conditions) in time for action to be taken. In urban areas, this type of system, together with a network of analyzers outside of the refinery, is pertinent to the safety of the zone surrounding the refinery.

28.3.1.2 ONLINE ANALYZERS FOR OPTIMAL UNIT OPERATION

The objective of a major portion of APC applications is the maintenance of the setpoints despite variations arising elsewhere, with many of these variations caused by product quality and the associated product giveaways. Hence, it is essential to be able to measure quality on an online mode for feedback and feedforward APC strategies. For a long time, this has been one of the bottlenecks for the low level of APC implementations in refineries. Examples are most commonly found in relation to the units listed in Table 28.3.

It is acknowledged that the use of online analyzers in relation to APC gives rise to many problems, particularly the justification of the initial investment. Quite recently, there are other options that have become available, and this chapter sheds light on two such technologies—NIR and soft sensors—the latter are most frequently based on neural networks.

28.3.1.3 ONLINE ANALYZERS FOR QUALITY CONTROL OF COMMERCIAL PRODUCTS

In general, the quality control by online analyzers for commercial products in refineries concerns two aspects:

1. Control of intermediate products to achieve RTO of the operating or blending conditions of the process units (or deferred optimization via intermediate tankage); and
2. Control to ensure that the finished products for shipment outside of the refinery are on-specification ("on-specs") because any failure to meet specification requirements could lead to heavy commercial penalties or even judicial ones (the latter in the instance of violation of some environmental regulations).

With regards to the latter, unlike the application of APC on process units, quality control of the finished products is the final stage of the whole refining manufacturing process; hence, APC at this stage must ensure that the products conform to the commercial specifications. For that reason, the use of online analyzers in offsite areas, notably in the tank farm and product blending areas, is important for two major reasons. First, absolute measurement of quality parameters in comparison with the commercial specifications must be made (because some APC applications only necessitate relative measurements). Second, the installation of inline blending eliminates the use of excessive tankage and reduces stocks. The lack of availability of online analyzers in the blender has an effect on the lifting schedules of crude oil charge into the CDUs. Technological progress of online analyzers has witnessed increasing reliability, diversity, and performance. As a result, many specification characteristics for intermediate and finished products can now be controlled online, including octane number, relative density, volatility, distillation curve, viscosity, and even chromatographic analysis.

TABLE 28.3—Quality Control Parameters for APC Implementation on Process Units

Process unit	Parameter for Quality Control
Atmospheric distillation unit	Quality of sidestreams
Catalytic reformer	Increase in octane number of reformate over feedstock
Fluidized catalytic cracker	Main fractionation column operation
Hydocracker	Reactor temperature exotherms
Hydrofiner	H_2S levels of recycle gas
Alkylation unit	*i*-butane recycle ratio
Binary fractionation columns	Column operation

28.3.2 NIR Spectroscopy

The development of NIR spectroscopy technology at the end of the 1980s resulted in considerable advancement in the use of online analyzers. This technique, which previously has been mainly used in the food industry, enables the properties of products to be predicted by the identification and treatment of their spectroscopy signature. The procedure involves passing a sample of the product through an optic cell so as to obtain an adsorption spectrum. Unlike other analytical methods, NIR spectrometry effectively provides a fingerprint of the complex hydrocarbon mixtures contained in a sample that is tested.

With the benefit of over 15 years of experience on the application of NIR technology in refineries, its uses are poised to increase for the following reasons. Its repeatability is better than that of ASTM test methods, and, for a certain number of critical applications, it is possible to guarantee an NIR/ASTM reproducibility compatible with its use for online certification, which underlines the precision of the method in testing RON. NIR technology can be used for the measurement of characteristics such as coking index for steam cracking and "crackability" index for catalytic cracking. Because it determines chemical composition, NIR technology can also assess blending indices for the principal qualities of motor gasoline, gas oil, and fuel oil pools.

The time required to obtain the test result is relatively much less than for the traditional methods, particularly for octane numbers and cold temperature properties. Maintenance costs are of an order of magnitude less than for the ASTM test equipment, especially compared with the CFR motors.

The atmospheric distillation application is of obvious interest for the application of the NIR technology because the details of the true fractionation of the distillation column need to be known in real time because of the following two reasons: (1) to have the true boiling point (TBP) of a crude oil mixture leaving the desalter constantly available and (2) similarly, to have the critical quality characteristics of the sidestreams (with the notable exception of the residue) available. If these data can be produced on crude blends in the feed tankage well before a change, then much more accurate planning and scheduling for production target-setting is possible. The application's ability for performing prediction is particularly important for refineries with frequent changes of crude oil.

Today, it is possible to use NIR for the measurement of blending indices for the most critical properties of each motor gasoline or gas oil component. This development has resulted in (1) a reduction in the frequency of the analysis of the contents of the components tanks, (2) greater precision in blend formulation because of online measurement of component properties, (3) direct loading of large parcels to vessels from the delivery line without using finished product tanks, and (4) rapid convergence of multivariable control tools [3]. Major vendors for NIR systems include Thermo Fisher Scientific and ABB.

28.3.3 Distributed Control Systems

In DCS, process measurements and control functions such as multiple PID loops are connected to application processors, which are networked throughout the plant. A GUI makes it easier for operators to view data, create plots, change setpoints, and respond to alarms. In addition to process control, modern DCS software includes sophisticated trending and data storage.

The digitalization of control loops and the representation of unit operations onscreen, which the distributed DCS systems have achieved since their introduction in 1975, have increased operating flexibility significantly and revolutionized the organization of refinery control rooms. The first demonstration of their reliability is when they replaced the panels, which had previously been the norm, as well as individual controllers. Their value has been subsequently increased by the addition of extra functions that include (1) modules for recording data over a period of time, (2) calculation modules that provide equipment with the capability of implementing control strategies, and (3) interfaces with higher level systems.

DCS manufacturers and vendors maintain a constant program of research and development (R&D) to improve the DCS performance and to go further in transforming them into true computer networks operating on normal industrial standards. Most DCS systems installed today are built around powerful UNIX workstations and are increasingly based on top-of-the-range personal computers using the Windows NT or Windows 2000 operating systems for servers. Major DCS vendors include Honeywell, Yokogawa, ABB, Foxboro, Siemens, and Emerson Process Management.

The authors now have over 30 years of experience with DCS—this timeframe itself is evidence that DCS is highly suitable for use in refinery control rooms because of its reliability, response time, and even ergonomics. Nonetheless, improvement efforts are still ongoing, one of which concerns the integration of DCS in the overall refinery systems architecture and the entailed division of functions between the DCS and the programmable control devices, in addition to reinforcing its interface functions with processing and its storage function of process data [2].

28.4 CONCLUSIONS

The continuing growth in the capacities of computerized systems for engineering computations and communication indicates that there are few technical limits to the use of IT in refinery operations. Many applications have now been established over several years, and, as in other industrial and service sectors, many new and highly innovative applications are continually under trial for full-scale implementation. Nonetheless, the critical issues that remain to be addressed, as emphasized by Valleur [3], concern the following: (1) the choice of technologies to be made, (2) the nature of the provision of support in the long term, and (3) the impact of these technologies on the organization of the remaining manual tasks to be handled by the reduced number of refinery personnel.

28.5 FINAL REMARKS AND THE WAY FORWARD

At best, the current utilization of IT in refineries represents only a fraction of its true potential. Furthermore, the IT tools available rapidly become technically obsolete because of their very short lifecycle (akin to personal computers). The most important issue faced by refiners is that of making the best choice out of the many IT tools available, training for the staff, and maintenance of the systems and the overall plant to ensure effectiveness and efficiency over a long period. The abundance of technologies for the implementation of computerized systems in refineries is proving to be a difficulty in itself, giving rise to the following issues: (1) how technologies are to be chosen for a particular application, (2) how new technologies are to be integrated into a homogeneous system, and (3) how their durability is to be assured without excessive maintenance costs. These questions, and those of the choice of the applications and the sequence in which they should be implemented, ought to be considered within the framework of master plans elaborated before the development of the specifications and the installation of the systems.

Nevertheless, it goes unarguable that the applications of a wide spectrum of computer-assisted automated tools and systems have been a powerful force in revolutionizing today's oil refineries into an integral entity in the energy value chain. However, the technical aspects highlighted and stressed in this chapter are only part of the complete story. In fact, the work patterns of all refinery personnel are constantly revolutionized by the introduction of computerized systems, in which the most difficult aspect to manage by far is the human impact brought about by such systems. If they are introduced without prior consultation and agreement, automation and decision-making tools will inevitably be seen as threatening jobs that have hitherto been handled by a person. A master plan that is publicly disseminated, intensive training in the new roles to be undertaken, and an upgrading of positions, in line with the new responsibilities, are essential ingredients for successful implementation of computer-based applications in refineries. At the same time, individual capability and suitability for the revised roles demands careful assessment.

ACKNOWLEDGMENTS

Cheng Seong Khor acknowledges Universiti Teknologi PETRONAS for the support and resources made available for the completion of this work.

References

[1] Pompéi, C., "Functional and Organizational Analysis," in *Refinery Operation and Management*, J.-P. Favennec, Ed., R. Baker, Trans. Petroleum Refining Series, Editions Technip, Paris, 2001, pp. 455–509.

[2] Valleur, M., "Automation, Process Control and Information Technology," in *Refinery Operation and Management*, J.-P. Favennec, Ed., R. Baker, Trans. Petroleum Refining Series, Editions Technip, Paris, 2001, pp. 275–304.

[3] Valleur, M., "Applications and Their Implementation," in *Refinery Operation and Management*, J.-P. Favennec, Ed., R. Baker, Trans. Petroleum Refining Series, Editions Technip, Paris, 2001, pp. 305–361.

[4] Favennec, J.-P., Ed., *Refinery Operation and Management*, R. Baker, Trans., Petroleum Refining Series, Editions Technip, Paris, 2001.

[5] Reklaitis, G.V., and Koppel, L.B., "Role and Prospects for Intelligent Systems in Integrated Process Operations," in *Intelligent Systems in Process Engineering*, G. Stephanopoulos, V. Venkatasubramanian, and J. Davis, Eds., *AIChE Symp. Series 92*, Vol. 312, 1996, pp. 71–84.

[6] Bodington, C.E., Ed., *Planning, Scheduling, and Control Integration in the Process Industries*, McGraw-Hill, New York, 1995.

[7] Moro, L.F.L., "Process Technology in the Petroleum Refining Industry—Current Situation and Future Trends," *Comp. Chem. Eng.*, Vol. 27, 2003, pp. 1303–1305.

[8] Bemporad, A., and Morari, M., "Control of Systems Integrating Logic, Dynamics, and Constraints," *Automatica*, Vol. 35, 1999, pp. 407–427.

[9] Oldenburg, J., and Marquardt, W., "Disjunctive Modeling for Optimal Control of Hybrid Systems," *Comp. Chem. Eng.*, Vol. 32, 2008, pp. 2346–2364.

[10] Stein, O., Oldenburg, J., and Marquardt, W., "Continuous Reformulations of Discrete–Continuous Optimization Problems," *Comp. Chem. Eng.*, Vol. 28, 2004, pp. 1951–1966.

[11] Binder, T., Blank, L, Dahmen, W., and Marquardt, W., "On the Regularization of Dynamic Data Reconciliation Problems," *J. Proc. Control*, Vol. 12, 2002, pp. 557–567.

[12] Özyurt, D.B. and Pike, R.W., "Theory and Practice of Simultaneous Data Reconciliation and Gross Error Detection for Chemical Processes," *Comput. Chem. Eng.*, Vol. 28, 2004, pp. 381–402.

[13] Kelly, J.D., and Mann, J.L., "Crude Oil Blend Scheduling Optimization: an Application with Multi-Million Dollar Benefits," *Hydrocarbon Process*, 2003, pp. 72–79.

[14] Garcia, C.E., Ramaker, B.L., and Pollard, J.F., "Total Process Control—Beyond the Design of Model Predictive Controllers," presented at *Chemical Process Control CPC IV*, South Padre Island, TX, 1991.

[15] Venkatasubramanian, V., Rengaswamy, R., Kavuri, S.N., and Yin, K., "A Review of Process Fault Detection and Diagnosis, Part I: Quantitative Model-Based Methods," *Comput. Chem. Eng.*, Vol. 27, 2003, pp. 293–311.

[16] Venkatasubramanian, V., Rengaswamy, R., Kavuri, S.N., and Yin, K., "A Review of Process Fault Detection and Diagnosis, Part III: Process History Based Methods," *Comput. Chem. Eng.*, Vol. 27, 2003, pp. 327–346.

[17] Mahalec, V., and Marlin, T., "Real-Time Economic Optimization (RTO) of Process Operations: The Long Road to a Commercial Success," Presented at *Canadian Society of Chemical Engineers Annual Meeting*, 2006.

[18] SimSci-Esscor, "ROMeo: Rigorous Online Modeling with Equation-Based Optimization," 2007, http://www.ips.invensys.com/en/products/processdesign/Documents/ROMeobrochurenew.pdf (accessed October 12, 2008).

[19] Biegler, L.T., "Dynamic Optimization for Enterprise-Wide Optimization," 2006, http://egon.cheme.cmu.edu/ewocp/docs/ewo_talkBiegler.pdf (accessed September 21, 2008).

[20] Cutler, C.R., and Ramaker, B.L., "DMC—A Computer Control Algorithm," Paper No. 516, In *Proceedings of the AIChE 1979 Houston Meeting*, DMC, Inc., New York, 1979.

[21] Cutler, C.R., and Ramaker, B.L., "Dynamic Matrix Control—a Computer Control Algorithm," Paper WP5-B, *Joint Automatic Control Conference Preprints*, San Francisco, 1980.

[22] Shobrys, D.E., and White, D.C., "Planning, Scheduling and Control Systems: Why Can They Not Work Together," Comput. Chem. Eng., Vol. 24, 2000, pp. 163–173.

[23] Karuppiah, R., Furman, K.C., and Grossmann, I.E., "Global Optimization for Scheduling Refinery Crude Oil Operations," *Comput. Chem. Eng.*, Vol. 32, 2008, pp. 2745–2766.

[24] Méndez, C.A., Grossmann, I.E., Harjunkoski, I., and Kaboré, P., "A Simultaneous Optimization Approach for Off-Line Blending and Scheduling of Oil-Refinery Operations," *Comput. Chem. Eng.*, Vol. 30, 2006, pp. 614–634.

[25] Reddy, P.C.P., Karimi, I.A., and Srinivasan, R., "Novel Solution Approach for Optimizing Crude Oil Operations," *AIChE J.*, Vol. 50, 2004, pp. 1177–1197.

[26] Jia, Z., and Ierapetritou, M.G., "Mixed-Integer Linear Programming Model for Gasoline Blending and Distribution Scheduling," *Ind. Eng. Chem. Res.*, Vol. 42, 2003, pp. 825–835.

[27] Maravelias, C.T., and Grossmann, I.E., "A Hybrid MILP/CP Decomposition Approach for the Continuous Time Scheduling of Multipurpose Batch Plants," *Comp. Chem. Eng.*, Vol. 28, 2004, pp. 1921–1949.

[28] Li, J., Li, W., Karimi, I.A., and Srinivasan, R., "Improving the Robustness and Efficiency of Crude Scheduling Algorithms," *AIChE J.*, Vol. 53, 2007, pp. 2659–2680.

[29] Grossmann, I.E., "Advances in Logic-Based Optimization Approaches to Process Integration and Supply Chain Management," in *Chemical Engineering: Trends and Developments*, M.A. Galan and E. Del Valle, Eds., Wiley, West Sussex, UK, 2005, pp. 299–322.

[30] Bixby, R., and Rothberg, E., "Progress in Computational Mixed Integer Programming—A Look Back from the Other Side of the Tipping Point," *Ann. Oper. Res.*, Vol. 149, 2007, pp. 37–41.

[31] Grossmann, I.E., "Enterprise-Wide Optimization: A New Frontier in Process Systems Engineering," *AIChE J.*, Vol. 51, 2005, pp. 1846–1857.

[32] Li, W., Hui, C.-W., and Li, A.-X., "Integrating CDU, FCC, and Product Blending Models into Refinery Planning," *Comp. Chem. Eng.*, Vol. 29, 2005, pp. 2010–2028.

[33] Reddy, P.C.P., Karimi, I.A., and Srinivasan, R., "Novel Solution Approach for Optimizing Crude Oil Operations," *AIChE J.*, Vol. 50, 2004, pp. 1177–1197.

[34] Reddy, P., Karimi, A., and Srinivasan, R., "A New Continuous-Time Formulation for Scheduling Crude Oil Operations," *Chem. Eng. Sci.*, Vol. 59, 2004, pp. 1325–1341.

[35] Jackson, J., and Grossmann, I.E., "High-Level Optimization Model for the Retrofit Planning of Process Networks," *Ind. Eng. Chem. Res.*, Vol. 41, 2002, pp. 3762–3770.

[36] Timpe, C.H., and Kallrath, J., "Optimal Planning in Large Multi-Site Production Networks," *Eur. J. Oper. Res.*, Vol. 126, 2000, pp. 422–435.

[37] Zhang, N., and Zhu, X.X., "A Novel Modelling and Decomposition Strategy for Overall Refinery Optimisation," *Comp. Chem. Eng.*, Vol. 24, 2000, pp. 1543–1548.

[38] Maravelias, C.T., and Sung, C., "Integration of Production Planning and Scheduling: Overview, Challenges, and Opportunities," presented at *Foundations of Computer-Aided Process Operations (FOCAPO)* 2008 at Royal Sonesta Boston, Cambridge, MA, July 1, 2008.

[39] Harjunkoski, I., Nyström, R., and Horch, A., "Integration of Scheduling and Control—Theory or Practice?" presented at *Foundations of Computer-Aided Process Operations (FOCAPO)*, at Royal Sonesta Boston, Cambridge, MA, July 1, 2008.

[40] Terrazas-Moreno, S., Flores-Tlacuahuac, A., and Grossmann, I.E., "Lagrangean Heuristic for the Scheduling and Control of Polymerization Reactors," *AIChE J.*, Vol. 54, 2008, pp. 163–182.

[41] Terrazas-Moreno, S., Flores-Tlacuahuac, A., and Grossmann, I.E., "Simultaneous Cyclic Scheduling and Optimal Control of Polymerization Reactors," *AIChE J.*, Vol. 53, 2007, pp. 2301–2315.

[42] Flores-Tlacuahuac, A., and Grossmann, I.E., "Simultaneous Design, Scheduling, and Optimal Control of a Methyl–Methacrylate Continuous Polymerization Reactor," 2008, http://egon.cheme.cmu.edu/Papers/scdc-v2.pdf (accessed August 30, 2008).

[43] Flores-Tlacuahuac, A., and Grossmann, I.E., "Simultaneous Cyclic Scheduling and Control of a Multiproduct CSTR," *Ind. Eng. Chem. Res.*, Vol. 45, 2006, pp. 6698–6712.

[44] Karuppiah, R., Furman, K.C., and Grossmann, I.E., "Global Optimization for Scheduling Refinery Crude Oil Operations," *Comp. Chem. Eng.*, Vol. 32, 2008, pp. 2745–2766.

[45] Li, J., Li, W., Karimi, I.A., and Srinivasan, R., "Improving the Robustness and Efficiency of Crude Scheduling Algorithms," *AIChE J.*, Vol. 53, 2007, pp. 2659–2680.

[46] Furman, K., Jia, Z., and Ierapetritou, M.G., "A Robust Event-Based Continuous Time Formulation for Tank Transfer Scheduling," *Ind. Eng. Chem. Res.*, Vol. 46, 2007, pp. 9126–9136.

[47] Moro, L.F.L., and Pinto, J.M., "Mixed-Integer Programming Approach for Short-Term Crude Oil Scheduling," *Ind. Eng. Chem. Res.*, Vol. 43, 2004, pp. 85–94.

[48] Jia, Z., Ierapetritou, M.G., and Kelly, J.D., "Refinery Short-Term Scheduling Using Continuous Time Formulation: Crude-Oil Operations," *Ind. Eng. Chem. Res.*, Vol. 42, 2003, pp. 3085–3097.

[49] Li, W., Hui, C.-W., Hua, B., and Tong, Z., "Scheduling Crude Oil Unloading, Storage, and Processing," *Ind. Eng. Chem. Res.*, Vol. 42, 2002, pp. 3085–3097.

[50] Shah, N., "Mathematical Programming Techniques for Crude Oil Scheduling," *Comp. Chem. Eng.*, Vol. 20 (Suppl.), 1996, pp. S1227–S1232.

[51] Lee, H., Pinto, J.M., Grossmann, I.E., and Park, S., "Mixed-Integer Linear Programming Model for Refinery Short-Term Scheduling of Crude Oil Unloading with Inventory Management," *Ind. Eng. Chem. Res.*, Vol. 35, 1996, pp. 1630–1641.

[52] Neiro, S.M.S., and Pinto, J.M., "Multiperiod Optimization for Production Planning of Petroleum Refineries," *Chem. Eng. Comm.*, Vol. 192, 2005, pp. 62–88.

[53] Neiro, S.M.S., and Pinto, J.M., "A General Modeling Framework for the Operational Planning of Petroleum Supply Chains," *Comp. Chem. Eng.*, Vol. 28, 2004, pp. 871–896.

[54] Li, W., Hui, C.-W., and Li, A.-X., "Integrating CDU, FCC, and Product Blending Models into Refinery Planning," *Comp. Chem. Eng.*, Vol. 29, 2005, pp. 2010–2028.

[55] Jia, Z., and Ierapetritou, M.G., "Efficient Short-Term Scheduling of Refinery Operations Based on a Continuous Time Formulation," *Comp. Chem. Eng.*, Vol. 28, 2004, pp. 1001–1019.

[56] Joly, M., Moro, L.F.L., and Pinto, J.M., "Planning and Scheduling for Petroleum Refineries Using Mathematical Programming," *Braz. J. Chem. Eng.*, Vol. 19, 2002, pp. 207–228.

[57] Pinto, J.M., Joly, M., and Moro, L.F.L., "Planning and Scheduling Models for Refinery Operations," *Comp. Chem. Eng.*, Vol. 24, 2000, pp. 2259–2276.

[58] Meyer, C.A., and Floudas, C.A., "Global Optimization of a Combinatorially Complex Generalized Pooling Problem," *AIChE J.*, Vol. 52, 2006, pp. 1027–1037.

[59] Adhya, N., Tawarmalani, M., and Sahinidis, N.V., "A Lagrangian Approach to the Pooling Problem," *Ind. Eng. Chem. Res.*, Vol. 38, 1999, pp. 1956–1972.

[60] Tawarmalani, M., and Sahinidis, N.V., *Convexification and Global Optimization in Continuous and Mixed-Integer Nonlinear Programming: Theory, Algorithms, Software, and Applications*, Kluwer Academic, Dordrecht, The Netherlands, 2002.

[61] Bechtel Corporation, *Process Industry Modeling System (PIMS): User's Manual Version 6.0*. Houston, TX, 1993.

[62] AspenTech, "Aspen PIMS™," http://www.aspentech.com/products/aspen-pims.cfm (accessed October 29, 2008).

[63] AspenTech, "Aspen Orion XT™," http://www.aspentech.com/products/aspen-orion-xt.cfm (accessed October 29, 2008).

[64] AspenTech, "Aspen MBO™," http://www.aspentech.com/products/aspen-mbo.cfm (accessed October 29, 2008).

[65] Bonner & Moore, Inc., *Refinery and Petrochemical Modeling System (RPMS): A System Description*, Bonner & Moore Management Science, Houston, TX, 1979.

[66] Haverly, C.A., "OMNI Model Management System," *Ann. Oper. Res.*, Vol. 104, 2001, pp. 127–140.

[67] Haverly Systems, Inc., "OmniSuite® Product Page," http://www.haverly.com/OmniSuite.htm (accessed October 3, 2008).

[68] Haverly Systems, Inc., "Haverly Products," http://www.haverly.com/product.htm (accessed October 3, 2008).

[69] Haverly Systems, Inc., "GRTMPS, V4 (G4)," http://www.haverly.com/grtmps.htm (accessed October 3, 2008).

[70] Jones, C.V., and Baker, T.E., "MIMI/G: A Graphical Environment for Mathematical Programming and Modeling," *Interfaces*, Vol. 26, 1996, p. 90.

[71] AllBusiness, "Invensys and ChevronTexaco Sign Marketing Agreement for PETRO Refinery Planning System," http://www.allbusiness.com/company-activities-management/management-benchmarking/5921349-1.html (accessed September 29, 2008).

[72] Palmer, K.H., Boudwin, N.K., Patton, H.A., Sammes, J.D., Rowland, A.J., and Smith, D.M., "A Model-Management Framework for Mathematical Programming," John Wiley & Sons, New York, 1984.

[73] Association for Computing Machinery, "Computing Reviews," http://www.reviews.com/review/review_review.cfm?review_id=108820 (accessed July 31, 2008).

[74] Engineering Software Solutions limited (ESSCo), "DataGen," http://www.essco.co.uk/products/datagen.htm (accessed October 3, 2008).

[75] Drilling and Refining Process Engineering & Consultancy, "Projects," http://drpec.com/Project.htm (accessed November 6, 2008).

[76] Ingenious, "ProPlan—Refinery Optimization Services," http://ingeniousinc.com/ProPlan.phpererrrre (accessed November 9, 2008).

[77] Ingenious, "ProSched—Advanced Planning and Scheduling," http://ingeniousinc.com/ProSched.php (accessed November 9, 2008).

[78] Centre for Process Integration, School of Chemical Engineering and Analytical Science, The University of Manchester, "REFOPT," http://www.ceas.manchester.ac.uk/research/centres/centreforprocessintegration/software/packages/refopt/ (accessed October 3, 2008).

[79] Virtual Materials Group, "Virtual Materials Process Simulation," http://www.virtualmaterials.com/vmgsim.html (accessed October 3, 2008).

[80] Hallale, N., Moore, I. and Vauk, D., "Hydrogen: Under New Management," in *Practical Advances in Petroleum Processing*, Vol. 2, C.S. Hsu and P.R. Robinson, Eds., Springer Science+Business Media, Inc., New York, 2006, pp. 371–392.

[81] Perkins, J.D. and Sargent, R.W., "SPEEDUP: A Computer Program for Dynamic Simulation and Design of Chemical Processes," *AIChE Symp*. Ser. 214, 1982, pp. 1–11.

[82] Kröner, A., Holl, P., Marquardt, W., and Gilles, E.D., "DIVA—An Open Architecture for Dynamic Simulation," *Comp. Chem. Eng.*, Vol. 14, 1990, pp. 1289–1925.

[83] Barton, P.I., and Pantelides, C.C., "Modeling of Combined Discrete/Continuous Processes," *AIChE J.*, Vol. 40, 1994, pp. 966–979.

[84] Allgor, R.J., Berrera, M.D., Barton, P.I., and Evans, L.B., "Optimal Batch Process Development," *Comp. Chem. Eng.*, Vol. 20, 1996, pp. 885–896.

[85] Longwell, E.J., "Dynamic Modeling for Process Control and Operability," *Adv. Instrument. Control.*, Vol. 48, 1993, p. 1323.

[86] Martinson, W.S., and Barton, P.I., "Distributed Models in Plantwide Dynamic Simulators," *AIChE J.*, Vol. 6, 2001, pp. 1372–1386.

[87] Gidwani, K.K., and Beckman, R.F., "Evaluation of Refinery Control Systems," *ISA Trans.*, Vol. 33, 1994, pp. 217–225.

29

Environmental Issues Related to the Petroleum Refining Industry

Cheng Seong Khor[1] and Ali Elkamel[2]

LIST OF ABBREVIATIONS AND NOTATIONS

API	American Petroleum Institute
BOD	Biochemical oxygen demand
CDU	Crude distillation unit
CO	Carbon monoxide
COD	Chemical oxygen demand
CO_2	Carbon dioxide
CFR	Code of Federal Regulations
CN	Cyanides
CPI	Corrugated plate interceptor
DAF	Dissolved air flotation
DOE	U.S. Department of Energy
DS	Dissolved solids
EPA	U.S. Environmental Protection Agency
FCC	Fluid (or fluidized) catalytic cracking unit (or fluid catalytic cracker)
GHG	Greenhouse gases
H_2	Hydrogen gas
H_2S	Hydrogen sulfide
H_2SO_4	Sulfuric acid
HAP	Hazardous air pollutants
HC	Hydrocarbons
HF	Hydrofluoric acid
IAF	Induced air flotation
MEK	Methyl ethyl ketone
N_2	Nitrogen
NH_3	Ammonia
NO_x	Oxides of nitrogen
O_2	Oxygen
O&G	Oil and grease
RO	Reverse osmosis
SO_2	Sulfur dioxide
SO_x	Oxides of sulfur
SS	Suspended solids
VOC	Volatile organic compounds
WW	Wastewater
WWT	Wastewater treatment
WWTP	Wastewater treatment plant

29.1 INTRODUCTION

29.1.1 Orientation and Focus of the Chapter

This chapter focuses on a qualitative exposition of the environmental issues that are increasingly affected by and affecting the oil product business of the petroleum refining value chain, including global climate change due to greenhouse gas (GHG) emissions, particularly CO_2, from refineries. The overall framework of the chapter is largely influenced by the excellent work of the U.S. Department of Energy (DOE) [1], Jones [2], Wong and Hung [3], and Nemerow and Agardy [4], which all serve as the primary technical references for this work. This article also provides references to a few authoritative and comprehensive reports that are consulted in developing its contents, mainly those published by the U.S. Environmental Protection Agency (EPA), the DOE, and API, as can be found in the *References* section.

29.1.2 Current Developments and Trends in Environmental-Related Issues in Petroleum Refineries

The petroleum refining industry is a strong contributor to the global and local economy and supplies a major part of the energy required for world development. However, environmental pollution due to large industrial activity, including oil refining, which deteriorates the ecology and the environment, is an issue of global concern. As with the case of most manufacturing industries around the world, oil refineries have been facing the challenges of improving their environmental performance and complying with a substantial array of health, safety, and environmental (HSE) regulations. The industry spent an approximate average of \$10.3 billion (USD) in the year 2004 on environmental compliance, an increase of approximately 2.4 % from its 2003 expenditures, and participates in several public and private initiatives aimed at improving environmental performance [1].

For the past decade or so, the refining industry has faced considerable economic pressures mainly arising from concerns over global climate change that are largely due to GHG emissions, particularly CO_2, in addition to compliance with new HSE regulations. Pollution control and regulatory authorities have been imposing specific standard limits for the individual pollutant emission concentration and discharge rate. However, such an approach does not consider the combined effect of all of the pollutants; therefore, the actual net environmental effect of the operation of the refining industry cannot be fully and meaningfully evaluated [5]. In principle, to achieve true sustainable development, the overall environmental effect

---

[1] Center for Process Systems Engineering, Imperial College, London

[2] Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

of the industry must be minimized so that waste minimization at the source could be evaluated as the first option as compared to end-of-pipe treatment. Hence, this chapter strives to provide an analysis encompassing all of the major types of pollution that involve refineries to provide a comprehensive picture and understanding of the issues that are important and significant for deciding on holistic approaches toward mitigating the environmental effects of the refining industry. To begin, Table 29.1 summarizes the major types of pollutants and wastes generated from refineries, the constituents and amounts of which depend on various factors, primarily crude sources, crude oil capacity, number of refining processes, and the associated operating conditions.

29.2 WATER POLLUTION IN PETROLEUM REFINERIES

29.2.1 Refinery Aqueous Effluents of Wastewater and Biosolids: Sources, Characteristics, and Effects

29.2.1.1 REFINERY WASTEWATER

The refining industry consumes enormous quantities of water, and it is generally second only to that of the steel industry in terms of total industrial water consumption in the United States and many other industrialized countries. Virtually every refinery operation, from crude distillation through final waste treatment, requires a reliable supply of large volumes of water for various purposes, including steam generation, process cooling, and end-product manu-

TABLE 29.1—Major Types of Refinery Pollutants and Wastes

Pollutant/Waste	Example of Source
Aqueous effluents	• Wastewater from normal process operations (e.g., process area wastewater from steam stripping operations, sour water treatment unit, and demineralization resin regeneration [i.e., “demin regen”] • Wastewater from utility operations (e.g., blowdown and sidestream filter backwash of cooling towers) • Contaminated storm water runoff • Sanitary sewage waste • Ballast water blowdown • Miscellaneous discharges • Free and emulsified oil from leaks, spills, tank drawoff, and other sources • Emulsions incident to chemical treatment • Condensate waters from distillate separators and tank drawoff • Alkaline waters • Acid waters
Solid wastes	• Spent filtering clays • Coke (coking fines) from equipment tubes, towers, and other locations • Waste catalyst and catalyst fines • Biomass • Contaminated soils or solids • Pond sediments • API separator sludge • Spent catalysts from hydroprocessing and fluid catalytic cracker • Primary sludges • Slop oil emulsion solids • Tank-bottom sludges • Tank bottoms • Sludge from the WWTP (dewatered by pressure filtration) • Bottom sediments and water from crude storage tanks • Spent amines • Spent acids and caustics • Spent clay filter media (especially for simpler refineries) • Spent glycol • Spent Stretford solution and sulfur
Wastes (in general)	• Spent oil • Special chemicals from byproduct chemical manufacturing • Spent caustics (or waste caustics) and caustic sludges from (1) treatment of oils with alkaline reagents to remove acidic components and (2) sweetening processing of oils to convert or remove mercaptans • Acid sludges from H_2SO_4 treatment of oils • Dissolved air flotation float (which contains oil, precipitated minerals, sand, etc.)
Biosolids	• Activated sludge • Sludge from biological treatment plants, biopонds, and aerated lagoon
Atmospheric emissions	• Volatile organic compounds • Fuel gas • Acid gases: H_2S and SO_x (primarily SO_2) • NH_3 • NO_x (primarily NO_2) • HC (evaporation) • Others: CO, fine catalyst particulates, CO_2, HCl, smog, acid rain, ozone, lead

Sources: [3 (p. 157), 4, 6–9]

facturing. Consequently, huge volumes of aqueous effluents in the form of wastewater and biosolids, including hazardous wastes, are generated from refineries. Despite the huge volume of wastes generated, almost 80–90 % of the total water used by an average refinery is solely for cooling purposes, and this water is not contaminated except by leaks in the lines. However, the combined refinery wastes typically contain (1) crude oil and its various fractions, forming the contaminant generally categorized as oil and grease; (2) organic compounds; and (3) dissolved or suspended minerals [4].

29.2.1.2 REFINERY BIOSOLIDS AND HAZARDOUS WASTES

Wastewater influent streams include sludge, which is waste solids that must be removed and subsequently disposed of, but often ultimately entail beneficial reuse. Strictly speaking, these substances should be referred to as wastewater biosolids because of their reuse value (because the term "sludge" implies waste products). Thus, these solid particles suspended in water must be properly treated. In fact, biosolid management has become an important part of the wastewater treatment process. Some of these waste biosolids are hazardous, especially those containing hydrocarbons and heavy metals, and require special management and disposal.

Table 29.2 lists the major sources and characteristics of refinery wastewater and biosolids according to typical refinery process units. Table 29.3 summarizes the consequences of refinery toxic wastewater pollutants. Table 29.4 presents a sense of magnitude of refinery wastewater flow and characteristics (chiefly in terms of contaminant concentrations) and is largely adapted with updates from the excellent qualitative evaluation presented in reference 3.

Figure 29.1 is a schematic diagram indicating representative sources of aqueous effluents in overall refinery systems. Figure 29.2 illustrates representative sources of biosolids in refinery wastewater treatment systems.

29.2.2 Refinery Aqueous Effluents: Environmental Regulations and Reduction, Control, and Treatment Techniques

Wastewater streams are usually discharged to a centralized wastewater treatment system, but some of these streams (e.g., sour water) are treated first in what is termed as the opposing design philosophy of a distributed wastewater treatment system. Centralized treatment implies that all of the wastewater streams are collected and treated in a common facility, whereas in distributed treatment, streams are either treated separately or only partially mixed, which reduces the treatment flow rate to be processed as compared with the former system. The trend of the industry in the past has been to reduce wastewater production by improving the design, operations, and management of the centralized systems, rather than to provide individual treatment for each process unit. Today, it has become a priority to consider the distributed systems, in which wastewater streams are segregated for the regeneration of water, coupled with efforts for water reclaim, direct reuse, regeneration–reuse, and regeneration–recycle. According to reference 10, this decentralized practice in turn serves to reduce investment because the capital cost of most treatment operations is directly proportional to the total flow of the inlet wastewater [11].

Wastewater discharge from refineries is subject to three categories of regulatory limitations, as stipulated in Table 29.5 with the associated reduction, control, and treatment techniques presented. In general, the management of aqueous effluents from refineries conventionally involves three possible approaches: (1) in-plant source control, (2) segregation and pretreatment, and (3) end-of-pipe treatment [3].

29.3 AIR POLLUTION IN PETROLEUM REFINERIES

29.3.1 Refinery Atmospheric Emissions: Sources, Characteristics, and Consequences

Refineries are concerned about atmospheric emissions to fulfill their dual responsibilities of the production of products that involves a minimum release of toxic or unacceptable emissions, either when used or stored, and at the same time, identifying, controlling, and reducing undesirable emissions from refining operations and processes. For example, emissions that result from leaking equipment and process vents include air toxics and hazardous air pollutants, the major constituents of which are NH_3, H_2SO_4, *n*-hexane, toluene, and propylene. Generally, most oil refineries do not involve very hazardous emissions such as those usually released from a petrochemical or chemical plant. In most refineries, the source of air pollution is fuel burning (i.e., the burning of heavy hydrocarbon oils that may contain high levels of sulfur or nitrogen compounds or both). Table 29.6 lists the major sources and characteristics of refinery atmospheric emissions according to the type of emission with the associated monitoring, reduction, control, and treatment techniques. Table 29.7 provides a summary of other major air pollutants emitted by refineries [2].

Almost paradoxically, the emissions of SO_x and NO_x from the combustion of refinery products outside of the refinery are much higher than the emissions from the refining processes themselves. HC emissions from the transportation sector, while refueling and in running motor vehicles, are also considerably higher than during the steps from production to the filling station. Nonetheless, in general, the current trend has reflected a reduction in the total amount of emissions from refineries. Significant reduction has also been estimated for distribution and refueling activities [15].

29.3.2 Monitoring, Reducing, and Controlling Air Pollution Caused by Refining Processes

The refining sector in general has been able to manage emissions such as the release of particulates from certain units (e.g., fluid catalytic crackers and cokers). In all if not most cases, pollution control in refineries starts with an environmentally conscious design of the processes and the systems that result in their proper operations. In terms of legislation, the U.S. Clean Air Act (CAA) of 1970 and its amendments in 1977 and 1990 (CAAA) have a significant effect on the U.S. oil refining industry, covering the refining processes and the formulation of refined products. Its effects have also been cascaded to refineries in other parts of the world [1,2]. The interested reader may refer to Table 29.10 in the Appendix for a partial list of major regulations that affect the U.S. refining industry.

TABLE 29.2—Sources and Characteristics of Refinery Aqueous Effluents

Process Unit	**Source of Aqueous Effluents (with contaminant in brackets)**	**Biosolid**
1. Storage tanks for crude oil, intermediate products, and final products	• Wastewater [free oil, emulsified oil, SS; high COD] • Leaks, spills, salt filters (for product drying), tank cleaning • Wastewater from intermediate product storage: [polysulfide, iron-sulfide SS] • Wastewater from finished product storage: [high in BOD, alkaline, tetraethyl lead]	• Tank-bottom sediments
2. Ballast water storage (discharge from tankers shipping intermediate and final products)	• Ballast waters [organics, e.g., water-soluble alcohol, brackish water, sediments; high COD, DS]	• Residual fuels
3. Topping/separation processes		
3.1. Crude oil desalter	• Hot salty continuous process wastewater stream from desalter; potential thermal pollutant (temperature often exceeds 95°C) [emulsified oil (occasionally free oil), H_2S, NH_3, phenol, sulfides, and SS, leading to relatively high BOD and COD concentrations; contains enough chlorides and other dissolved materials to contribute to DS problems in discharges to freshwater bodies]	• Crude oil/desalter sludge [iron rust, clay, sand, water, emulsified oil and wax, heavy metals]
3.2. Crude oil distillation (atmospheric and vacuum)	• Oily sour water from fractionators [H_2S, NH_3, SS, chlorides, mercaptans, phenol] • Spent caustic	• Little or none generated
3.2.1. Prefractionation and atmospheric distillation (topping or skimming)	• Process area wastewater carried over to prefractionation tower from desalting process (e.g., pump glands, area drains)	• None
3.2.2. Three-stage crude distillation	• Water drawn off from overhead accumulators before recirculation or transfer of HC to other fractionators [sulfides and NH_3 (especially sour crudes processing), oil, chlorides, mercaptans, phenols] • Discharge from oil sampling lines (should be separable but may form emulsions in sewer) • Oil emulsions formed in barometric condensers used to create reduced pressures in vacuum distillation units (not with surface condensers)	• None
3.3. Thermal cracker	• Water separated from HC vapor and sent to sewer system at overhead accumulator on fractionator • Sour water • Decking water (oil) • Process area wastewater [contains various oils and fractions; may be high in BOD, COD, NH_3, phenol, sulfides, and alkalinity]	• None
3.4. Visbreaker	• Sour wastewater from the fractionator [H_2S, NH_3, phenol, SS, dissolved solids]	• Little or none generated
3.5. Coker	• Coke-laden water from decoking operations in delayed cokers [H_2S, NH_3, SS, cyanides] (*Note*: fluid coking produces little or no effluents)	• Coke dust [carbon particles and HC] may not be a waste because coke fines may be a product
3.6. Unsaturated gas plant for FCC	• Sour and phenolic wastewater from (1) overhead accumulators on fractionators or gas concentration units and (2) steam strippers [high in oil, SS, sulfides, phenols, cyanides, H_2S, NH_3 (produces alkaline wastewater with high BOD and COD)] • Spent caustic • Process wastewater	• Spent catalysts [metals from crude oil and HC] • Spent catalyst fines from electrostatic precipitators [aluminum silicate and metals]
3.7. H_2 production plant for catalytic hydrocracker	• Sour wastewater from the fractionator and hydrogen separator • Process wastewater • [sulfides, SS]	• Spent catalysts [metals from crude oil and HC]

(Continued)

TABLE 29.2—Sources and Characteristics of Refinery Aqueous Effluents (Continued)

Process Unit	Source of Aqueous Effluents (with contaminant in brackets)	Biosolid
4. Combination/rearrangement processes		
4.1. Polymerization	• Caustic and acid wastes [S, mercaptans, NH_3]	• None
4.2. Saturated gas plant for alkylation	• Wastewater from water wash of reactor HC products [SS, DS, H_2S, oils] • For H_2SO_4 units: spent caustics • For HF units: water drawn off from overhead accumulators on fractionator	• Neutralized alkylation sludge (H_2SO_4, HC)
4.3. Reformer (catalytic)	• Process wastewater from overhead accumulator on stripping tower for removing light HC fractions from reactor effluent [alkaline; high in oil, SS; low in H_2S, NH_3, mercaptans]	• Spent catalysts [metals and H_2]
4.4. Isomerization	• No major pollutant: sour water [low in H_2S, NH_3], chloride salts, and caustic wash water [overall low in phenolics, BOD, COD]	• Calcium chloride sludge from neutralized HCl gas
4.5. Ether production	• Pretreatment wash water (N_2 contaminants)	• Spent catalysts [metals]
4.6. Catalytic hydrotreater	• Sour wastewater from fractionator and H_2 separator [SS, H_2S, NH_3, phenols]	• Spent catalyst fines [aluminum silicate and metals]
4.7. Sweetening/Merox process	• Little or no wastewater generated	• Spent caustics; residual oil–disulfide mixture
4.8. Sulfur removal (Claus process)	• Process wastewater [H_2S, NH_3]	• Hazardous air emissions—H_2S, carbonyl sulfide (COS), and carbon disulfide (CS_2) • Fugitive solvent emissions may be toxic (e.g., diethanolamine)
5. Specialty product manufacturing		
5.1. Lubricating oil manufacturing and finishing (deasphalting, solvent extraction, dewaxing)	• Steam stripping wastewater [oil and solvents] • Solvent recovery wastewater [oil and propane]	• Little or none • Fugitive solvent emissions may be toxic [toluene, methyl ethyl ketone (MEK), methyl isobutyl ketone]
5.2. Grease manufacturing	• Wash water from batch units [soap, oil] • Little wastewater • Pump leaks [little oil]	• None
5.3. Asphalt production	• Wastewater [high in oil, BOD, COD; low in phenol]	• None
5.4. Drying and sweetening	• Spent caustics [high in phenols, H_2S, BOD, COD] • Water wash of treated product and regeneration of treating solution [low in oil, treating material]	• None
5.5. Blending and packaging	• Wash waters from washing railroad tank cars or tankers before loading finished products [high in emulsified oil] • Sludges from finished gasoline storage tanks [high in lead if tetraethyl lead is used as major additive]	• None
5.6. Hydrogen production	• Desulfurization unit [oil, sulfur compounds, and phenol] • Water wash for free carbon removal in the partial oxidation subprocess	• None
5.7. Utility functions	• Boiler and cooling tower blowdowns [high in DS, SS, treatment chemicals; elevated temperatures]	• Waste brine and sludge from demineralization and other waste treatment systems [high in DS, SS, treatment chemicals]
5.8. Tankage area	• Tank dike area drains • Noncontaminated rain runoff	• None

Note: Spent caustics refers to alkaline wastes in the form of solution. *Source:* [1,2]

TABLE 29.3—Common Refinery Toxicants and the Corresponding Reduction, Control, and Treatment Techniques

Toxicant	Source and Consequence
Oil (heavy oil and other HC)	• Most problematic pollution in refinery water effluent • All refineries exercise most stringent methods to control and remove oil pollutants, often to the extent that treated effluent streams leaving refinery may be purer than incoming potable water consumed
Phenols	• Often formed in catalytic and thermal cracking • Highly toxic to aquatic life (at 1–10 ppm) • Unpleasant taste and odor to drinking water (at 50–100 ppb) • Can deactivate water treatment units such as trickle filters and activated sludge (at ≥200 ppm)
Caustic soda and derivatives	• Solutions containing NaOH are used in several refinery processes • Some inevitably enter the wastewater system • Toxic even in low concentrations • Spent caustics (e.g., sodium sulfide) leaving the processes are even more injurious
Aqueous solutions of ammonium salts	• Most common are NH_4SH and ammonium chloride—both salts are present in effluent water from CDU's overhead accumulator • However, sulfide salt is present in all aqueous effluents from cracking processes and hydrotreaters • Other ammonium salts also present in hydrocracking and deep oil hydrotreating
Acids in aqueous effluents	• Most common are from alkylation processes, which use either HF or H_2SO_4 • In some isomerization processes, HCl is used to promote the aluminum chloride catalyst • In certain older processes, SO_2 is used to remove aromatics • Typically leaves refineries as dilute H_2SO_4 effluent
Ketones, furfural, and urea	• Used in lube oil refining • MEK and urea are used in dewaxing processes; furfural in extraction processes for finished lube oil stock

29.3.3 Monitoring, Reducing, and Controlling Air Pollution Caused by Refinery Products

Because most of the air pollution from refineries is due to pollutants emitted by the refining products when they are utilized, a major effort in refinery design and operation is geared toward producing products that have a minimal effect on the environment. This has prompted research into refining technologies and product compositions that afford the means to alter the character of conventional refinery products [1,2]. Alfke et al. [15] consolidate some of the major conventional techniques for producing cleaner refining products that involve hydrodesulfurization of gasoline and middle distillates and reforming and isomerization for the production of high-octane components for unleaded gasoline, including the synthesis of suitable components such as the gasoline additive methyl tert butyl ether (MTBE).

29.4 NOISE POLLUTION IN PETROLEUM REFINERIES

29.4.1 Refinery Sound Emissions: Sources and Consequences

Noise pollution caused by refineries was only a minor issue in the past. It was a widely accepted practice then for the pumps and compressors to be installed in the open air and not in enclosed buildings because of the flammability of petroleum and its products. Also, because refineries were smaller, noise emissions from the units were relatively low. In addition, the sound radiation from furnaces and the associated burners produced relatively low sound levels in the refinery surroundings because of the compact construction of the main process plants. Moreover, the radiation was simultaneously screened by low-noise auxiliary installations of the tank farms at the refinery's periphery [15].

However, densely populated areas with relatively close distances between the industrial and residential areas have unavoidably given rise to increasingly serious noise pollution. Today, noise has been widely recognized as a major industrial and environmental problem in most processing plants, including refineries, because of the risk of hearing loss involved when workers are exposed to high noise levels [16]. Most refinery noise problems are caused by flare noise in the event of process disturbances [15]. Other major sources of the high noise levels in refineries can be attributed to compressors, fans, pumps, motors, steam turbines, gas turbines, furnaces, control valves, and piping systems in general.

29.4.2 Refinery Sound Emissions: Environmental Regulations and Reduction, Control, and Treatment Techniques

The noise-generating mechanism for each piece of refinery equipment is complex, but in most cases, the noise levels can be reduced to desired limits through the implementation of proper noise control measures. Important measures for noise reduction include the following considerations in design and operations:

- Low-noise burners and additional noise insulation on process heaters and piping;
- Sound hoods on driver motors and turbines of pumps and compressors;
- Complete "in-housing" that entails placing all related and relevant equipment in closed spaces; however, it is noteworthy that such practices may give rise to safety problems because firefighting is more difficult and the danger of explosion is greater in closed rooms;
- Sound insulation on control valves; and

TABLE 29.4—Qualitative Evaluation of Refinery Wastewater Flow and Characteristics

Source of waste	Flow	Free Oil	Emulsified Oil	BOD	COD	Phenol	Sulfide	Ammonia	Chloride	Suspended Solids	pH	Temperature	Acidity	Alkalinity
Crude oil and product storage	••	•••	••	•	•••	•	○	○	○	••	○	○	○	○
Crude desalting	••	•	•••	••	••	•	•••	••	•••	•••	•	•••	○	•
Crude distillation	•••	••	•••	•	•	••	•••	•••	•	•	•	••	○	•
Thermal cracking	•	•	○	•	•	•	•	•	•	•	••	••	○	••
Catalytic cracking	•••	•	•	••	••	•••	•••	•••	•	•	•••	••	○	•••
Hydrocracking	•	○	○	○	○	••	••	••	○	••	○	••	○	○
Polymerization	•	•	○	•	•	○	•	•	•	•	•	•	•	○
Alkylation	••	•	○	•	•	○	••	•	••	••	••	•	••	○
Isomerization	•	○	○	•	•	•	•	•	•	○	○	○	○	○
Reforming	•	•	○	○	○	•	•	•	○	○	○	•	○	○
Solvent refining	•	○	•	○	•	•	○	○	○	○	•	○	○	•
Asphalt blowing	•••	•••	○	•••	•••	•	○	○	○	○	○	○	○	○
Dewaxing	•	•	○	•••	•••	•	○	○	○	○	○	○	○	○
Hydrotreating	•	○	○	•	•	••	••	••	○	•	••	○	○	•
Drying and sweetening	•••	○	•	•••	•	••	○	•	○	••	••	○	•	•

Note: ••• = major contribution, •• = moderate contribution, • = minor contribution, ○ = insignificant. *Source:* Table modified after [2]. Information also from [9].

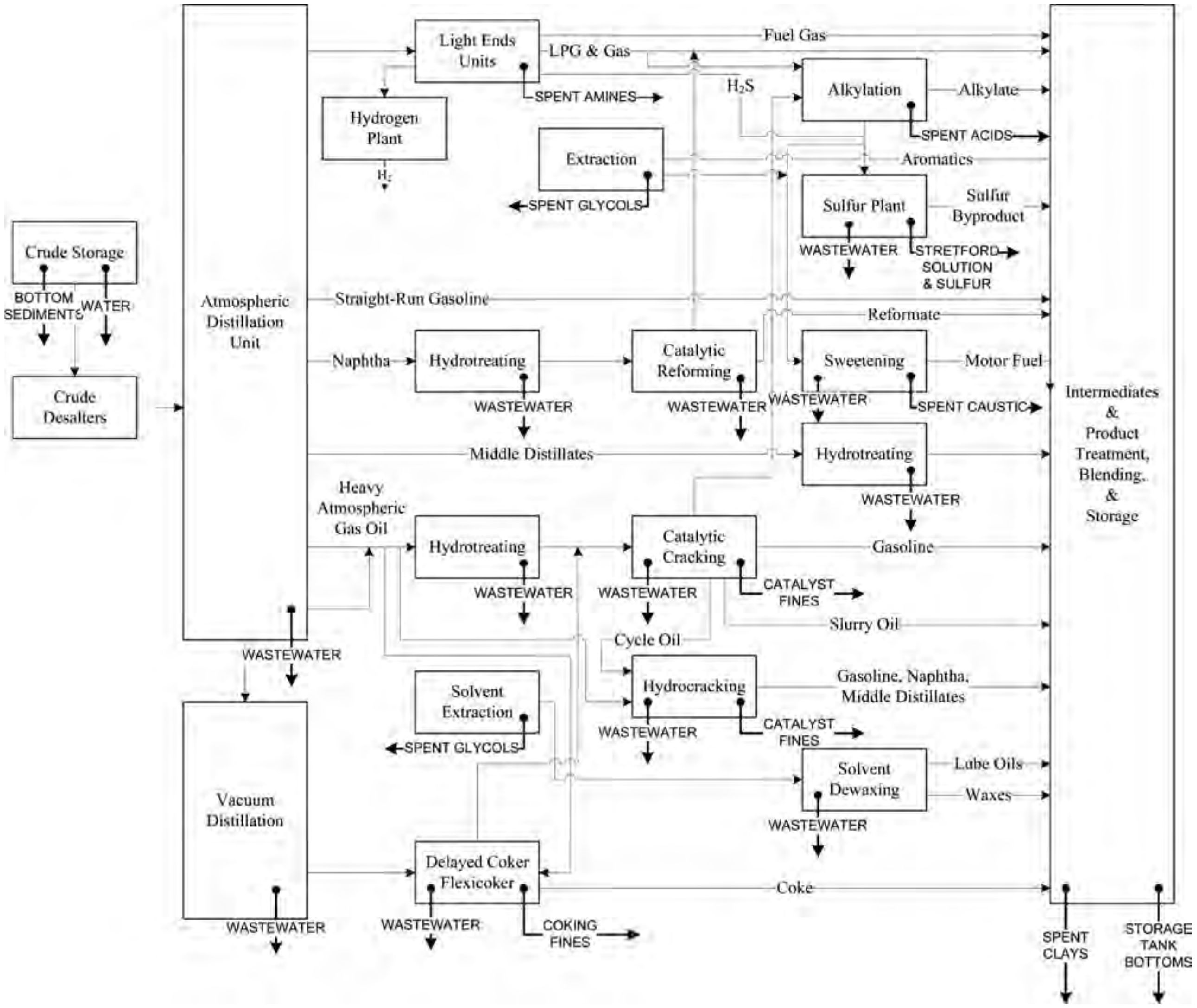


Figure 29.1—Schematic diagram indicating representative sources of aqueous effluents in overall refinery systems. Note that most biosolids from refineries are considered hazardous wastes in the United States. *Source:* Figure based on [3].

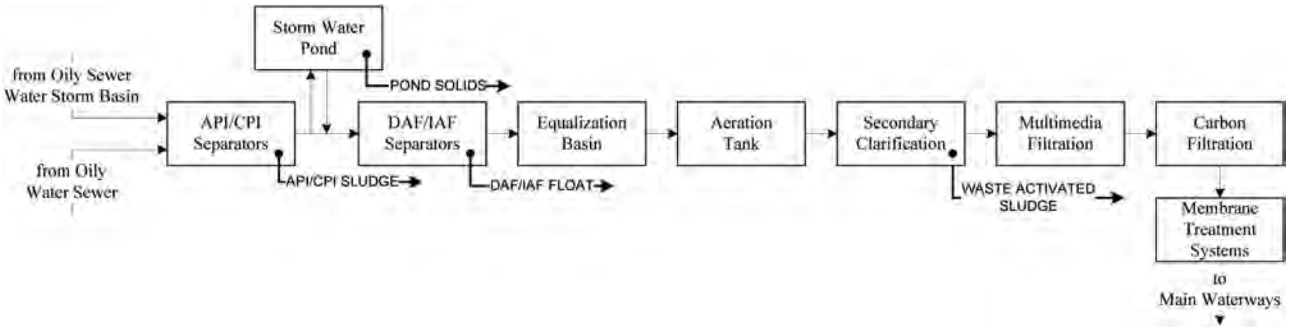


Figure 29.2—Schematic diagram indicating representative sources of biosolids in refinery wastewater treatment systems, which include floats from dissolved air flotation, induced air flotation units, and pond and tank sediments. All of these wastes except activated sludge are classified as hazardous wastes because of their oil contents. *Source:* Figure based on [3].

- Low-noise flare stack tips for elevated flares or additional ground flares.

A noise reduction by 10 dB(A) (that is, a reduction of the observable noise level by approximately one half) may be possible depending on the specific refinery, its existing noise abatement measures, and the state of the art, although such an effort will usually involve considerable expenditure. Nonetheless, because of the growing environmental awareness among the public and stricter legislation requirements, further measures ought to be implemented in the future to reduce sound emissions [15].

TABLE 29.5—Environmental Regulations on Refinery Wastewater Discharge and the Corresponding Reduction, Control, and Treatment Techniques

Category of Regulation (in United States)	Reduction, Control, and Treatment Technique	Example of Technique
1. Effluent limitations for industrial point source on significant wastewater constituents that are based on water quality impact and treatability in conventional treatment systems • e.g., EPA's Effluent Guidelines and Standards for the Petroleum Refining Industry under 40 CFR Part 419 (May 9, 1974) (*Note:* "point source" refers to water pollution sources or dischargers that can be collected and routed in pipes or channels, e.g., industrial and municipal effluents)	***In-plant source control:*** Onsite processes for reducing overall pollutant load for subsequent end-of-pipe treatment before discharge	• Good housekeeping • Process modifications • ***Wastewater reuse–recycle:*** Effective strategy for reducing overall pollutant loadings but water quality is critical—contaminants present must be compatible with reuse (i.e., contaminant concentrations must not be greater than level permissible for reuse)
2. Pretreatment discharge requirements • e.g., EPA's Effluent Guidelines and Standards for the Petroleum Refining Industry under 40 CFR Part 419	***Segregation and pretreatment:*** • Reduces or eliminates a pollutant before it is diluted in main WWT stream • Provides opportunity for material recovery • First step is segregation of major WWT streams to implement distributed WWT treatment system	• Sour water stripping • Spent caustic neutralizers • Spent caustic oxidizers • Ballast water separation • Slop oil treatment

3. Effluent limitations for certain bodies of effluent-receiving waters that are based on water-quality-limiting segments
• e.g., EPA's Public Law 92-500
	End-of-pipe treatment: final stage for meeting regulatory discharge requirements and for protection of stream water quality	• API separators or other similar oil–water separating devices
		• Secondary treatment, e.g., chemical coagulation; filtration; trickling filter; dissolved (DAF) and induced (IAF) air flotation; aerators (e.g., aerated lagoon); equalization; parallel and corrugated plate separation/interception; waste stabilization pond; activated sludge; rotating biological contactor; activated carbon adsorption
		• ***Advanced treatment processes:*** Control of whole effluent toxicity, cyanide control, heavy metals removal
		• ***Treatment modifications due to newer regulations:*** Primary sludge listing; revised toxicity characteristics (TC) rule; National Emission Standards for Hazardous Air Pollutants (NESHAP) for benzene
		• ***Treatment for reuse–recycle and zero discharge:***
		  • Involves reclaim, reuse, and recycle of water for cooling, steam generation, and process use
		  • Main obstacle of zero liquid discharge: generation of large amount of solid waste, mostly salt from wastewater

Source: Table data modified after [3,12–14].

With increasing awareness of the noise problem and its effect on the general public, regulations on noise standards have been adopted in many countries throughout the world. In the United States, the Occupational Safety and Health Act (OSHA) of 1970 (29 CFR 1910.95) and the Noise Control Act of 1972 and its later amendments have served as basic guidelines for noise control requirements. The former (OSHA) contains the maximal permissible sound pressure levels for each daily time of exposure. The latter, administered by EPA, is intended to establish federal noise emission standards. It serves as a broader scope of coordinating all noise control efforts and places the primary responsibility for noise control on the states (in the United States).

29.5 ENVIRONMENTAL MANAGEMENT OF PETROLEUM REFINERIES

29.5.1 Environmental Impact Assessment Study of Petroleum Refining Industry

In general, an environmental impact assessment (EIA) is a study of the implied environmental impacts of a new facility

TABLE 29.6—Sources of Refinery Atmospheric Emissions and the Corresponding Reduction, Control, and Treatment Techniques

Type of Emission	Source	Air Pollutant	Reduction, Control, and Treatment Technique
Process vents	***Sulfur recovery units:*** Sulfur removal process (Claus process) and sulfur storage pit	SO_2	• Claus plants for sulfur recovery from H_2S followed by fine purification • Subsurface tiled pit for storing liquid sulfur product from sulfur plant (which is covered by concrete or other suitable slabs) are sealed to prevent emission of SO_2 that is always present above liquid sulfur • Accumulated SO_2 is normally vented off to a small bullet partially filled with water • H_2SO_4 formed is either used for caustic neutralization or sold to other users
	• During manufacturing, e.g., from chemical reactions • Fugitive emissions from visbreaker and catalytic reformer • Spent catalyst regeneration in catalytic reformer and FCC (the latter in exit stack of steam strippers and CO boilers due to disruption caused by air surges) • Saturated gas plant for alkylation • Isomerization • Sweetening in Merox process	Fuel gas, H_2S, NH_3, SO_x (SO_2), NO_x, HC, CO, VOC, and fine catalyst particulates	FCC emissions can be reused by burning CO and volatiles as boiler fuel; gases are then passed through electrostatic precipitator or cyclone separator to remove particles
Combustion	Fuel burning including for electricity generation	CO_2	A wide variety of measures depending on type of fuel
Equipment leaks	Leaking involving valves, pumps, seals, packing, pressure relief valves, piping joints, poorly maintained flanged joints and control valves, and other process devices throughout refinery	VOC (e.g., NH_3, benzene, toluene, propylene, xylene)	Leak detection and repair program
Storage tanks for crude oil, intermediate products, and final products that are open or poorly ventilated	• During transfer of crude oil and products • Filling facilities of railcars and road tankers • Ship loading and unloading facilities in the jetty area • LPG loading	• Major source of VOC • HC (evaporation)	• HC vapor recovery systems for storage and loading of volatile products • Properly installed floating roofs and floating covers in storage tanks • Extension of closed inert gas circulating system to all fixed roof tanks as inert blanket prevents VOC emission during filling (*Note:* Inert blanket is often required in intermediate tanks for which the contents are feed for processes needing to eliminate O_2) • Float make-or-break valves of the spheres and bullets on the refinery fuel gas main of LPG storage are floated • ***Automatic shutoff on loading arm nozzles at loading facilities (similar to those in public filling stations):*** Operates using a level sensitive device that closes filling valve at prescribed filling level in tank • ***Flash recycle system:*** Route flashed LPG vapor under pressure control to compressor and cooler assembly where it is liquefied and returned to LPG feed stream (system continues to operate throughout loading activity, acting as loading relief system)

(Continued)

TABLE 29.6—Sources of Refinery Atmospheric Emissions and the Corresponding Reduction, Control, and Treatment Techniques (Continued)

Type of Emission	Source	Air Pollutant	Reduction, Control, and Treatment Technique
Wastewaters	• Fugitive emissions from tanks, treatment ponds, sewer system drains • Treatment of oil–water separators • Cooling water towers	H_2S, NH_3, and light HC	• Drainage to wastewater treatment plants • Closed sampling systems, laboratory analysis, and online instruments for pollutant measurement in air and wastewater
Flue gas or stack gas or process tail gas from heaters and furnaces (fired heaters)	• Crude oil desalter • Crude oil distillation (atmospheric and vacuum) • Thermal cracker • Coker • FCC • H_2 production plant for catalytic hydrocracker • Catalytic reformer • Isomerization • Catalytic hydrotreater • Lubricating oil manufacturing and finishing (deasphalting, solvent extraction, dewaxing)	SO_x (especially SO_2)	• Reduce SO_x and NO_x emissions from refinery furnaces • Reduce sulfur content of fuel oil to permissible levels for flue gas emitted when burnt in fire box • Blend with hydrotreated middle distillate streams (gas oil or kerosine) to reduce total stream sulfur • Customize planning and scheduling of operations to fuel criteria
		NO_x	• Optimize minimal excess air required for proper heater operation • Optimize heater fire box geometry to lower or at least maintain required excess air criteria • Use low NO_x burners • Design stack height to ensure that emission fallout avoids populated areas • Common refinery engineering practice now is to use computer simulation programs that define contour maps (i.e., fallout contours at ground level distances from fired heater stacks) in layout studies during design stages for locating process units and fired heaters on plant site
		CO, HC, particulates, HCl (possible in fuel gas from isomerization)	
Flue gas from boilers	• Isomerization • Ether production	CO, SO_x, NO_x, HC, and particulates	
Particulate emissions	Coker (during decoking)	Particulates	
Steam ejector	Vacuum distillation unit	HC, SO_2	Closed systems for discharge of HC gases (via a flare)
Breakdown of protection equipment	FCC particularly cyclone separators located in critical areas (e.g., at reactor outlet and regenerator flue gas outlet)	SO_2, CO, particulates	Shutdown for repair
Flare and incinerator	Sulfur removal (Claus process)	HC	Closed systems for discharge of HC gases (via a flare)
Fugitive solvents and fugitive propane	Lubricating oil manufacturing and finishing	HC	Closed systems for discharge of HC gases (via a flare) and liquids
Acid gas from sour gases treating	Drying and sweetening	High in H_2S	Flared, burned, or processed for elemental sulfur recovery
Partial oxidation	Hydrogen production	CO_2	
Draining of bottoms from road tankers and railcars	Slop system	VOC	• Steam out facilities on vessels carrying heavy petroleum cuts • Route vents to flare header

Note: VOC refers to chemicals such as NH_3, benzene, toluene, propylene, xylene, methylene chloride, and methyl chloroform. n.a. indicates that no information is available in the open literature regarding a probable reduction, control, and treatment technique. *Source:* Table data modified after [1,2].

TABLE 29.7—Other Major Refinery Air Pollutants

Refinery Air Pollutant	Source (include refinery products)	Health Effect	Environmental Effect	Property Damage
Smog formers and VOC	• Rail and road tanker filling facilities • Ship loading and unloading facilities in jetty area • Product loading facilities • Tank farm • Handling of light HC streams (e.g., LPG loading) • Fuels burning (e.g., gasoline, oil, wood coal, natural gas); cars and other motor vehicles; solvents; paint glues; certain products used at work or at home	Serious illness (e.g., cancer)	• Reduce visibility • Damage plants and trees (caused by formaldehyde and ethylene)	—
Acid rain (encompasses acid snow, acid fog or mist, acid gas, and acid dust)	Heavy HC burning (e.g., fuel oils)	Breathing and lung problems (especially to asthmatics)	• Damage plants, animal life, and lakes • Hazy skies	Eats away at stone buildings and statues
Ozone (ground-level ozone is principal component of smog)	Chemical reactions of pollutants; VOC; NO_x	Breathing problems; reduced lung function; asthma; eye irritation; stuffy nose; reduced resistance to colds and other infections; accelerated aging of lung tissue	Similar to smog	Damage rubber, fabrics, etc.
Nitrogen dioxide (NO_2; a type of NO_x); smog-forming chemicals	Fuel burning; cars (especially NO_2)	Lung damage; illnesses of respiratory system (breathing passages and lungs)	Damage trees and lakes (it is an ingredient of acid rain [acid aerosols]); reduced visibility	Acid aerosols can eat away stone used on buildings, statues, monuments, etc.
CO	Fuel burning	Reduced ability of blood to bring O_2 to body cells and tissues; particularly hazardous to people with heart/circulatory (blood vessel) problems and damaged lungs/breathing passages	Impair transport of O_2 in plants and animals even at low concentrations	Little effect
Particulate matter (e.g., dusts, smoke, soot, ashes)	Fuel burning (e.g., wood, diesel); industrial plants; agriculture (plowing, burning off fields); unpaved roads	Nose and throat irritation; lung damage; bronchitis; early death	Main cause of haze—reduced visibility	Dirty and discolor structures and other property (e.g., clothes, furniture)
Lead	Leaded gasoline (being phased out); paint (houses, cars); smelters (metal refineries); manufacture of lead storage batteries	Damaged brain and other nervous system components; children are at particular risk; cancer in animals; digestive and other health problems	Harm wildlife	Blood
CO_2 (*Note:* Not monitored by EPA or CAA)	Combustion		Climate change	

Source: Table data modified after [2].

or operation. In the context of the refining industry, the primary purpose of an EIA is to evaluate the potential effect of constructing a new or grass-root refinery project to assure the stakeholders that the environment will not be unduly threatened by the refinery development project. EIAs have become common requirements for financial institutions, government agencies, and other stakeholders involved in a large-scale project such as a new oil refining facility [17]. It can be extremely effective in ensuring the minimization of environmental impacts on the community in the most cost-effective manner. It also serves to ensure that the industry, government, and local community channels of communication are opened and remain established throughout the life of a refinery project [18]. These goals are accomplished via the public documents, which typically constitute EIAs, that incorporate the following aspects in detail: (1) a description and scope of the project, (2) all relevant environmental regulatory requirements, (3) a study and documentation of existing environmental conditions, (4) a description of any potential environmental impacts of a project, (5) plans and programs to manage and mitigate the potential environmental impacts, (6) a monitoring plan to ensure compliance with these environmental management programs, and (7) establishment of communications channels with government agencies and the community [19].

29.5.2 Life Cycle Impact Assessment for Petroleum Refining Products

The concept of life cycle assessment (LCA) serves to evaluate the environmental effects associated with any given activity from the initial gathering of raw material(s) from the Earth until the point at which all residuals are returned to the Earth. In the case of the oil refining industry, an example of LCA involves a study on the life cycle of the product kerosine that spans the oil exploration, development, and production stage to the stage in which it is used in a commercial jet aircraft [20]. This particular work uses the LCA approach of Eco-indicator 95 by PRé Consultants, which is the predecessor version of the popular LCA method of Eco-indicator 99 [21].

Life cycle impact assessment (LCIA) is a part of LCA that evaluates the combined environmental effect of pollutants of different events of an activity on the basis of inventory analysis. Using the LCIA approach, a single potential environmental impact (PEI) score for a refinery operation can be determined. Such a PEI score represents the environmental deterioration considering all of the relevant pollutants and all types of impacts. It can also be used to optimize design configurations of new refineries to minimize environmental effects. This unique score holds the potential of being established as a benchmark by the regulatory bodies for the limit value of pollution by the refining industry (or any industry for that matter). This numerical PEI value can ultimately be used for comparison among different industries; hence, it can be utilized for improving environmental compliance of the multitude of processes involved in oil refining [5]. An example of an LCIA method is ReCiPe 2008, also by PRé Consultants [22].

29.5.3 CO_2 Management in Petroleum Refineries

CO_2 emissions from refineries account for approximately 4 % of the global CO_2 emissions, close to 1 billion t of CO_2 per year. This places the refining sector as third among stationary CO_2 producers, after the power generation sector and the cement industry. With increasingly stringent environmental regulations, oil refining is likely to be featured in any legislation aimed at curbing CO_2 emissions, especially because legislators tend to group refining with power generation and other stationary CO_2 sources [23]. Table 29.8 provides a breakdown of CO_2 emissions in percentages according to oil-refining-related activities.

TABLE 29.8—CO_2 Emissions from Oil-Refining-Related Activities

CO_2 Emission Source	Percentage of CO_2 Emission (%)
Oil products and combustion	91.72
Oil refining processes	4.95
Crude oil transportation (shipping)	2.29
Oil products distribution (shipping)	1.03

Source: Table data modified after [24].

Concurrently, refineries are facing many new and challenging situations, including such trends as

- Increased markets for heavy crude oils that have resulted in increased use of and heightened capacity demand for conversion units, particularly hydrocrackers and FCCs, and consequently, a need to increase the associated hydrogen consumption; and
- Clean-fuel legislation that enforces reduction of sulfur content in fuel products for the production of ultra-low sulfur (ULS) gasoline and diesel fuels, which again require a greater amount of hydrogen [25].

Thus, the world refining industry must deal with tradeoffs between emissions of pollutants with global effects (in the former because of the increased energy use at refineries to remove contaminants from oil products) and emissions of pollutants with local effects (in the latter because of fuel specifications). The overall issue becomes compounded because hydrogen production is often a large source of CO_2 emissions from refineries. For example, the enforced reduction in the sulfur content of diesel and gasoline between 2002 and 2009 has increased the energy use of Brazil's refining industry by approximately 30 %, with a similar pattern observed in its CO_2 emissions [26].

Nonetheless, there are real economic benefits to refineries for adopting a CO_2 management and reduction strategy, primarily the economic gains through conventional measures involving energy conservation and CO_2 utilization. Phillips [24] advocates the use of gasification technology for relatively easy CO_2 capture in a single site by utilizing a relatively simple amine-based scrubbing technology that produces hydrogen in the form of syngas and that enables destruction of low-value heavy crude residues in addition to other environmental benefits. On the basis of the same premise, potentially promising technology options include the development of CO_2 treatment processes using non-hydrogen-consuming techniques. Table 29.9 discusses the reduction, control, and treatment techniques for major CO_2 emission sources from refineries.

There are also incentives to be reaped through participation in the emerging cap and trade market of the carbon

TABLE 29.9—Major CO_2 Emission Sources from Refineries and the Corresponding Reduction, Control, and Treatment Techniques

Source of CO_2 Emission	Reduction, Control, and Treatment Technique
Onsite H_2 production for numerous refining processes	Optimization of H_2 required for hydrocracking and catalytic cracking reactions
Coke burning from FCC regenerator	Process changes involving • ***Coke (concarbon) management:*** Minimize coke yield while maintaining product slate • ***Capacity management:*** (1) reduce unit capacity and (2) separate feedstock into high-coke and low-coke yields • Use alternative hydrocracking technologies
Utilities for onsite production of steam and electricity	Optimization of utility use
Fuels burning in furnaces and utility boilers to provide heat for separation of liquid feed and processes such as reforming and cracking	Fuel replacement for the dirtier heavy high-sulfur fuel oil by opting for the cleaner energy sources of natural gas and H_2-rich fuel (although conceptually acceptable, this is an arguably expensive and perhaps even impractical measure to implement)

Sources: [23,25,27,28]

emissions trading scheme, as provided under the execution of the Kyoto Protocol. Such participations are particularly advantageous simply because, on average, the costs of CO_2 capture or removal in refineries on the basis of available amine-based technology is approximately 3–4 times higher than current trading values of carbon emission credits. The accord also provides two other cost-effective project-based means for achieving CO_2 emissions targets: Joint Implementation (JI) and Clean Development Mechanism (CDM). Other spillover benefits from using a formal program for CO_2 capture and sequestration include the upholding of corporate social responsibility (CSR) for an organization.

29.5.4 Ongoing Environmental Management Initiatives in the Petroleum Industry

In 2003, the API members established the API Climate Challenge Programs to develop rigorous industry-wide tools and procedures for estimating and tracking emissions and to reduce emissions through increased energy efficiency, use of alternative energy, and development of new technologies for the elimination or sequestration of emissions [1]. As part of the program, member refiners committed to improving their energy efficiency by 10 % between 2002 and 2012 [29]. Members have also established clean water committees that collaborate with industry, governmental, and other groups to address a broad range of water quality issues, including biomonitoring research, production effluent guidelines, soil or groundwater research, and emergency preparedness and response [30]. Recently, API has provided a suite of tools for the estimation, accounting, and reporting of emissions comprising (1) a compendium of methodologies [31], (2) software that was originally developed by Chevron Corporation with Battelle's assistance [32], and (3) a set of guidelines jointly developed with the International Petroleum Industry Environmental Conservation Association (IPIECA) and the International Association of Oil and Gas Producers [33]. With the emergence of mandatory reporting programs and economic instruments that rely on precise knowledge of GHG emissions (and emission reductions), a supplementary publication [34] is provided to address measurement uncertainty and statistical calculation methods.

29.6 CONCLUSIONS

As society matures and industry moves forward in the modern era, it is foreseeable that environmental considerations will continue to increasingly assume the central stage in the drive to pursue sustainable development. Hence, to arrive at informed decision-making in using the appropriate initiatives to tackle the multifarious environmental issues of pollution and climate-change-inducing emissions, it is vital for refiners to understand the fundamental aspects of a particular type of pollution, which encompass the sources, characteristics, and consequences of the three major types of pollution affecting the industry, namely water, air, and noise, and the associated legal regulations. With that, strategies on suitable monitoring, reduction, control, and treatment techniques can be formulated in devising a framework of approaches and measures for an effective and efficient refinery environmental management program. Ultimately, these environmental issues of multiple origins ought to be addressed via an integrated systems approach rather than as separate problems.

APPENDIX

TABLE 29.10—U.S. Federal and State Legislation Requirements Affecting the Environmental Impacts of the Refining Industry

• Clean Water Act (CWA) • Safe Drinking Water Act
• Clean Air Act 1963 • Clean Air Act of 1970 (CAA) and regulations • Clean Air Act Amendments of 1977 and 1990 (CAAA) and regulations thereunder • Clear Skies Act of 2003
• Resource Conservation and Recovery Act (RCRA) • Superfund: Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) • Emergency Planning and Community Right-to-Know (EPCRA) • Occupational Safety and Health Act (OSHA) • Toxic Substances Control Act (TSCA) • Oil Pollution Act • Spill Prevention Control and Countermeasure Plans

REFERENCES

[1] U.S. Department of Energy, *Energy and Environmental Profile of the U.S. Petroleum Refining Industry*, Energetics Incorporated, Columbia, MD, 2007.

[2] Jones, D.S.J., "Environmental Control and Engineering in Petroleum Refining," in Jones, D.S.J., and Pujadó, P.R., Eds., *Handbook of Petroleum Processing*, Springer, Dordrecht, The Netherlands, 2006, pp. 611–673.

[3] Wong, J.M., and Yung-Tse, H., "Treatment of Oilfield and Refinery Wastes," in Wang, L.K., Hung, Y.T., Lo, H.H., and Yapijakis, C., Eds., *Handbook of Industrial and Hazardous Wastes Treatment*, 2nd ed., Marcel Dekker, New York, 2004.

[4] Nemerow, N.L., and Agardy, F.J., *Strategies of Industrial and Hazardous Waste Management*, Van Nostrand Reinhold, New York, 1998, pp. 491–499.

[5] Dutta, A., Dikshit, A.K., Ray, S., and Bandyopadhyay, M., "Environmental Impact Assessment and Its Minimization in a Refinery Using Life Cycle Impact Analysis Approach," *Int. J. Life Cycle Assess.*, Vol. 7, 2002, pp. 185–186.

[6] *Management of Residual Materials: 1995—Petroleum Refining Performance*, API Publication No. 339, API, Washington, DC, 1997.

[7] *The Generation and Management of Residual Materials: 1991—Petroleum Refining Performance*, API Publication No. 329, API, Washington, DC, 1994.

[8] Wong, J.M., "Hazardous Waste Minimization (SB 14) in California Petroleum Refineries," in *Proceedings of the 50th Purdue International Waste Conference*, Chelsea, MN, Lewis Publishers, 1993.

[9] Ford, D.L, "Water Pollution Control in the Petroleum Industry," in Azad, H.S., Ed., *Industrial Wastewater Management Handbook*, McGraw-Hill, New York, 1976.

[10] McLaughlin, L.A., McLaughlin, H.S., and Groff, K.A., "Develop an Effective Wastewater Treatment Strategy," *Chem. Eng. Prog.*, September, 1992, pp. 34–42.

[11] Galan, B., and Grossmann, I.E., "Optimal Design of Distributed Wastewater Treatment Networks," *Ind. Eng. Chemistry Res.*, Vol. 37, 1998, pp. 4036–4048.

[12] Wong, J.M., "Petrochemicals," *Water Environ. Res.*, Vol. 71, 1998, pp. 828–833.

[13] Ortolano, L., *Environmental Regulation and Impact Assessment*, Wiley, New York, 1997.

[14] Sittig, M., *Petroleum Refining Industry Energy Saving and Environmental Control*, Noyes Data Corporation, Park Ridge, NJ, 1978.

[15] Alfke, G., Irion, W.W., and Neuwirth, O.S., "Oil Refining," in Elvers, B., Ed., *Handbook of Fuels: Energy Sources for Transportation*, Wiley, Weinheim, Germany, 2008.

[16] Celly, J., and Zambrano, J., "Hearing Loss: A Case Study on the Burden of the Oil Industry," Paper SPE 111613 presented at the *2008 SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production*, Nice, France, April 15–17, 2008.

[17] *Environmental Assessment Source Book Volume 3: Guideline or Environmental Assessment of Energy and Industry Projects*, World Bank, Geneva, Switzerland, 1996.

[18] United Nations Environmental Program, *Environmental Impact Assessment Manual*, 2nd ed., Earthprint Publisher, Stevenridge, UK, 2002.

[19] Mohamed, L., and Al-Thukair, A.A., "Environmental Assessments in the Oil and Gas Industry," *Water, Air, Soil Pollut.*, Vol. 9, 2009, 99–105.

[20] Koroneos, C., Dompros, A., Roumbas, G., and Moussiopoulos, N., "Life Cycle Assessment of Kerosene Used in Aviation," *Int. J. Life Cycle Assess.*, Vol. 10, 2005, pp. 417–424.

[21] Goedkoop, M., Effting, S., and Collignon, M., *The Eco-Indicator 99: A Damage Oriented Method for Life Cycle Impact Assessment—Manual for Designers*, 2nd ed., 2000, http://www.pre.nl/eco-indicator99/default.htm (accessed July 9, 2010).

[22] Goedkoop, M., Heijungs, R., Huijbregts, M., De Schryver, A., Struijs, J., and van Zelm, R., *ReCiPe 2008: A Life Cycle Impact Assessment Method Which Comprises Harmonized Category Indicators at the Midpoint and the Endpoint Level*, 1st ed., 2009, Report 1: Characterisation, http://www.lcia-recipe.net (accessed March 17, 2009).

[23] van Straelen, J., Geuzebroek, F., Goodchild, N., Protopapas, G., and Mahony, L., "CO_2 Capture for Refineries, A Practical Approach," *Energy Procedia*, Vol. 1, 2009, pp. 179–185.

[24] Phillips, G., "CO_2 Management in Refineries," 2002, http://canmetenergy-canmetenergie.nrcan-rncan.gc.ca/fichier/78901/co$_2$_management_in_refineries.pdf (accessed August 5, 2009).

[25] Alhajri, I., "Integration of Hydrogen and CO_2 Management within Refinery Planning," PhD Thesis, University of Waterloo, Ontario, Canada, 2008.

[26] Szklo, A. and Schaeffer, R., "Fuel Specification, Energy Consumption and CO_2 Emission in Oil Refineries," *Energy*, Vol. 32, 2007, pp. 1075–1092.

[27] Stockle, M., Carter, D., and Jounes, L., "Optimising Refinery CO_2 Emissions," *Petrol. Technol. Quart.*, Winter, 2008, pp. 123–130.

[28] Mertens, J.N., Minks, K., and Spoor, R.M., "Refinery CO_2 Challenges," *Petrol. Technol. Quart*, Summer, 2006, pp. 113–121.

[29] API, *Climate Challenge: A Progress Report*, December, 2005, http://api-ec.api.org/ehs/climate/new/index.cfm (accessed July 11, 2009).

[30] API, *Environmental Record of Performance—2009* (updated October 9, 2009), http://www.api.org/ehs/performance/environmental-record.cfm (accessed August 31, 2009).

[31] API, *Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Natural Gas Industry,* August 2009, http://www.api.org/ehs/climate/response/index.cfm (accessed August 31, 2009).

[32] API, *SANGEA™ Emissions Estimating System*, June, 2004, Software, http://ghg.api.org/ (accessed August 31, 2009).

[33] International Petroleum Industry Environmental Conservation Association, International Association of Oil and Gas Producers, and API, prepared by Battelle. *Petroleum Industry Guidelines for Reporting Greenhouse Gas Emissions,* December, 2003, http://www.ipieca.org (accessed August 31, 2009).

[34] API, *Addressing Uncertainty in Oil & Gas Industry GHG Inventories: Technical Considerations and Calculation Methods*, http://www.api.org/ehs/climate/response /index.cfm (accessed August 10, 2009).

30

Safety Issues Related to Petroleum Refineries

Joel M. Haight[1]

30.1 INTRODUCTION AND HISTORY

Petroleum refineries operate in an industry category often referred to as the process industry. Although all of the incidents that will be discussed here are not petroleum refinery related, because of similar processing methodologies, their applicability to refining and their effect on the safety and health programs are the same. Historic process incidents are well documented, and their impact on today's safety approaches in petroleum refineries is significant enough that it is important to at least summarize some of them. Although it would make sense to cover these incidents chronologically from the earliest to the most recent, a recent incident in the refining industry was so significant that we should start with it.

On March 23, 2005, an explosion and fire occurred at the British Petroleum refinery in Texas City, TX. There were 15 people killed, and the damage was significant. This incident did not necessarily prompt people to generate new regulations, but it did force a major re-emphasis of compliance with the appropriate process safety regulations and standards. During a postmaintenance turnaround startup, in an isomerization unit, a vessel was overfilled with a flammable intermediate product called raffinate. The vessel contents were routed to a blow-down drum, which subsequently overfilled and the raffinate ignited, killing 15 people and injuring many. This was a complex incident, and it is beyond the scope of this chapter to cover it all in detail. However, it did highlight many safety-related problems, such as operating procedures, facility siting, communication, supervision, and preventive maintenance, to name a few [1].

Two incidents in Europe during the 1970s brought about some of the attention that eventually led to a more significant regulatory contribution (e.g., revisions to the Seveso Directive, the United Kingdom's Health and Safety Executive's Safety Case, and the United States' Occupational Safety and Health Administration (OSHA) Process Safety Management of Highly Hazardous Chemicals regulation) to the process safety problem. In June 1974, an incident occurred at the Nypro, Ltd. Caprolactam plant in Flixborough, United Kingdom. There were 28 fatalities and 89 injuries in the plant and outside in the community. There was physical damage to more than 1800 homes and 167 businesses in the plant area. In this case, the large fire occurred after a temporary bellows joint and line between two reactors in a cyclohexane oxidation plant failed. When the connection failed, containment was lost, and a significant amount of cyclohexane escaped and subsequently ignited. Before this incident, there was no analysis done to determine if this temporary line and bellows connection could safely operate under the intended process conditions (120 psig and 145°C). It could not, but it was unknowingly operated and failed. This organization did not evaluate the safety-related implications of managing changes. When significant changes are made to a process, they can lead to inadvertent and undesired consequences upstream and downstream of the change as well as to the revised part of the process. There should be a process in place to ensure that these changes are evaluated for unintended consequences. This evaluation process is called management of change [2].

The second 1970s incident for discussion occurred approximately 2 years after Flixborough in Seveso, Italy. Approximately 2 kg of dioxin were released to the atmosphere through a reactor's pressure relief valve. It was reported in various sources that the operating crew had gone home for the weekend without completing the last step in this batch recipe. As a last step, manufacturing this batch required the addition of quench water. Without water to control the reaction rate, the unattended reaction continued, generating heat and overpressuring the reaction vessel. The pressure relief valve on the vessel protected the reactor against rupture; however, 2 kilograms of 2,3,7,8-tetrachlorodibenzopara-dioxin was discharged to the atmosphere. Wind carried the dioxin into the town and countryside. This incident highlighted the importance of having up-to-date standard operating procedures that are read, understood, and used. It also showed the necessity of training employees about the hazards they are working with and about proper emergency response [2].

In 1984, a notable and significant process incident occurred in Bhopal, India at a Union Carbide plant. On December 3, methyl isocyanate (MIC) was vented to the atmosphere from a vent gas scrubber after a runaway reaction exceeded the scrubber's capacity. It is reported that more than 2500 people died and 20,000 people were injured as a result of exposure to MIC. The subsequent investigation showed that a runaway reaction occurred in the MIC tanks after water was reportedly added to the tank. The safety systems, a pressure relief valve, a vent gas scrubber, and a flare were reportedly poorly maintained. The relief valve worked to vent the pressure, but the scrubber was overwhelmed and the flare was down for maintenance. This incident highlighted several safety-related issues that needed improvement. A preventive maintenance program and an effective emergency preparedness and response plan (working with the community to notify the public was ineffectual) did not appear to be in place or working. The plant was built over a mile away from the community, but the

---

[1] The Pennsylvania State University, University Park, PA, USA

community eventually moved right to the plant boundaries, which also increased the number of overexposures [2].

An explosion occurred at a Phillips Petroleum high-density polyethylene plant in 1989 in Pasadena, TX, when a large amount of a flammable mixture of ethylene, isobutene, hexane, and hydrogen were released and subsequently ignited. Twenty-three fatalities, 314 injuries, and more than $700 million in losses resulted. It was determined that a contract maintenance crew was attempting to unplug a settling leg in one of the polyethylene product systems. They apparently did not follow the defined safety procedure for such an operation. This incident highlighted several deficiencies in the system's design, the permit-to-work system was ineffective, there were no permanent combustible gas detection or alarms available, and building spacing was questionable in terms of absolute distance and a high occupancy (the control room) [2].

Some notable recent incidents that contribute to the need for maintaining an effective safety and health intervention program in petroleum refineries include

- A July 2007 fire and explosion at the Barton Solvents Facility in Valley Center, KS, where a static spark discharge during a loading/unloading operation in a flammable solvent storage operation ignited the vapor space of one of the facility's storage tanks. The ensuing fire ignited the flammable vapor in several other tanks in the storage facility, resulting in significant damage and a long period of downtime. An understanding of and control of static generation and discharge is a critical content area in any refinery safety and health program. Loading and unloading of static-accumulating refined products is an activity that warrants attention in petroleum refining operations [1].
- A February 2007 explosion and fire at the Valero McKee Refinery in Sunray, TX, at a propane deasphalting unit highlighted the importance of proper management of change practices and preventive maintenance activities. A dead leg in a line that was created when a section of piping was blocked during the early 1990s allowed the accumulation of water in a propane line, which froze during a cold snap. The expansion associated with the formation of ice cracked the line, allowing the escape of propane when the ice melted. The propane found an ignition source in a nearby boiler room, and the resulting fire ignited flammable materials in several other locations as other fire-damaged equipment in the radiant heat impact zone released additional flammable contents. The resulting injuries included three serious burns and 11 minor injuries, but approximately $50 million in losses resulted from downtime and reduced capacity over the next several months [1].
- A June 2006 incident in Raleigh, MS, in which three workers were fatally injured and one was seriously injured highlighted the importance of proper isolation of equipment for maintenance. It also showed the importance of the regulations regarding the proper access to elevated work sites. Three people were killed when a welder ignited the flammable vapors evaporating from a vessel near his welding site. Those killed were contract maintenance people; two were standing on a ladder being used by the welder (a work platform that does not meet the appropriate regulations) and one was a supervisor overseeing the job [1].

There continue to be incidents that clearly show us that we have not yet solved the safety problem in refineries and other process industries. A November 2005 incident occurred at the Valero refinery in Delaware City, DE, in which two workers were asphyxiated upon entering a tank containing nitrogen in violation of confined space entry requirements. An October 2005 explosion and fire at the Formosa Plastics Plant in Point Comfort, TX, where a worker who was driving a forklift struck a valve on a system containing propylene, which allowed a significant amount of flammable propylene to escape and ignite. Two workers were burned, 14 received minor injuries, and the ensuing fire resulted in extensive damage and 5 months of downtime. In January 2006, at a wastewater treatment plant in Daytona Beach, FL, a fire resulted from the ignition of methanol being released from a tank beneath a hot work job to repair a hurricane-damaged roof above the tank. A worker operating a torch to cut sections of the damaged roof ignited methanol vapors, and the resulting fire and explosion killed two workers and severely injured a third [1].

There were also several more historic incidents in industries involving injuries (including many fatal) and loss of containment of flammable or toxic material that have had an effect on the approaches used in the petroleum refinery safety today, such as a liquefied petroleum gas (LPG) explosion in Mexico City in 1984, a North Sea offshore oil platform explosion in 1988, and a fuel tank rupture in Pittsburgh, PA, in 1988 [2].

The catastrophic incidents are more publicized and may be considered more newsworthy than the day-to-day injuries that are much more prevalent in daily refinery operations; however, it is necessary to consider the effect of these day-to-day incidents. The National Safety Council reports that the cost of injuries in general industry was as high as $156 billion during 2006 [3].

Incidents teach and have taught us much about their future prevention, and more importantly, the earlier ones seemed to have provided the motivation for industry and government to aggressively address the catastrophic loss potential associated with the petroleum refining industry specifically and the chemical process industry in general. They helped generate enthusiasm around the development of several consensus and regulatory standards that have since become so much a way of life in the chemical process industry that they are now the way business is done in these important industries.

30.2 PETROLEUM REFINERY HAZARDS

30.2.1 Flammability

This author has heard refineries described jokingly as "controlled bombs." It is not really a joke, but in many ways, one could say this is to a certain extent true. The main products of a petroleum refinery are, by their very nature and expected specifications, flammable and in some cases explosive. This quality is inherent in the crude oil raw material, and it is made more so through the processing of many of the products, certainly with gasoline, jet fuel, diesel, and heating oil products. The processing of these flammables is done through many steps, many of which involve high pressure, high temperature, or both. High temperature and pressure alone can increase the magnitude of the hazards associated with the process. However, loss of containment can also occur as raw materials, intermediate products, and final products flow through the system. This includes filling into and draining from vessels being heated and cooled and undergoing state changes. These process hazards, combined with numerous potential ignition sources throughout the refinery, create the need for aggressive proactive safety and health programs.

30.2.2 Toxicity

A petroleum refinery, again, by its very nature presents some significant health hazards because of the toxicity of the raw materials, intermediate products, side reaction products, catalysts, additives, wastes, and final products. Hydrocarbon exposure in general is of concern because many of the specific hydrocarbons are central nervous system depressants. However, certain categories of hydrocarbons possess carcinogenic potential as well; the aromatics, namely benzene, is a leukemia concern and the polynuclear aromatic hydrocarbons have shown mutagenic potential [4,5].

The two contaminants that warrant significant respect result from waste streams. Many crude oils contain sulfur, and as the crude is processed, it evolves hydrogen sulfide, one of the more pervasive and toxic refinery exposure contaminants. Hydrogen sulfide has been responsible for many fatalities over the years. It ties up the hemoglobin in the blood once inhaled, and it can be fatal at high enough concentrations (immediately dangerous to life or health [IDLH] = 400 ppm) [6]. As the sulfur is removed from the crude and is processed to elemental sulfur in most cases, sulfur dioxide also evolves. Although many people subjectively do not put it in the same category of toxicity as hydrogen sulfide, it in fact carries a lower IDLH concentration [4,5].

Heavy metals present in crude streams (e.g., nickel, chromium, etc.) can have carcinogenic or mutagenic potential. Many of the wastes, corrosion inhibitors, and system additives should be evaluated for exposure and carcinogenic or mutagenic potential, such as aniline, selenium, hydrazine, arsenic, etc. Because heat is such a major part of refinery operations, much of the equipment and piping are and have been insulated. Although asbestos is no longer used, it is present in many older refinery insulations. Its carcinogenic potential is well documented. Ceramic fiber insulation is used in many high-temperature applications such as firebox lining in furnaces or hot process reactors. This material breaks down into various silica-based structures that can cause respiratory concerns [4,5].

Carbon monoxide and nitrogen are two interesting exposure contaminants that warrant some discussion here. Nitrogen was responsible for approximately 80 fatalities in U.S. industries during the period from 1992 to 2002. This is important because nitrogen makes up approximately 78% of the air that we breathe. However, it is a simple asphyxiant that excludes oxygen, and therefore workers exposed to nitrogen to the point where the oxygen concentration falls below approximately 16% are at great risk of suffocation. Nitrogen is used in many places in a refinery; however, one important place from a health and safety concern is in vessels that must be inerted because of the need to keep flammable hydrocarbons inside while work is being done. Sometimes a catalyst must remain inside of the vessel while work commences, and if the hydrocarbon cannot be removed, the oxygen must be so that ignition cannot occur. This means normal human breathing cannot occur either. Entry can only be done under strict protective requirements including the use of closely monitored, supplied breathing air [1,4,5].

Carbon monoxide can exist anyplace that combustion occurs. This is also of great concern inside of vessels that are undergoing welding or burning. It is also of some concern in any place where combustion and an enclosure on an inside environment exists. It too is an asphyxiant, but it does its damage by binding to the hemoglobin in place of oxygen, resulting in the cells being starved of oxygen. It is also of particular concern because it is colorless and odorless (not like the rotten egg smell of hydrogen sulfide) and cannot be detected without the proper gas testing equipment. Supplied air respiratory protection is appropriate for use around known concentrations of carbon monoxide [4,5].

30.2.3 Physical, Ergonomic, and Human Factor Hazards

The petroleum refinery is a collection of very large equipment; many elevated work areas; congested work areas; and much equipment that is hot and heavy or requires the use of large power tools or equipment to access, open, or move. It also is an operation that uses extensive high-technology computer control systems to operate, with each area testing the physical and cognitive skills and capacities of the work force. During maintenance turnarounds, the refinery is often filled (sometimes congested) with contract workers who may not be as familiar with the hazards or the work area as the workers who are there every day all year round [2].

Material handling hazards with heavy equipment (sprains and strains), elevated work hazards (falls and dropped objects), heavy lifts (dropped objects), inaccessible equipment controls (ergonomic strain or falling), operating computer control systems (errors, eyestrain, ergonomic hazards of the workstation, i.e., carpal tunnel syndrome, cupital tunnel syndrome, etc.), excavation (cave-ins, crushing injuries), and extensive use of electricity (electrocution hazards) are all safety- and health-related concerns in a petroleum refinery. In general, maintenance work can result in any of the above noted consequences [2].

30.2.4 Burns

The petroleum refinery can present many burn hazards, both thermal and chemical burns. Because so much of the refinery process involves heat, there are burn hazards associated with coming into contact with any hot surface—vessels, piping, steam turbines, or other hot surface. The refinery is the site of many furnace operations, therefore direct fire-related burns are also a potential concern. Chemical burns are not as well understood as thermal burns; we learn about not touching the hot stove as children, but we do not always get full instruction on acid or caustic burns as we are growing up. Acids, caustics, and other primary irritants are used in or result from refinery operations. These materials can oxidize human tissue if exposed to great enough concentrations and for a long enough time. They are used as catalysts (hydrofluoric or sulfuric acid—alkylation processes), as chemical cleaning agents (inside of vessels—preparation for maintenance), as corrosion inhibitors, etc. Although the main objective of a safety and health effort is to keep the chemical burn material in the process, this is an area where many companies provide and expect the use of appropriate personal protective equipment (goggles, gloves, chemical suits, etc.) to further protect employees from this hazard [4].

30.2.5 Release of Marshaled Energy

There are many opportunities for workers to be injured or overexposed to various forms of energy in a petroleum refinery. It can be as simple as an electrocution for contacting live electrical equipment or other energized equipment in the process of being shut down. However, electrical energy is not the only hazard worthy of our respect. Steam under pressure, toxic chemicals, and moving parts of equipment can also be energy-related hazards if released in an uncontrolled manner while shutting down or starting up equipment. Entry into equipment that contains or can contain released energy to inspect or repair internal components introduces the hazards associated with exposure to the atmosphere that can exist within a confined space (e.g., oxygen deficiency, flammable concentrations, toxic concentrations of hydrogen sulfide, sulfur dioxide, etc.). The atmospheric hazards can exist at the beginning of the entry or they may develop as the work progresses. If the space is not properly cleaned and isolated, it may not be safe to enter. If the work being done is something such as welding or burning (where oxygen is consumed and/or carbon monoxide is generated), a hazardous atmosphere may develop. When equipment is being prepared for maintenance, the process can be complex and extensive. There are many hazards, and not all of them are visible [4].

30.3 REGULATIONS AND CONSENSUS STANDARDS

The foundation of safety in petroleum refineries is formed first by governmental regulations, and then by consensus standards and general, industry-wide, good engineering practices. OSHA has promulgated regulations covering nearly every aspect of safety and health in the modern petroleum refinery. These regulations are supported by the U.S. Environmental Protection Agency (EPA)'s regulations covering mostly environmental and health-related concerns. The regulations that seem to have a significant effect on the petroleum refinery are as follows:

- *OSHA general industry regulations* [7]: OSHA's Process Safety Management of Highly Hazardous Chemicals regulation (PSM; 29 CFR 1910.119), which took effect in 1992, includes
  - 29 CFR 1919.120 Hazardous Waste Operations and Emergency Response.
  - 29 CFR 1910.1200 Hazard Communication Standard
  - 29 CFR 1910.28 Scaffolding
  - 29 CFR 1910.38 Emergency Action Plans
  - 29 CFR 1910 Subpart G Occupational Health and Environmental Control
  - 29 CFR 1910 Subpart I Personal Protective Equipment
  - 29 CFR 1910 Subpart H Hazardous Materials.
  - 29 CFR 1910.146 Permit Controlled Confined Spaces
  - 29 CFR 1910.147 The Control of Hazardous Energy Sources (Lock out Tagout)
  - 29 CFR 1910 Subpart L Fire Protection
  - 29 CFR 1910 Subpart O Machining and Machine Guarding
  - 29 CFR 1910 Subpart S Electrical
  - 29 CFR 1910 Subpart Z Toxic and Hazardous Substances
- *Also from OSHA construction regulations*:
  - 29 CFR 1926 Subpart L Scaffolds
  - 29 CFR 1926 Subpart M Fall Protection
  - 29 CFR 1926 Subpart P Excavations
  - 29 CFR 1926 Subpart R Steel Erection
- *From EPA (not all-inclusive)* [8]: EPA's Risk Management Program (RMP; 40 CFR Subpart B), which took effect in 1996, includes
  - Emergency Planning and Community Right to Know Act (EPCRA) Section 313 Industry Guidance: Petroleum Terminals and Bulk Storage Facilities
  - Spill Prevention, Control and Countermeasure (SPCC) rule at 40 CFR Part 112.

These performance standards are similar and had industry input through the former Chemical Manufacturers Association [now the American Chemistry Council (ACC)] and the American Petroleum Institute (API), among others. These standards assist industry in preventing (and minimizing the consequences or likelihood of occurrence) catastrophic incidents and injuries like those that occurred in India, the United Kingdom, Mexico, Italy, the United States, and other places [7,8].

The U.S. Chemical Safety and Hazard Investigation Board (CSB) is a relatively recent addition to the safety and health effort for the U.S. refining industry. It was authorized by the Clean Air Act in 1990 and became operational in January 1998. The CSB is an independent federal agency that, through its investigations of incidents, seeks to prevent process-related chemical accidents in the future. They do this by identifying root causes and issuing recommendations to correct those causes. Their work is well publicized, and when they issue an investigation report, it is made available to the public. They are not a regulatory body, but their recommendations are taken seriously in the petroleum refining industry [1].

Consensus standards and voluntary programs also help to support refining efforts. The Responsible Care Program of the ACC helped get companies to address protecting not only workers, but also their plant neighbors, their customers, and the rest of the community. Although they do not directly apply to the refining industry, many of their methods and programs have been adopted by the petroleum refiners. They promote this wider view through practices such as product stewardship and emergency preparedness and response. OSHA's Voluntary Protection Program (VPP) promotes the use of safety management systems and encourages active employee involvement in the management of safety and in preventing injuries [7].

Consensus and industry organizations have contributed greatly to the safety and health efforts of the petroleum refining industry. The API developed Recommended Practice 750 Process Hazards Management [9] (which preceded the OSHA PSM standard), Recommended Practice 752 on Facility Siting [10], and API Recommended Practice 650 on Welded Steel Tanks for Oil Storage [11], among others. The American Institute of Chemical Engineers' (AIChE) Center for Chemical Process Safety (CCPS) developed a complete series of textbooks that provide guidance (and "how-to" information) on the 14 elements of OSHA's PSM standard. They also sponsor conferences, seminars, and symposiums; publish proceedings; and provide industry with valuable process safety resources [2].

30.4 REGULATORY AND MANAGEMENT PRACTICES FOR SAFETY AND HEALTH

30.4.1 Labor or Personnel Safety

Today's safety and health programs in petroleum refineries are gravitating toward a management systems approach that incorporates the traditional safety program elements, but it also allows the program to be managed using modern oversight and measurement techniques along with extensive employee involvement. The general content of a typical safety and health program includes a safety training component, an inspection and audit provision or both, an awareness and motivation component, a work control provision (permit-to-work system), a behavioral observation component, a hazard analysis component, and an incident investigation component. These components are addressed using various techniques that are so varied and extensive that they cannot be completely covered in this chapter. Each component is treated extensively in many complete texts, which one can refer to for further information. This part of the chapter will treat, to some extent, behavioral safety and permit-to-work systems. However, it is important to mention that housekeeping and compliance inspections, safety meetings, safety incentive programs, job safety analyses, and safety committees are often found as part of a refinery safety and health program [7,12–15].

30.4.2 Behavioral Safety

A safety and health program element in refineries that seems to have become popular in the last 15–20 years is the element referred to generally as "behavioral safety." It has various proprietary names and it is supported by many consultants who specialize in the area. The general description of the approach and the goals may not provide the reader with enough information to establish a behavioral safety program, but it will provide enough to allow the reader to understand the concept and to pursue further information if desired. In the opinion of the author, the element has its strengths in two areas. The first is that it is usually considered a "grassroots" program developed for the employees by the employees. It involves one-on-one peer evaluations and is not managed from above. The other strength is that it involves an observation step in the process. What better way to evaluate behavior than to watch a person doing his or her real job? Work observation is one of the strongest tools in the quest to measure and evaluate human behavior, and the observation tool is used for this purpose in many disciplines. With observations, one gets a realistic picture of how a job is actually done. With peers observing peers, one is more likely to observe true behavior [16].

The process usually involves the selection of a core team of developers from among the employees. These employees then develop a critical inventory of behaviors that they are interested in observing. The "critical" term refers to those behaviors that the team believes could have an effect on the relative level of safety of the task. The team then develops a definition for safe behavior versus at-risk behavior for each of the entries in the critical behavior index or list. Once the behaviors and their safe or at-risk nature have been identified and defined, they are published in a checklist for observers to use while observing their peers performing their jobs [16].

If the person being observed performs his or her task safely, according to the behavior index, the observer would give the behavior a "safe" rating. If it is not performed safely, the observer would identify and record on the checklist the particular behavior that was putting the worker at risk. The observer then discusses the findings with the person being observed, and together they develop an action plan to correct the at-risk nature of the behavior or the task. This, in and of itself, can reduce at-risk behavior in the operation, and most users of the system would probably claim that it has reduced at-risk behaviors. However, there is more that can be gained by analyzing the data that are collected during this process. Through various analytical techniques, an organization can determine if safe behavior is at acceptable levels or if it is improving toward the safe level, what types of behavior are showing up in the at-risk category more often than desired, whether or not suggested action plans are working, etc. With proper management and analysis of the data collected, the behavioral safety program can be a valuable tool in the quest to improve human performance in the refinery [16].

A process such as this also has its drawbacks. Hopkins (2006) warns us that many of these programs are operated under the assumption that unsafe behaviors are the only causes of accidents that are worth studying [17]. Hopkins (2006) also suggests that unsafe behavior is often just the last link in the causal chain and it is not necessarily the link that most accurately explains the real cause of accidents [17]. Hopkins (2006) suggests in his study that behavioral safety programs might be more effective if they involve observation of the managers [17].

30.4.3 Permit-to-Work Systems

Permit-to-work systems are a staple in any safety and health program in a refinery. There are many hazards associated with maintenance work in a refinery, and a work control program can help reduce the risk of these hazards manifesting themselves in the form of an injury, fire, or explosion. When maintenance is done in a refinery, equipment must be shut down, cleaned, and isolated before work can be started. If this shutting down, cleaning, and isolating is not done properly and all participants and affected workers are not informed of what is going on, some of the high pressure, high temperature, electric shock, toxic or flammable chemicals, or steam energy can be released. This loss of containment is where the injury, fire, or explosion consequences can occur. So although there are varying practices used in the refining industry, OSHA regulations cover the basic requirements for hot work, locking, and tagging-out equipment; entering confined spaces; excavations; elevated work or work done from scaffolds or both. For most work, the basic process involves the following steps or something similar:

- Shut down the equipment (pump, compressor, turbine, etc.; align appropriate valves and push the start/stop switch, button, etc.; close the main switch in the motor control center); lock switches closed; and tag the equipment and appropriate switch or control at the motor control center.
- Align all suction/discharge or inlet and outlet valves (open and close appropriate valves) to drain the equipment of liquid content.

- Steam, purge, or otherwise remove all vapor contaminants.
- When equipment is clean, install blinds (or blanks as they are sometimes called) at the appropriate flanges, close block valves, open bleeder valves, and then lock and tag the valves open or closed as appropriate.
- Cover drains or other sources so that flammable material cannot flow back into the area.
- If an entry into a permit-required space or hot work is being done, test the atmosphere for the appropriate contaminants (i.e., flammables and toxics, or both, and oxygen deficiency as appropriate).
- Provide respiratory and other protective equipment, and provide entry standby personnel, fire watch personnel, or other back-up people to aid in communications and rescue if needed.
- Provide any necessary communications (radios) and rescue equipment.
- Ensure all permits, tags, warning signs, etc. are completed and approved/signed by the appropriate authorities.

These are basic steps, and individual programs will have much more detail and include more or different actions. It is important to note that OSHA requires a lock-out/tag-out procedure for each piece of equipment in which energy can be released and injure a worker while he/she is performing maintenance or tests on the equipment [2,7,18].

Excavation work and elevated work, although not always under a permit-to-work system for all companies, do warrant special attention because of their unique hazards. For excavation, the biggest concern is collapse with workers inside, and for elevated work, of course, the concern is falls. There are many issues around excavations that must be addressed to ensure that collapse does not occur. These issues include soil type (stable or unstable), presence of water, force created by the weight of the equipment and spoil pile on the sides of the excavation, shoring, angled cutbacks, escape, sensitive occupancies such as nearby gas lines, etc., vibration, and atmospheric concerns. For elevated work, height and guarding are important; decision between life-lines or scaffolding, footing and stability, fall life-line drop distance, and task mobility while being tied off are a few of the issues that must be addressed. Each of these issues can be addressed in a procedure, a permit system, or both that requires task participants to communicate with each other and check each other's input, analysis, approval, etc. [7].

30.4.4 Management Systems

In large organizations, such as we find with many U.S. refineries, the safety "problem" should be managed with the use of a systematic approach. This is already the way many refineries manage the safety and injury prevention business, as the following sections will describe. However, the Chemical Safety and Hazard Investigation Board (CSB) has determined that not all refineries manage their safety and health system well [19]. Blair (2004) found that through all of the CSB Investigations, many companies fail to perform effective hazard reviews of their processes and facilities, they do not adequately investigate and follow up after incidents occur, they do not adequately train their employees, and they fail to implement sound and effective mechanical integrity programs. Although many have seen that it is appropriate to establish a management system for safety and health management, it seems that there is still work to do to effectively implement this system [19].

30.4.5 Process Safety

Although the two main management systems that have driven process safety in petroleum refineries are regulations, the way the industry has implemented them since 1992 represents an effective way to manage process safety and still comply with the regulations. The regulations are OSHA's PSM and EPA's RMP regulations. Although they took effect at different times, they are similar in what they require from industry. They both address many aspects of how business operates. It appears to this author that over the last 17 years industry representatives have made complying with these regulations more the way business is done rather than an additional task for the sake of compliance.

30.4.5.1 OSHA'S PROCESS SAFETY MANAGEMENT OF HIGHLY HAZARDOUS CHEMICALS

OSHA's PSM regulation 29 CFR 1910.119 covers 14 elements. Although operations are required to determine if they are covered by the regulation by reviewing the applicability section of the regulation (29 CFR 1910.119 (a)), most petroleum refineries in the United States are covered [7].

The Employee Participation (29 CFR 1910.119 (c)) element describes the requirements for employees who could be affected by an incident. Covered employers are required to provide affected employees access to pertinent PSM information and allow them to have input to its development and use. Affected employees must be trained in the standard's content. This element complements the OSHA VPP effort because both require employees to actively engage and participate in the safety and health program. Employee participation in PSM implementation must be documented [7].

The Process Safety Information (PSI) (29 CFR 1910.119 (d)) requires each covered operation to produce, maintain, and use information associated with the chemicals, process technology information, and covered equipment information. Among others, this information includes Material Safety Data Sheets (MSDS), Piping and Instrument Diagrams (P&ID), Block Flow Diagrams, relief valve design and sizing information, ventilation system information, data sheets on pumps (pump curve data, etc.), compressors, pressure vessel ratings, and safe operating and design limits for equipment. The information must be kept up to date and available to employees who work at or on the covered process [7].

The Process Hazards Analysis (PHA) (29 CFR 1910.119 (e)) element requires that a covered process be analyzed to identify hazards that could lead to a catastrophic incident. Acceptable analytical techniques, according to OSHA, are what-if studies, what-if/checklists studies, hazard and operability (HAZOP) studies, failure mode and effects analysis (FMEA), and fault tree analysis (FTA). Other techniques may be acceptable. An initial analysis must be performed by a trained, multidisciplinary team of analysts and then the study must be revalidated every 5 years. The team identifies hazards, determines potential consequences, identifies existing safeguards, determines the risk associated with each identified hazard, and recommends corrective action if the risk is considered to be too high. Corrective actions are then evaluated by a management team for resolution (justifiably decline or accept and implement on a timely basis) [7].

The Operating Procedures (29 CFR 1910.119 (f)) element requires that the operation of a covered process be guided by written, up-to-date (must be certified annually as being up-to-date) operating procedures that are used by the employees who operate that process. They must cover normal operations, start-up, emergency shutdown, temporary operations, and start-up after a maintenance turnaround. They must cover safe operating limits for critical process parameters, how to prevent operation outside of those limits, and what to do if the limits are exceeded. Users must be trained in the contents of the procedure [7].

The Training element (29 CFR 1910.119 (g)) requires that operators of a covered process be trained in its safe operation. They must receive initial training and then receive refresher training at least every 3 years after the initial training. The training must include the Operating Procedure and any Management of Change–driven changes to the process. Trainees must show that they have understood the training [7].

The Contractors (29 CFR 1910.119 (h)) element requires that companies that use contractors for work on a covered process must consider the contractors' past safety performance before selecting them. The company must then ensure that the contractor employees are qualified to do the work and that the contract employees understand the hazards they will be working with or near. Regular audits of the contractor performance are required as well as keeping the contractor's incident records [7].

If a refinery process is started up for the first time or undergoes a maintenance turnaround, it must receive a Pre-Start-up Safety Review (PSSR) (29 CFR 1910.119 (i)). This element is integrated with the Management of Change element and it is intended to help ensure that anytime there is a change to the process, it is reviewed and documented. The intent is to ensure that necessary changes to operating procedures have been made, that operators have been trained, that required updates to the PSI have been made, that PHA corrective action recommendations have been resolved and completed, and that all required design specifications have been followed [7].

The Mechanical Integrity (29 CFR 1910.119 (j)) element includes the requirements to maintain the integrity of existing equipment throughout its useful life. Critical equipment must be identified and tracked. Implementation of inspection, testing, and preventive maintenance programs is required. A quality assurance practice must be in place to ensure that equipment, spare parts, lubricants, and other consumable maintenance materials, etc. are built properly and manufactured to specifications for dimensions, materials of construction, composition, strength, etc. Regular and contract employees must be trained to perform the intended maintenance, inspections, and testing, and deficiencies in equipment of the program must be managed [7].

The Hot Work Permit (29 CFR 1910.119 (k)) element addresses work that involves use of an ignition source in areas where flammables could be present. It also addresses energy isolation for work on covered equipment (where flammability is of concern). This element supports the existing hot work regulation 29 CFR 1910.252. Hot work is managed in a system in which the permits convey safety-related information (protective equipment requirements, special atmospheric testing, approval signatures, etc.) and preventive actions (seal drains, assign a fire watch, contain sparks, etc.) to those performing hot work. Permits for hot work require those involved in the task to review the permit and, in some cases, approve and sign it [7].

The Management of Change (29 CFR 1910.119 (l)) element requires an evaluation of each change to ensure that it will not introduce any safety-related concerns. It also requires that the documents containing any process safety information be revised and that employees are informed of and, in some cases, trained as needed to operate new equipment, etc. It applies to changes in equipment; raw materials; intermediates; and products, methods, or procedures and can apply to changes in consumable supplies such as lubricants, gaskets, O-rings, etc. [7].

The Incident Investigation (29 CFR 1910.119 (m)) element requires that all process incidents (such as fire, explosion, or toxic release in which people are injured or killed; or equipment, facilities, or the community are damaged) that either occurred or could have occurred be investigated. An investigation, done by a multidisciplinary team with the appropriate expertise, must begin within 48 h of occurrence. The team determines the causes and develops recommended corrective actions to help keep the incident from happening again. The team puts together a report of the findings, conclusions, and recommended corrective actions, along with the details of the incident, and makes it available to employees who may be affected by this or a similar incident [7].

The Emergency Preparedness and Response (29 CFR 1910.119 (n)) element is important to anyone who can be affected by an incident requiring evacuation or at least a response. This element supports two other OSHA emergency-response-related regulations: 29 CFR 1910.38 (Emergency Action Plans) and 29 CFR 1910.120 (Hazardous Waste Operations and Emergency Response). The objective is to help ensure that affected employees are informed about alarms and alarm notification, actual response (fire fighters, air monitoring specialists, etc.), notification of outside response organizations, evacuation procedures, damage assessment, and clean-up. The program must be written, and training and critiqued practice sessions must be performed for all affected [7].

The Compliance Audit (29 CFR 1910.119 (o)) element requires that overall program performance be evaluated every 3 years [7].

There is also a Trade Secret (29 CFR 1910.119 (p)) provision to allow companies to protect competitive advantage associated with their chemical formulations. However, they are required to disclose PSI for any hazards associated with that process or process materials [7].

30.4.5.2 EPA'S RISK MANAGEMENT PROGRAM

EPA's Risk Management Program (RMP) regulation (40 CFR Subpart B) is similar to OSHA's PSM standard. Its intent is also to prevent accidental releases of toxic or flammable material, but to off-site receptors. RMP's major elements include its Hazard Assessment, Prevention Program, Emergency Response Program, and documentation maintained on-site and submitted to federal, state, and local environmental authorities [2,8].

The Hazard Assessment element requires a consequence analysis be done for a worst-case event (an event involving the release of the entire contents of the largest vessel in 10 min under the worst atmospheric conditions). Covered processes are allowed then to analyze an alternative case (more likely to occur, but usually with less severe consequences) [2,8].

The Prevention Program has 11 of the same PSM elements, but it has no Employee Participation, Contractor Safety, Hot Work Permit, or Trade Secret elements [2,8].

Implementation of these two regulations accounts for much of the safety- and health-related effort in a petroleum refinery. Although they are regulatory requirements, they form the basis of the management systems used by most refineries in the United States to manage the catastrophic risk associated with process conditions that may increase the potential for loss of containment. Although these management activities are thought to be effective, there are additional engineered approaches that also warrant coverage.

30.5 ENGINEERING APPROACHES TO SAFETY AND HEALTH

Engineered prevention interventions are also used to reduce the risk of incidents in the petroleum refinery. The systems or design specifications and practices that contribute to the safety and health effort include (but are not limited to) pressure relief systems and flares, automated control systems including detection and alarm systems, piping and equipment or material specifications, purging and ventilation systems, fire suppression systems, explosion venting systems, positive pressure buildings, and equipment layout and siting practices [2].

A National Institute of Occupational Safety and Health (NIOSH) initiative also stresses an engineered approach to safety and health with its “Prevention-Through-Design” initiative [20]. Howard (2008) stresses the importance of designing out hazards in the early design phase of every project [20]. This also seems to support the OSHA hierarchy of control that places the highest value on engineering out the hazard and then allows companies to use administrative controls and protective equipment after engineered controls have been explored [7].

30.5.1 Pressure Relief Systems

Many refinery vessels operate at pressures above atmospheric, and each vessel is rated to safely contain a range of pressures. The pressure can increase dramatically in an exothermic runaway reaction or an external fire. In vacuum systems, the pressure can also decrease below safe limits. If the maximum rated pressure is exceeded (or the minimum pressure is reduced into excessive vacuum), the vessel can potentially rupture and release its contents. For these potential pressure swings, it is typical to install on a vessel a pressure relief device (pressure vessel) or vacuum breaker (for atmospheric vessel). Although these devices are generally used to protect the vessel from damage, they can also be used to protect personnel from exposure to the contents of the vessel and minimize loss of product or other material if they vent to an enclosed system [21]. The choice of what type to use is beyond the scope of this chapter; however, the Crowl and Louvar (2002) book provides a summary of design issues and advantages and disadvantages [21].

Pressure relief devices (or pressure safety valve—PSV is a common acronym to describe them) must be designed—meaning they must be properly sized (capacity) and the discharge location is critical. The PSVs are usually sized for an external fire or some type of internal process upset such as the uncontrolled exothermic reaction noted above. A decision must also be made about whether to discharge to the atmosphere or to a closed system that includes a scrubber, a flare, or in some cases a water tank. If discharging to the atmosphere, one must ensure that it does not discharge to high-traffic or high-occupancy areas (facility siting decisions should be made here), to a building air intake, or in the area of potential ignitions sources if the vented material is flammable. Crowl and Louvar (2002) address these design decisions in more detail [21].

30.5.2 Automated Control Systems (Including Interlocks, Detection, and Alarm Systems)

Petroleum refineries are controlled extensively using automated control systems. Automated computer controlled systems have long been used in refineries to control pressures, temperatures, flows, levels, process stream concentrations, etc. It has been said, and it seems most people recognize, that the automation performs the control function more efficiently, more effectively, and more safely than humans. For this reason, automated systems are relied upon extensively for their contribution to the safety and health effort. There is debate about the optimal mix of automated versus manual functions for optimal performance: the human must be involved to some extent because the computer cannot be programmed to recognize all safety-related upsets [22–24].

A control system is designed to detect when process conditions are trending outside of the intended limits. For example, if during a distillation operation, the temperature goes above a specified limit at a specific level in the tower, a temperature indicator/controller generates a signal that a transmitter then sends to possibly the steam flow control valve at the reboiler, telling it to trend toward closed or to a flow control valve on the reflux loop telling it to trend toward open, etc. This can be accomplished without human intervention. If there is a leak, a detection system measures the concentration of a flammable material in the air, and at a prescribed concentration it sends a signal to a sprinkler system or an alarm enunciator or control room screen alerting operators to the problem [22–24].

In larger upsets, control operators can easily become overwhelmed with alarms in a very short period of time. In one case in the author’s experience, a furnace tube rupture was determined to have generated over 300 alarm signals in one 5-min period. Operators are unable to address all of those. One effective design philosophy and management strategy to address alarm overload is called abnormal situation management (ASM). An ASM system can be built and integrated into a normal process control system. Control system engineers try to anticipate the actions that an experienced operator would take to head off an incident and then attempt to design these responses into the control system. They contain an alarm priority protocol that is intended to recognize and then suppress low-priority alarms to make it easier for the operators to acknowledge and address the higher priority alarms. The objective of this strategy and system is to reduce the information overload on the operator while still minimizing the risk of catastrophic incident. This allows the operator to focus more of their valuable time where it needs to be to avert an upset [2,7].

Automated systems contribute significantly to the overall refinery safety effort; however, one must understand the limits of automation, its energy source (electricity, water instrument air, etc.), its failure mode (open, closed, on, or off, etc.), whether an alarm is registered where the upset occurred (possibly in a location where no one would see or hear it) or in the control room, which is occupied 24 hours per day [22–24].

30.5.3 Piping Specifications

Piping must contain the pressure and the toxic or flammable material that it carries. In piping, the process stream is almost always flowing (instead of sitting in a vessel). This keeps a dynamic load on the pipe and that load must be considered when determining the materials of construction, the thickness, the flange ratings, etc. Piping can rupture; corrode through; leak at a weld, flange, or other connection point; and can even leak through its walls (if the molecular size of the process stream is small, e.g., hydrogen). To keep the conveying material from getting out of the pipe, the piping for each particular application must be designed to handle the stresses (both environmental and process stream) to which it will be exposed. These specifications are written in several ways and are different for each company, but they all usually include an identifying number that is shown on the piping and instrument diagram. This number is coded to indicate a description of the safe range of process stream contents and conditions (maximum and minimum temperatures, maximum and minimum pressures, flow rates, etc.) and materials of construction (minimize the risk of corrosion attack). The specification also usually includes a description of the required wall thickness, type, material, and size of gaskets, O-rings and fittings, pipe joining technique, etc. These specifications also provide information about the valve types to be used and any other connections or appurtenances (thermowells or injection points, etc.). All of these requirements are intended to ensure that containment is not lost through failure of the piping [25].

Many piping specifications are found in consensus standards such as the American National Standards Institute (ANSI), ANSI B31.3, Chemical Plant and Petroleum Piping Code [26], the American Petroleum Institute (API)'s API 5L Specifications for Lined Pipe [27], or the National Fire Protection Association (NFPA)'s NFPA 30 Flammable and Combustible Liquids Code [28]. These can form the foundation for an individual company's specifications. Adjustments to the consensus standard specification may be necessary because of differences in plant operating conditions and history [25].

30.5.4 Inerting, Purging, and Ventilation

Refinery vessels and other process containers must be opened periodically for inspection, maintenance, or both. Vessels are most often drained and cleaned, but sometimes residual toxic or flammable vapors remain. Under certain conditions, work must be performed in these vessels where residual material cannot be fully removed. In some cases, flammable concentrations must remain (e.g., some catalysts cannot be water-washed or steamed) during entry. Because flammables may not be completely removed, other protection methods must be used to minimize human exposure. To accomplish this, many refineries use inerting, purging, and ventilating to remove oxygen or add more oxygen, depending on the situation. If all of the flammable material cannot be removed, a vessel is inerted with a material such as nitrogen or carbon dioxide to reduce oxygen concentrations to a point where ignition is not possible. In some cases, a hot nitrogen purge is used to remove heavier hydrocarbons from vessel internals or from catalysts. Other general types of purges such as vacuum and pressure purges are used to remove toxic or flammables from a work environment as well. It is critical that the purged material be safely discharged to an appropriate location or closed system. There are many routing options depending upon the material. It may be routed through a collection medium such as a bag house, electrostatic precipitator, incinerator, or flare system [2,21].

General dilution and local exhaust ventilation are two removal techniques used to remove contaminants (toxic or flammable) from a work space. This is done more on a local scale to protect employees rather than the public. Ventilation systems are sized based on space dimensions, expected contaminant loading, necessary capture velocity, physical and chemical properties of the contaminant, and extent and time of the space. Ventilation system discharge must also be appropriately managed to ensure it is not discharged to traffic or flammable areas [2,29].

30.5.5 Explosion Venting and Explosion-Proof Equipment

Process operating areas can be given special designations such as XP (explosion proof) or non-XP. An XP designation means that flammable vapors could be present under upset or other intermittent conditions. This is comparable to the National Electric Code's Class 1 Division 2 area designation. In these areas, safety-related measures must be taken to minimize fire and explosion risk, such as elimination or factory sealing of equipment that could be ignition sources, installing explosion-proof housing around electrical equipment (this is housing that can withstand an internal explosion), or providing explosion venting capability. This does not prevent an explosion, but it does reduce damage when the explosion occurs because the overpressure is vented in a controlled manner. This could be accomplished with a welded or riveted panel on an atmospheric vessel wall or a weak seam weld on a tank roof-to-wall seam, among many other approaches. In each case, the weak component provides a designed vent area because it opens for venting the overpressure to protect the equipment [2,21,30].

When electrically driven equipment is operated in an XP or electrically classified area, it must be rated for that environment. This means that the electrical ignition source associated with the equipment must be sealed away from the flammable vapors to prevent them from infiltrating the housing. The integrity of these seals dictates whether the equipment can be operated in an environment where flammable vapors are always presents [National Electric Code (NEC) Class 1 Division 1 area] or where flammable vapors could be present (NEC Class 1 Division 2) [2,21,30].

30.5.6 Fire Suppression Systems

If a fire occurs in a refinery, the consequences can be catastrophic. Therefore, although it is most important to prevent fires, some attention must be given to controlling and suppressing fires if they do ignite. There are many types of fire suppression systems in use in refineries, and therefore design decision-making becomes necessary. The engineer must determine if a water-based system will be needed or if a non-water-based system is more appropriate. They will need to decide between automatic and manual systems or between wet pipe and dry pipe systems. They will also need to decide how fast the system needs to respond and whether the system is to extinguish the fire or merely control it until the fire department arrives. Actual design decisions are beyond the scope of this chapter; however, the NFPA's *Fire Protection Handbook* and the Society of Fire Protection Engineers' *Handbook of Fire Protection Engineering* can provide all of the information necessary to design a fire suppression system [2,30].

In general, refineries are protected by fire hydrants, water monitors, and hose reels. In most cases, refinery fires are fought manually. In some cases, with liquefied petroleum gas vessels, for example, a deluge system is installed over the vessel to help keep the vessel cool in a fire to prevent a boiling liquid expanding vapor explosion (BLEVE). Sprinkler systems can be used over critical motor-operated isolation valves, in compressor buildings, or in critical pump rooms where operators may be trapped if they enter to try to fight a fire. Non-water-based systems are found in control rooms where computer equipment is found, in electrical rooms, or in records-retention areas where water damage is a concern [30,31].

30.5.7 Facility Siting and Equipment Spacing

In refineries, in the event of an explosion, release, or fire, there is a concern for adjacent units, areas, buildings, and other occupancies in general because of the potential for knock-on or domino effects. Consideration for the effects from an adjacent fire, explosion, or other release, facility siting, as described in the API's Recommended Practice 752 addresses the potential for collateral damage in adjacent units or occupancies. The analytical practice of facility siting focuses on equipment and building spacing. It sometimes involves a consequence analyses step to determine the extent of the vulnerability zone associated with dispersion of toxic or flammable vapor cloud, the blast overpressure impact, or radiant heat effects. One first determines credible release scenarios that will be considered, then they determine the extent of its vulnerability zone from the release, and then they identify buildings or facilities inside of that zone. After the buildings in the vulnerability zone are identified, the facility siting analyst must determine if that building is occupied to the level (number of people hours) reaching unacceptable risk (acceptability is suggested in the API RP 752 Consensus Standard). If the risk of impact is considered unacceptable, a decision is made to remove the activity to a location outside of the vulnerability zone, move the building or function to a location outside of the vulnerability zone, pressurize the building, change the process to minimize the likelihood of the release scenario's occurrence, strengthen the blast resistance or vapor tightness of the building, or install a barrier between the source and the occupied building. This is a design decision-making process that is based on the extent of the risk and the feasibility of the countermeasures [32].

Equipment spacing practices involve determining safe distances between equipment in a refinery to keep flammables away from ignition sources, to keep two reactive chemicals away from each other, etc. It is best to accomplish this step during the design phase. The response taken will be based on the forecasted vapor cloud travel distance, presence of an ignition source, and the compatibility between materials handled in the process being studied. One would like to provide as much distance as possible between individual pieces of equipment; however, this uses more real estate and involves more cost associated with longer piping runs and process inefficiencies. There are tradeoffs, and if one can install rated electrical equipment near a flammable vapor source, this may be less expensive than doubling the distance between them and be just as safe. Proper application of protective spacing protocols can lower the risk of fire [32].

30.5.8 Other Protective Systems

Other loss prevention practices, procedures, devices, etc. that can be considered for implementation as needed include

- Static electricity controls—bonding and grounding, relaxation and increasing process stream conductivity with additives
- Corrosion prevention—material selection, addition of corrosion inhibitors, cathodic protection, galvanic corrosion prevention and non-destructive and destructive inspection protocols
- Remote impounding of flammable liquids—containment and drainage away from process equipment

Please consult the references for this chapter to learn more about these and other types of protection systems [2].

30.6 CONCLUSIONS

Safety in petroleum refineries has come a long way in the last half century. It is now, thanks to regulatory and industry input, a more managed function than it ever was. The OSHA PSM standard and the EPA RMP have become an integral part of the overall safety and health program in U.S. petroleum refineries. Permit-to-work systems, behavioral safety programs, inspection, and preventive or predictive maintenance programs have contributed greatly to injury reduction. We have learned much through too many catastrophic incidents, and the engineering and management systems approaches have contributed much to the improvement of safety and health in petroleum refineries.

REFERENCES

[1] "U.S. Chemical Safety Board," www.csb.gov. (accessed on August 29, 2008).

[2] Haight, J.M., "Loss Prevention in Chemical Processing," in *Encyclopedia of Chemical Processing*, E. Sunggyu Lee, Ed., Taylor & Francis, Inc., New York, Vol. 3, 2005, pp. 1483–1492.

[3] "National Safety Council," www.nsc.org. (accessed on August, 2008).

[4] Haight, J.M., "Occupational Health Risks in Crude Oil and Natural Gas Extraction," in *Encyclopedia of Energy*, Elsevier Science, Academic Press, San Diego, CA, 2004, pp. 477–487.

[5] Lipton, S., Lynch, J., *Health Hazard Control in the Chemical Process Industry*, John Wiley and Sons, New York, 1987, pp. 76–77.

[6] *Threshold Limit Value Guide*, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 2008.

[7] "Occupational Safety and Health Administration," www.osha.gov (accessed August 1, 2008).

[8] "U.S. Environmental Protection Agency," www.epa.gov (accessed August 10, 2008).

[9] *Recommended Practice API 750 Management of Process Hazards*, American Petroleum Institute, Washington, DC, 1990.

[10] *Recommended Practice API 752 Management of Hazards Associated with Location of Process Plant Permanent Buildings*, American Petroleum Institute, Washington, DC, 2009.

[11] *Recommended Practice API 650-2009, Welded Tanks for Oil Storage*, American Petroleum Institute, Washington, DC, 2009.

[12] Haight, J.M., and Thomas, R.E., "Intervention Effectiveness Research—A Review of the Literature on Leading Indicators," *Chemical Health and Safety*, Vol. 10, 2003, pp. 21–25.

[13] Haight, J.M., Thomas, R.E., Smith, L.A., Bulfin, R.L., and Hopkins, B.L., "Evaluating the Effectiveness of Loss Prevention Interventions: Developing the Mathematical Relationship between Interventions and Incident Rates for the Design of a Loss Prevention System (Phase 1)," *Profess. Safety J. Am. Soc. Safety Eng.*, Vol. 46, 2001, pp. 38–44.

[14] Iyer, P.S., Haight, J.M., del Castillo, E., Tink, B.W., and Hawkins, P.W., "A Research Model—Forecasting Incident Rates from Optimized Safety Program Intervention Strategies," *J. Safety Res.*, Vol. 36, 2005, pp. 341–351.

[15] Iyer, P., Haight, J.M., Del Castillo, E., Tink, B.W., and Hawkins, P.W., "Intervention Effectiveness Research: Understanding and Optimizing Industrial Safety Programs Using Leading Indicators," *J. Am. Chem. Soc.*, Vol. 11, 2004, pp. 9–19.

[16] Agraz-Boenekar, R., Groves, W.A., and Haight, J.M., "An Examination of Observations and Incidence Rates for a Behavior Based Safety Program," *J. Safety, Health Environ. Res.*, Vol. 4, 2007, http://www.asse.org/academicsjournal/archive/vol4no3/docs/fall07-feature05.pdf.

[17] Hopkins, A., "What Are We to Make of Safe Behavior Programs," *Safety Sci.*, Vol. 44, 2006, pp. 583–597.

[18] Erny, W., "Work Authorization in Refineries, by Design—Engineering Practice Specialty," *Am. Soc. Safety Eng.*, Vol. 1, Winter 2001–2002, pp. 1, 6–7.

[19] Blair, A., "Management System Failures in Incidents Investigated by the U.S. Chemical Safety and Hazard Investigation Board," *Process Safety Prog.*, Vol. 23, 2004, pp. 232–236.

[20] Howard, J., "Prevention through Design—Introduction," *J. Safety Res.*, Vol. 39, 2008, pp. 113.

[21] Crowl, D.A., and Louvar, J.F., *Chemical Process Safety: Fundamentals with Applications*, 2nd ed. Prentice Hall International Series in the Physical and Chemical Engineering Sciences, Prentice Hall PTR, Upper Saddle River, NJ, 2002, pp. 27–29, 225–428.

[22] Haight, J.M., and Caringi, R.G., "Automation vs. Human Intervention—What Is the Best Mix for Optimum System Performance? A Case Study," *Int. J. Risk Assess. Manage.*, Vol. 7, 2007, pp. 708–721.

[23] Haight, J.M., "Do Automated Control Systems Reduce Human Error and Incidents?" *Profess. Safety J. Am. Soc. Safety Eng.*, Vol. 52, 2007, pp. 20–27.

[24] Haight, J.M., and Kecojevic, V., "Automation vs. Human Intervention—What Is the Best Fit for the Best Performance?" *Process Safety Prog.*, Vol. 24, 2005, pp. 45–51.

[25] O' Brien, T., and Luckiewicz, E., *Guidelines for Process Safety Fundamentals in General Plant Operations*, 1st ed., Center for Chemical Process Safety, American Institute of Chemical Engineers, New York, 1995, pp. 91–96, 103–114.

[26] *ANSI/ASME B31.3-2010, Process Piping*, American National Standards Institute, Washington, DC, 2010.

[27] *API 5L Line Piping*, 44th ed., American Petroleum Institute, Washington, DC, 2008.

[28] *Flammable and Combustible Liquids Code*, NFPA 30, National Fire Protection Association, Quincy, MA, 2008.

[29] *Industrial Ventilation: A Manual of Recommended Practices*, 23rd ed., American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1998, pp. 2-2–2-7, 2-13.

[30] DiNenno, P.J., Ed., *SFPE Handbook of Fire Protection Engineering*, 3rd ed., National Fire Protection Association and Society of Fire Protection Engineers, Quincy, MA, Bethesda, MD, 2002, pp. 4-1–4-72.

[31] Cote, A.E., Ed, *Fire Protection Handbook*, 18th ed., National Fire Protection Association, Quincy, MA, 1997, pp. 6-1–6-136.

[32] Flynn, A.M., Theodore, L., *Health, Safety, and Accident Management in the Chemical Process Industries*, 1st ed., Marcel Dekker, Inc., New York, 2002, pp. 1–77, 161–172.

31

Refinery Management

Folkert J. Herlyn[1]

31.1 INTRODUCTION

“The oil refining industry is at a crossroad in its history. World refining capacity was in surplus from the mid 1970s to the mid 1990s due to overinvestment in the early 1970s, a downturn in demand after the oil shocks of 1973–1974 and 1979–1980 and the Asian financial crisis. As a result of strong growth in demand for refined products in recent years, spare capacity is diminishing rapidly and production flexibility even faster. Allowing for maintenance, there is now little scope for further increasing utilization; thus, capacity additions will be essential to meet growing demand for refined products.” (Fatih Birol, Chief Economist and Head, Economic Analysis Division, International Energy Agency [IEA]) [1].

The crude price is currently in waves: skyrocketing over a period of months and falling drastically in an even shorter period. The pressures related to environmental matters from tightening regulatory requirements and impact from climate change are the highest ever.

The refinery’s management is further faced with

- Increased variety of crude oils (heavier, more sulfur)
- Increased complexity of operations from increased diversity of products
- Tighter rules on product specifications and lower sulfur content
- Uncertainty in future refinery margins – ups & downs, but
- Positive average growth

As a result, the refinery management is faced with changing external factors while the facility change projects to adjust to these factors are getting more complex and are taking longer.

A refinery operations manager of a large oil company, responsible for more than 10 plants, said in the 1980s: “The console operator has in his hands the set point knob for the profitability of the refinery. Let us do everything to support him.”

Is this still true after almost 30 years? Is it valid today after integrated value chain planning, advanced control, process optimization, and total productive maintenance processes may have been implemented?

31.2 LEADERSHIP

Much has been written on the subject of leadership and as evidenced by the many MBA and other business school programs offering leadership as a study module, it would seem that many business academics have views on what their students should learn to become effective leaders.

In the recent management school literature, the effective leader has been likened in some ways to an orchestra conductor. He/she has to somehow get a group of potentially diverse and talented people to work together toward a common output or goal. Will the conductor harness and blend all the gifts his or her players possess? Will the players accept the degree of creative expression they have? Will the audience enjoy the sound they make? (This is arguably the goal of the whole orchestra as an organization.) The conductor, as leader, has a clear determining influence on all of these questions.

His leadership is regular: his authority to lead is clear. His means of influencing the members of the orchestra may be either direct or indirect depending on individuals, the gap in their performance, and the urgency of the required performance improvement (increasingly direct as opening night approaches).

Less noticeable in an orchestra though are the irregular, indirect leaders we find in the workplace, most often relatively junior in level of official authority and compensation, but with a disproportionate degree of (often negative) influence among peers, subordinates, and thereby indirectly amongst more senior management. The refinery leadership must also align the aims and actions of these sometimes uncooperative and even unwilling “leaders” throughout the refinery organization.

So, the role of the refinery leadership (which might be a sole refinery manager, or more often, the refinery manager and his senior team of managers of each major refinery function such as operations, maintenance, and engineering) is then to encourage behaviors among the refinery population that will allow them to reach their goal (and similarly to discourage behaviors that work against achieving this goal). The effective refinery leadership will also further help the members of their organization by clearing away any undesirable obstacles in their path as these are brought to their attention.

To do this, the refinery leadership must possess a range of leadership qualities, preferably personally in the refinery manager, or if not, then certainly among his small cadre of senior managers upon whom he can rely. These leadership qualities should include:

- A clear sense of purpose (or mission): Clear goals, focus, and commitment.
- Results-oriented: Directing every action toward a mission; prioritizing activities to spend time where results most accrue.
- Cooperation: The ability to work well with others.

---

[1] Herlyn Consulting, Köln, Germany, www.herlyn.com

- Sense of humor: The ability to see and to share in the humorous aspect of a situation.
- Awareness of environment: The ability to understand the environment they lead in and how they affect and are affected by it (in our experience, a strong grounding in the technical / specific skills of refining is required to fully possess this capability).
- Integrity: The integration of outward actions and inner values.

So, we know what refinery leadership needs to do, and what qualities they'll need to possess to do it, but can we advise on the most important question: to where, or in which direction, should the refinery be led? (It's our position here that an organization progressing untroubled in steady-state might need management, but only if we have to change direction do we need leadership).

Again current management school literature would say that the direction in which an organization is to be led is best expressed as a "vision." And further, to be effective, a vision should:

- Appear as a simple, yet vibrant, image in the mind of the leader
- Describe a future state, credible and preferable to the present state
- Act as a bridge between the current state and a future optimum state
- Appear desirable enough to energize followers
- Succeed in speaking to followers at an emotional or spiritual level

A leader, or the group of leaders, will therefore encourage, aid, and influence their employees to move the organization successfully towards this vision as their goal with a plan (sometimes called strategic change plan, strategic plan, or simply strategy).

So, with a vision, let's say *to maximize the utilization of feedstock at minimum cost,* and with the required leadership qualities, and a plan (or strategy) to move the organization towards the vision, it should be plain sailing for the leadership of a refinery, shouldn't it?

31.3 STRATEGIES

31.3.1 Definition

A strategy is a long-term plan of action designed to achieve a particular goal or desired change/end-state. Implicit in all organizations are the ongoing activities within each function, department, or plant (the "how do we do things around here" statements) driven by its local management, which are causing the small incremental changes within that function, department, or plant from today's performance to tomorrow's. See Figure 31.1.

Some typical functional strategies for a refinery might be:

- Ensure safe operations and maintain plant reliability
- Ensure quality and operations excellence in all areas
- Continue to improve profitability and competitiveness
- Comply to internal and external regulations
- Progress work and projects smoothly and safely
- Further improve working environment and teamwork

So, in order for the refinery leadership to deliver its strategy (that is, to move the organization towards its vision of *maximizing the utilization of feedstock at minimum cost*), it must cause change at the level of these local/functional strategies into "how will we do things differently here?" statements. To do this, the refinery leadership must, of course, provide details, targets, and action plans, for each functional strategy so that those employees required to execute the plans during their routine operations activities understand what is required of them and can be motivated to do them as required. But more importantly, the detailed targets and action plans for each functional strategy must be linked to ensure that when they are realized, they also realize the broader refinery strategy towards ***maximizing the utilization of feedstock at minimum cost.***

31.3.2 Checklist for Functional Strategies

So, firstly, how do we ensure we have considered all the functional strategies, that is the local action plans for which we'll develop a statement of "how will we do things differently here?" One helpful approach is the use of a structure that groups the functional strategies into functional areas. If we think of three major business process functions: operations (which we'll use interchangeably with production), maintenance, and reliability, we can then divide each of these into, for example:

- Planning process
- Performance analysis and review process
- Ownership and accountabilities
- Technology
- Leverage

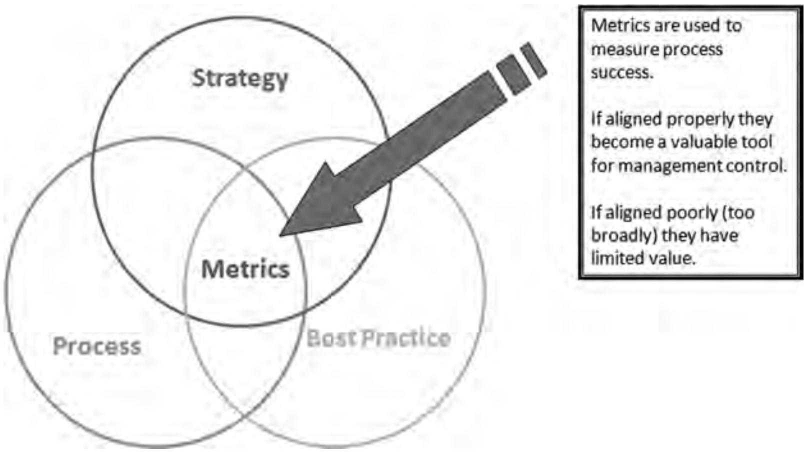


Figure 31.1—Strategy development elements.

TABLE 31.1—Checklist for Functional Strategies

Maintenance	**Reliability**	**Operations**
Planning process		
Central planning process	Central support process	Central support process
Expectation to maintenance excellence	Expectations to reliability excellence	Expectations to operations excellence
Project participation and planning	Project involvement related to reliability	Planning process integration
Shut down planning process	Reliability aspects in S/D planning process	Shut down planning synchronization
Cost optimization	Asset live cycle optimization	Production optimization
Performance analysis and review process		
Maintenance performance	Reliability performance	Production performance
Cost performance	Life cycle reliability vs. cost expectations	Cost performance
Equipment integrity performance	Integrity performance	Process integrity performance
Compliance to regulations		Compliance to regulations
Contractor performance measurement		Contractor support performance
Cost optimization	Cost optimization	Cost optimization
Ownership and Accountabilities		
Function and individual accountabilities	Function and individual accountabilities	Function and individual accountabilities
Governance	Governance	Governance
Data and communication ownership	Data and communication ownership	Data and communication ownership
Maintenance cost responsibilities	Life cycle cost awareness	Production cost responsibilities
Capitalization process on new investment	Capitalization process on new investment	Capitalization process on new investment
Support agreements	Support agreements	Support agreements
Technology		
Equipment technologies	Reliability analysis support tools	Process technologies
Monitoring technologies	Monitoring technologies	Advanced controls technologies
Asset management IT support tools		Process management IT support tools
Specialist IT tools and applications	Specialist IT tools and applications	Specialist IT tools and applications
Leverage		
Contractor philosophy	Service philosophy	Service philosophy
Spare parts outsourcing philosophy	Routine surveys and auditing	Auditing for integrity
Spare parts philosophy		Utility support and integration philosophy
Interface to engineering vendors	Interface to external support services	Interfaces to supporting functions
Information update process to as-built	Involvement in as-built updating	Information update process to as-built
Interfaces with other functions	Interfaces with other functions	Interfaces with other functions
Vendor assistance for technology support	Vendor assistance for technology support	Vendor assistance for technology support
Total productive maintenance	Total productive maintenance	Total productive maintenance
People (labor, specialist)		
Skill development	Skill development	Skill development
Training, external support	Training, external support	Training, external support

(Continued)

TABLE 31.1—Checklist for Functional Strategies (Continued)

Maintenance	Reliability	Operations
Compensation principles	Compensation principles	Compensation principles
Culture		
Planning and performance review cycle	Planning and performance review cycle	Planning and performance review cycle
Continuous improvement management	Continuous improvement management	Continuous improvement management
Quality management	Quality management	Quality management
Organizational learning	Organizational learning	Organizational learning

- People
- Culture

This second level of detail then demonstrates that each major business process can then be impacted by one, and sometimes more than one, functional strategy. An iterative check that each major business process has at least one function describing its own functional strategy to impact that business process will ensure that all functional strategies are described.

The value of this analysis comes when we recognize that, although each function (operations, maintenance, and reliability) accepts a charter to deliver its own functional strategies (see Table 31.1), they must at the same time realize the importance of working together with other functions to deliver the required change to the business process. None of them can be successful in isolation. Reliability, for example, is a shared responsibility between maintenance and operations, and a “how will we do things differently?” statement for the business process “improve reliability” would require input from both the maintenance and operations functions.

The development of functional strategies is an iterative process. Throughout the process, it is essential to involve key personnel to achieve their buy-in and to ensure their functional strategies focus on the main issues that must be addressed to deliver the refinery strategy.

31.4 BUSINESS PROCESSES

31.4.1 Introduction

Attempts to use business process analysis and BPM to re-engineer businesses down to the detailed refinery activities have cost some companies tens of man-years but were of limited value for developing optimization strategies. However, simple process models are used successfully for specifying information technology applications and structuring data resources.

Competitive benchmarking would not be easy without some form of structure aligned to business processes, and some simple business process models (BPMs) are effectively used to describe best practices and key performance indicators [2].

31.4.2 Scope

So, which business processes should we ensure we have functional strategies to address? This really requires us to look at whether the profitability of the refinery is really in the hands of the operator? If we look at Figure 31.2, which

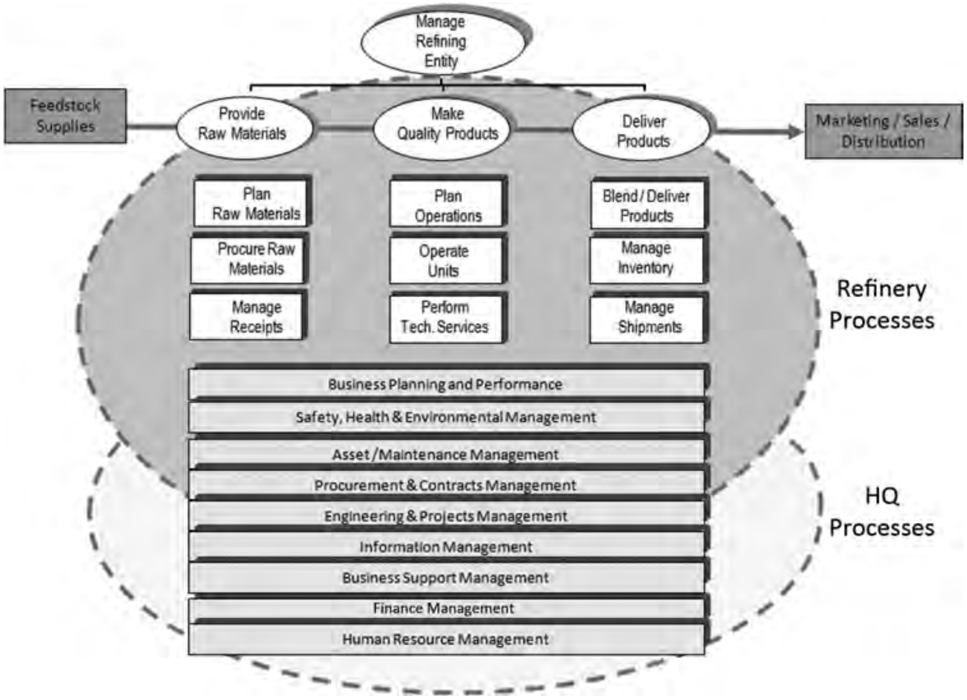


Figure 31.2—Major refining downstream processes.

includes the major refining downstream functions from feedstock supply to sales, we can see that a significant part of the processes are typically covered by headquarters organizations/functions and another large part by the refineries distributed within a country or a region. This sort of a diagram is helpful to define the scope of management for the refinery team. It makes clear that the primary businesses of the value chain between supplier (feedstock supplies) and the customer (distribution) does includes production (manage refining entity), and it shows all the other functions classically considered "support functions" by followers of Michel Porter. If we accept this, then it is entirely consistent that the profitability of the refinery is (largely) in the hands of the "operator."

Is there any value in analyzing the business processes of refining?

31.5 BENCHMARKING AND BEST PRACTICES

31.5.1 Introduction

Benchmarking (also "best practice benchmarking" or "process benchmarking") is a process used in management and particularly strategic management, in which organizations evaluate various aspects of their processes in relation to best practice, usually within their own sector. This then allows organizations to develop plans on how to adopt such best practice, usually with the aim of increasing some aspect of performance. Benchmarking may be a one-off event but is often treated as a continuous process in which organizations continually seek to challenge their practices.

Benchmarking is a powerful management tool because it overcomes "paradigm blindness" – the belief that "The way we do it is the best because this is the way we've always done it." [3]. Benchmarking opens organizations to new methods, ideas, and tools to improve their effectiveness. It helps crack through resistance to change by demonstrating other methods of solving problems than the one currently employed, and demonstrating that they work because they are being used by others.

31.5.2 Benchmarking Process Example

The process of benchmarking is shown in Figure 31.3. Assuming the best practices (reference practices) are collected, then they have to be adapted (conditioning) to the specific purpose. The comparison of the best practice with the actual state will results in proposals for actions to change current practices.

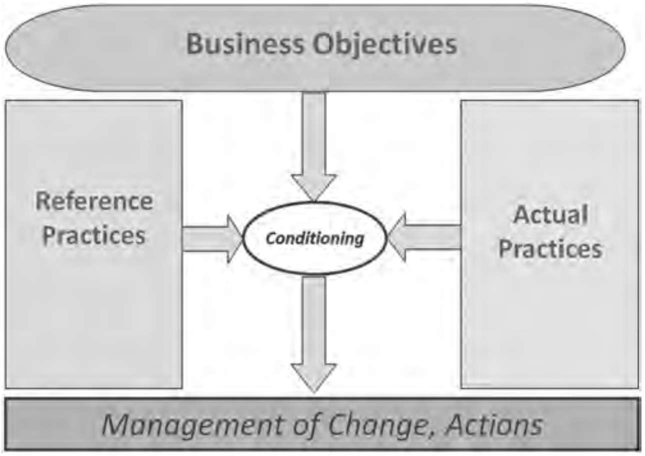


Figure 31.3—Benchmarking process example.

Large oil companies have built up benchmarking knowledge in such a way that they can compare a simulated reference refinery with the physical installation. If best practices are not available, then they will have to be collected, and there are a variety of places to look:

- Who performs the business process very well?
- Who has practices that are adaptable to your own organization?
- Who is most compatible to conduct the benchmark with?
- Obtain 80–90 % of what you need just from using resources of a different nature.
- Networks, consortium, internet, consulting companies, etc.

31.5.3 Best Practice Example

After the best practices have been collected and adjusted to the site's needs, they can be used to better understand the present situation. Each function may have 10–20 best practices that should be listed (one is shown in Table 31.2 by way of illustration) [4]:

TABLE 31.2—Best Practice Example Listing

Unit: Refinery				
Best Practices Hydrocarbon Processing Plant, Reliability Management Example				
Best Practices				
Business Process Model Number	**BP Name**	**Practice**	**How to**	**Enablers**
1,2	Reliability strategy is available	Establish a reliability strategy that defines the expectations for all functions in the organization which contribute to the process and maintenance excellence.	The reliability strategy includes shared goals from all functions of the organization. It formulates the concepts to achieve the goals. These concepts include (1) Reliability and maintenance concepts. (2) The organizational concept to ensure effective design, management and delivery of specified plant availability performance. (3) The computer systems concept associated with the other two concepts.	Site management strategies

The present situation may be scored relative to the best practices. Although the scoring is rather subjective, it assists in better quantifying the current state in comparison to best practices. The quantification leads more to focusing on areas that need highest attention. The outcome may look like Figure 31.4.

After the benchmarking, relative to best practice, has been completed, the usually experienced internal barriers to change are significantly reduced. It is a good way to get buy-in.

31.6 MEASUREMENTS: KEY PERFORMANCE INDICATORS (KPIS)

31.6.1 Introduction

The missing element to good strategy development is quantitative targets. This section outlines "measurements"– the important element to successful strategy development, implementation, and control of progress.

In an ideal world, people would know intuitively what was going well and what was not. Intuition would be part of the toolkit of skills brought to bear on problem resolution; decisions would be easy to take [5].

Unfortunately, this is not an ideal world. People live in a complex environment where cause and effect have become lost in the mass of data received, which must be processed before it is possible to act. For example, when overtime cost is up and maintenance on line performance is down, how does the leader know which thing to address and what to look for? Energy consumption has risen, and the total production output is less. Why is the energy consumption higher? With 1 % too much energy on a 100,000 bpd refinery costing about US$ 4 million/year, it is worth having performance indicators (PIs) that permit fast "drill down" of information into the system for analysis and decision making.

Measurement and evaluation of performance are central to control of hydrocarbon process plants. The refinery manager needs to be able to answer four basic questions:

- What is happening and what has happened?
- Why has it happened?
- Is it going to continue?
- What needs to be done about it?

If the first question can be answered by accurate performance measurements, then this same information can be usefully applied to better answer the remaining three.

31.6.2 Current Issues

All plants have formal or informal performance measures throughout the organization. They evolve over time and are available in for example daily, monthly, and yearly reports and other such means. Unfortunately, many indicators are not providing measures for the most important issues, or they have limited credibility due to inconsistent data or lack of timeliness. Others may be outdated and become a burden in reporting. Some people feel also overwhelmed with the amount of data that is printed in frequent reports or is available on network billboards. In many cases, there is neither visible structure for selection nor adequate management process for maintaining PIs to their full potential.

31.6.3 Opportunity

Carefully selected and managed performance indicators drive the efficiency and effectiveness of the organization towards success. About 50 to 100 indicators can provide the necessary knowledge for meaningful diagnosis. Additional measures (100 to 200 or more) permit "drill down" into the details of an issue as required. A good selection provides a balance between financial and technical performance information and between detail and overview (e.g., a good system of PIs should be designed to permit senior management to find condensed information to "control by exception" while the engineer uses the full information effectively to relate the actual value to the desired state). Such targets or criteria may be benchmarks, optimized process parameter settings, or quality-related information within ranges. Others may originate from the business strategy development process and need to be monitored over a longer period.

Overall, performance indicators are available in well-performing plants that satisfy all levels of the organization for transparency and timeliness. A roadmap on the best selection and setup of performance indicators is provided below.

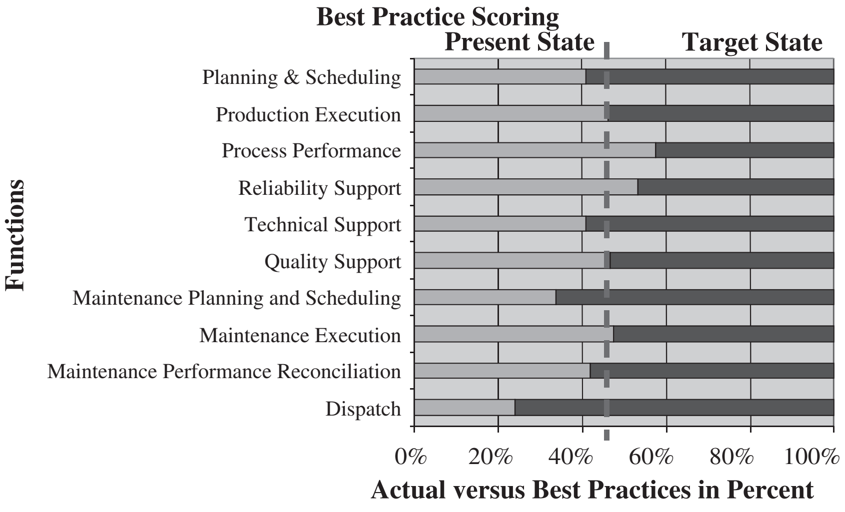


Figure 31.4—Best practice scoring example.

31.6.4 Business Perspective and Balanced Scorecard

At its core are the corporate and local business vision and the strategy. By measuring financial performance, organizational effectiveness, customer satisfaction, and operational efficiency the long-term refinery strategy can be linked to short-term actions within the functional strategies. The vision should set and the strategy should drive the components of the performance monitoring system. This system, sometimes also known as the balanced scorecard, makes visible an understanding of what is critical to survive and to succeed (see Figure 31.5) [6].

As shown above, the scorecard should, for example:

- Include financial and non-financial measures.
- Align departmental goals with vision and strategy.
- Reflect commitments to safety, reliability, environment, and customer service.
- Link measures throughout the organization.
- Be shared with as many staff as is practical.
- Involve staff members during design.
- Be maintained with a continuous improvement process.
- May be linked to compensation.

31.6.5 Getting from Business Vision to Performance Measures

The link between the vision and strategy and the metrics is provided through sample best practices (or other key practices measure), as explored in the previous section. The best practices provide the path to, or the targets for, the desired state of the business. If we want to understand performance, and track our progress along this path, we need to compare our performance against these targets. A simple measure of actual/current to historical performance is valuable, but in many cases not enough; without the target expressing the relationship with the business vision and strategies (Figure 31.5), it wouldn't be clear whether any deviation was in the desired direction or not.

The link from the vision "to be the best…" requires a series of individual functional strategies. These functional strategies will require action steps for getting the desired results. As an illustration, one such functional strategy might be to drive the cost down by reducing the energy consumption without penalties on product quality and plant reliability. The success of actions to achieve the reduced energy consumption must be monitored in real time, over time, and in relation to a target of, for example, the energy efficiency index (EEI). In case of deviation, the staff members will have to analyze the cause and take action to make changes.

A single measure such as the EEI for the total plant is not enough to gain sufficient knowledge to act on. "Drill down" information with sub-targets and measured data reflecting the type of feedstock, the products, and the plant configuration are necessary. Figure 31.7 provides an example of the "drill-down" structure needed for effective search of cause and effect of deviation (also shown in Figure 31.6).

Figure 31.5—Survive and succeed criteria viewpoint.

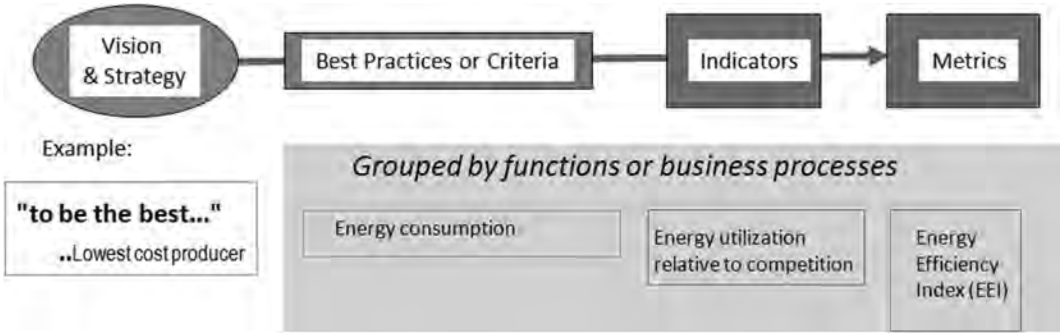


Figure 31.6—Vision linked to performance.

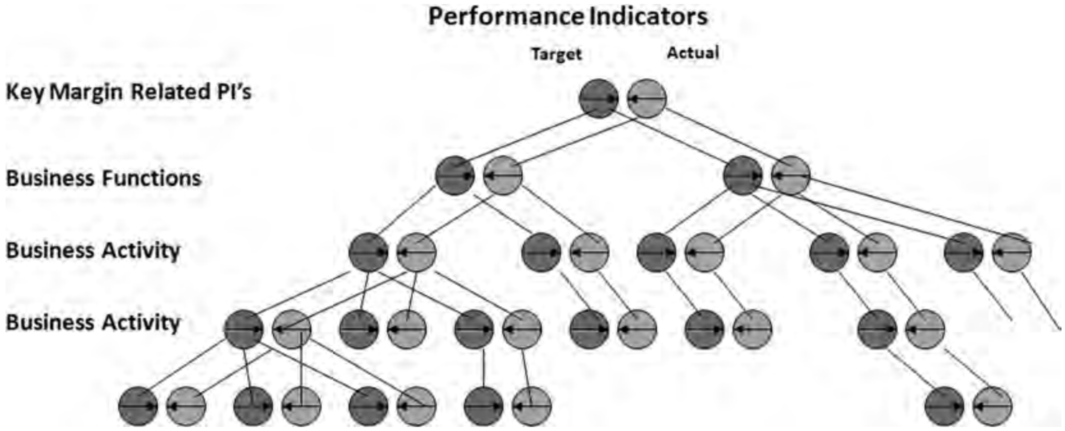


Figure 31.7—Target and actual comparison for "drill down."

Usually, the planning group will have the tools and capability to define the target of the energy index, and many others, precisely. Technical targets will also be provided for technical staff such as inspection and mechanical and process engineering personnel. Finally, each group will use its own performance indicators, all of which should be clearly linked to the business objectives.

31.7 CHANGE MANAGEMENT: STRATEGY IMPLEMENTATION

We posed the question earlier, "So why do so many good strategies fail, and what can be done to effectively lead these strategic plans?"

In our experience, there are three parts to developing a good strategy:

- Analyze the market (its current and future state projection), our current situation versus best practices, our desired changed state (with respect to our view of the market), next
- Develop the strategy (our plan of necessary change actions to get to our desired changed state), and
- Implement the strategy (make the necessary changes and monitor the effect of these).

Although we have spent time discussing in detail the first two steps, the toughest step by far is the implementation. The implementation of the strategic plan requires *management of change*. The key to the change is to change people's behavior and behavioral change requires a shift in their thinking. To achieve this may require many changes in the way things are currently done (by way of illustration, a change program in the maintenance function may have the behavior change objectives identified in Table 31.3). This might include or require changes to some "sacred cows" such as changes in compensation and authority: strategic change is difficult because people often perceive they will lose power and/or resources. But most importantly, it will require a change in people's perception of what their own contribution (and value) is to the business today, and in the future changed state.

Much has been written about *management of change*, and there are many academic/sociological models available which seek to provide explanations and guidance on how best to effect organizational change. But in our practical experience there are five prerequisites for any change program:

1. Plan: The change plan must be thought through with the same discipline as the development of the strategy that it will cause to happen.
2. Focus: The strategic change plan must set priorities. Too many tasks at once can overwhelm even the believers.
3. Accountabilities: Managers should be assigned specific change tasks and specific objectives to work towards. If they feel like their input to the change program is essential (which of course it is), this will help to ensure their buy-in.
4. Communication: Change can be a threat or an exciting journey. One must promote the benefits of change to the internal team as much as to the customers, and be realistic about any threats that may result.
5. Courage: When the change plan is defined and communicated, courage is needed to push the change program through.

This section has provided a methodology that will equip the refinery leadership with the ammunition to address the first four of these, and in so doing will provide

TABLE 31.3—Maintenance Example for Change Management

Current Behavior	Target Behavior
✓ Disruptive scheduling, coordination	✓ Job planning, controlled scheduling process
✓ Immediate response / failure focus	✓ Predictive/preventive vs. corrective
✓ Victim mentality	✓ Proactive
✓ No control	✓ In control
✓ Allocation of maintenance cost	✓ Charge for services rendered
✓ Buffer hourly staffing	✓ Optimal hourly staffing

them with the confidence to enable them to act in ways which demonstrate the fifth.

31.8 FURTHER AREAS TO SUPPORT SUCCESSFUL REFINERY MANAGEMENT

31.8.1 Management of Planning/Scheduling and Control

31.8.1.1 INTRODUCTION

A competitive refinery needs an optimal plan for use of labor and equipment, raw materials or feedstock, inbound/outbound transportation, storage capacity, and other constraints that may affect the decision of what to produce, when, and in what quantity, balancing the tradeoffs between all constraints to meet management goals.

The planning process is a loop ranging from, for example, crude selection to production, performance analysis of operations, and the shipment of the products. It is an important activity to synchronize all activities based on the customer product requirements. These requirements are usually defined by the market or the sales team. Figure 31.8 demonstrates the feedback process along the individual planning process steps.

31.8.1.2 CRUDE OIL SELECTION

The optimized crude selection for each refinery based on customer requirements is unique to each plant's configuration, logistical capabilities, and product slate and price variations. Refining optimization and crude selection in "Best Practice" refineries, utilize linear and nonlinear models. Short-term crude selection may be based on variable cost and profit opportunities. Not necessarily minimum cost but maximum utilization of facilities at maximum profit. Incremental capacity and crude/product opportunities may be analyzed on marginal economics of cost/profit model evaluations. These are complex calculations and include information from many sources such as:

- Crude assay data that define the crude quality
- Assays model feedback factors included from actual runs
- Plant configuration in the form of a model with yields and energy impact
- Processing and transportation data relationships easily structured
- Plant availability
- Cost and product/feedstock price information

The solution determines the optimal crude from availabilities and the related need of resources and sourcing patterns, considering capacities of production and distribution assets. Business objectives, such as cost minimization or profit maximization, are used to finally develop the plans.

Figure 31.8—Planning process.

With such a tool in hand, powerful scenario analysis is possible: it enables planners to develop and compare multiple scenarios for operations.

31.8.1.3 PLANNING AND SCHEDULING

The main plan driver is always the product requirements. Spot sales or long-term contracts define the frequency. The typical plan frequency is monthly, quarterly, and yearly with some updates within a month. Companies have realized that weekly planning is appropriate if the market changes quickly.

The plan data are used to develop the schedules. Those schedules must include logistics and distribution data in detail on a daily basis as well as maintenance/equipment availabilities from the maintenance planning/scheduling system. A main feature of today's scheduling systems is the blending optimization. The planning runs ensure the availabilities of blend components, but the blending optimizer calculates the most cost effective solution to meet the product requirements. Actual component qualities, inventory, and cost per component are included for blending optimizer output.

31.8.1.4 OPERATIONS AND SHIPMENT EXECUTION

With the schedules in hand, the operations and shipment instructions are transmitted for execution. A good, accurate planning system will provide trust in the instructions and ensure that the customer requirements are met and at the same time that the business strategies are implemented. As such, the planning system quality is the most valuable tool for the management to achieve its objectives.

31.8.1.5 PERFORMANCE MONITORING AND ANALYSIS

Performance monitoring includes all areas of the refining functions; however, the most critical one is the monitoring of the process in real time and over a longer time period. The source of data is usually the DCS (distributed control system) with digital gateway to an RTDB (real-time database system). The data are stored over time in hourly, daily, and monthly averages as predefined by the people that need it.

Performance monitoring means the comparison of, for example, process data to history data or to targets. The targets may be a result of complex process simulation or production plans and schedules. Performance monitoring is different if performed by different vertical business levels. The financial department is interested in the accounting data of production and its financial performance, while a maintenance person is interested in the corrosion of some equipment from pH control results or the vibration level of a pump. Figure 31.9 represents the different levels of performance and control areas to the process.

A prerequisite for all performance monitoring activities is the availability of recent, accurate, and sufficient data. The trend is to increase the real data input as instrumentation becomes less expensive and data analysis more automated. Usually, the DCS data are transferred to an RTDB for analysis. The RTDB receives and stores the data at regular intervals. The value has a time stamp and an identifier that represents a unique tag name. Above the RTDB system is the refinery shared database (relational database) that acts also as an integrator to many other applications and systems. Tools should be available for process analysis, such as

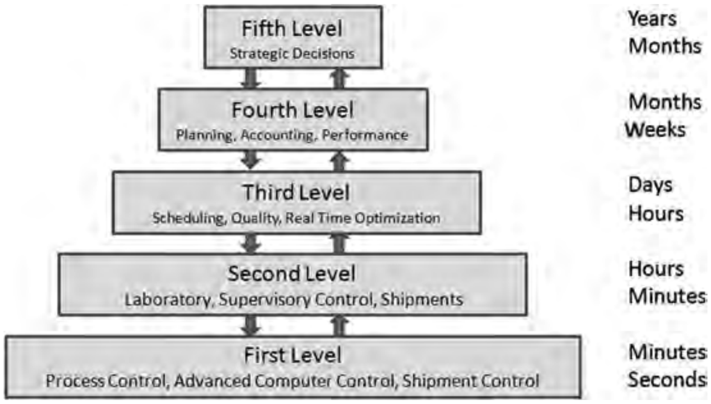


Figure 31.9—Information and control levels.

statistical quality control, data reconciliation, and process simulation (steady state and dynamic). The RTDB may also house all key performance indicator calculations that are described in previous sections.

At best, the planning and control process is continuously improved and aligned to the business objectives. If equipped and applied with appropriate information systems on the site networks, it is the most valuable tool not only for the refinery manager but also for each individual at site.

31.8.2 Safety, Environmental Management, Industrial Health, and Security

31.8.2.1 EXAMPLE INCIDENT DESCRIPTION

At approximately 1:20 p.m. on March 23, 2005, a series of explosions occurred at a refinery during the restarting of a hydrocarbon isomerization unit. Fifteen workers were killed and 180 others were injured. Many of the victims were in or around work trailers located near an atmospheric vent stack. The explosions occurred when a distillation tower flooded with hydrocarbons and was over-pressurized, causing a geyser-like release from the vent stack [7].

31.8.2.2 INCIDENT PREVENTION

The highest priority of refinery management is compliance to safety, environmental targets, health of personnel, and security. All of these functions to manage are related to survival.

31.8.2.3 RISK MANAGEMENT

It begins with a plan. A risk management plan (RMP) is a proactive identification and assessment of the potential incidents or hazards. An assessment is an analysis of the current potential and past dangers and incidents and near misses for safety, environmental issues, and industrial health. Based on this plan, a prevention program is developed to address and mitigate any potential hazards or possible incident within the assessment. The goal is to avoid any noncompliance to the internal goals and external regulations. Usually, a prevention program addresses 12 safety elements:

- Safety information
- Hazard analysis
- Operating and maintenance procedures
- Training
- Mechanical integrity
- Management of change
- Pre-startup safety reviews
- Compliance audits
- Incident investigations
- Employee participation
- Contractor safety
- Emergency response

31.8.2.4 INCIDENT INVESTIGATIONS

Root cause investigations of incidents must be conducted to understand the reason and to prevent any incident recurring for this or similar reasons. Root causes of the example described above are usually deficiencies in safety management systems but can be any factor that would have prevented the accident if that factor had not occurred. Other accident causes often involve equipment failures, human errors, unforeseen chemical reactions, or other hazards.

Each near miss and each incident will require root cause analysis by a team setup from in-house personnel and with support from external organizations. In the United States, for example, regulatory agencies such as the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA), industry organizations, and labor groups make recommendations for prevention as well as part of the analysis after an incident has occurred. It becomes apparent that a well-designed performance control system provides meaningful data also for better root cause analysis.

Practices and procedures: Effective organizational practices and procedures, such as encouraging the reporting of incidents and allocating adequate resources for safe operation, are required to make safety systems work successfully.

31.8.2.5 INTEGRITY AUDITS AND IMPLEMENTATION OF RECOMMENDATIONS

Operational and equipment integrity should not be compromised, including the training for personnel for handling. Cost-cutting measures have intervened with work to get things right: often reliability improvements and training are cut.

31.8.2.6 INCIDENT RESPONSE

Part of the practices and procedures include an emergency response system. In the event of an emergency, a refinery's first contacts are made to internal management and external agencies, This system is dictated by the emergency situation, applicable regulations, and response protocol. Persons may be contacted by phone, fax, or detection devices. These contacts decide on next steps that have been defined as part of the response system procedures. Automated phone and radio systems supplement fire and police notification tools, for example, to direct the community to either shelter in place or evacuate.

31.8.2.7 CULTURE

Finally, the organization's culture toward safety, environmental management, and industrial health, most noticeable in the provision of sufficient resources to achieve all commitments, is a key to success. A statement of the CSB Chairman Carolyn W. Merritt in the United States on March 20, 2007: *"Process safety programs to protect the lives of workers and the public deserve the same level of attention, investment, and scrutiny as companies now dedicate to maintaining their financial controls. The boards of directors of oil and chemical companies should examine every detail of their process safety programs to ensure that no other terrible tragedy (like the one described above) occurs."*

31.8.3 Cost Control

31.8.3.1 COST CONTROL ISSUES IDENTIFIED

A current concern of any manufacturer is cost. For managers faced with reducing cost, budgetary and actual cost reports are typically their only insight into cost reduction opportunities. Unfortunately, these tend to be vertically based; they represent the business on a departmental responsibility basis. There is often insufficient understanding of costs by unit or individual equipment. Mostly predetermined allocation is used to get at least some insight. For good cost control it is necessary to understand how much of the overall cost is related to, for example, the maintenance of individual equipment. How much is related to services from technology, engineering, and central technology organization, and to which equipment or project? Does it include shop floor work not counted for in a work order system? Without a drill-down system or proper actual cost, it will be difficult to trace the cost and who has requested work. Without proper cost allocation assignments based on the cause and effect principle with the drill-down capability, it is extremely difficult to control expenditures as there is less care taken in identifying really necessary spending, and less chance to understand waste in the system. In this situation, nobody is held accountable for costs getting out of control.

Clearly, a customer that is held accountable for resources requested will use those requests wisely. In a situation where costs are wrongly assigned, it may appear that costs exceed targets or costs have increased above industry average. This may in turn lead to corrective actions that, based on inaccurate costing information, may be unwise, for example, the conclusion to outsource some of the maintenance activities. It is unwise to act without clear understanding of the total picture and costs involved. As has been found during a wave of maintenance outsourcing recently, such decisions may be detrimental to the refinery's strategic objectives. Victims of these trends have often been shop services for the fleet and for repair of equipment with the assumption that outsourcing of these activities would be for the better.

31.8.3.2 ACTIVITY-BASED MANAGEMENT (ABM)

ABM, of which activity-based costing is only a part, has been shown in some circumstances to provide a more competitive operation. The principle of ABM is to run functions or departments, such as maintenance for example, as businesses within the business units and not as departments. ABM can play a critical role by improving a company's understanding of its product profitability, cross functional process cost, and proper performance measures.

ABM provides more than just valuable product cost information; it also highlights the consumption of resources from a cross-functional perspective (e.g., steam, electricity, laboratory sampling cost, and contractor cost). For example, the true cost of outsourcing to contractors is probably greater than the cost of a contractor hourly rate itself when one includes the accounting, logistical issues within maintenance, and contract services performed by internal individuals. Benefits from understanding this information include supporting outsourcing decisions, elimination of redundant activities, or developing programs to ensure that activities are performed more efficiently and effectively.

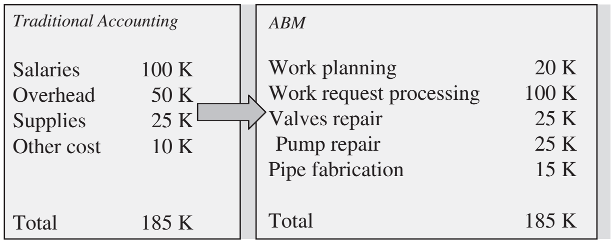
ABM concepts move the emphasis away from vertical department focus to a horizontal business process focus (see Figure 31.10). ABM concepts will shift away from an overhead based measure to a business product measure with insight into maintenance results as opposed to hours.

Within the maintenance function, cost control is possible if all activities are charged to the repair work order raised. That work order is equipment specific and closed after the work is completed. Standing work orders should be minimized, but all work should apply the work order system for recording. Once activities are understood managers can set up systems that help manage people to perform more preferred behavior (see Figure 31.11).

Tools need to be available to accomplish ABM; however, the system must be set up and loaded with sufficient base information to define the functions and set up the screens for easy use. A user-friendly information access system will encourage the users to analyze cost as part of their normal activity. Example:

Under ABM, the shop services provide services at cost per unit and bill the hours at true cost so that the repair cost can be compared to outside services. The safety valve shop no longer sells hours; it sells rebuilt valves charged to a specific work order. The shop may bill on price list just like their competitors. The price list is developed based on process value analysis. Additional process value analysis was also performed on outsourcing valves. Based on the results of such an analysis, outsourcing may not be the best way of servicing valves.

The laboratory cost may be allocated to sample types. It is apparent that the cost assignment based on cause and effect principle by the samples analyzed will trigger opportunities for optimization. If the sample frequency is too low, there may be lower yield recovery for the higher value



Traditional Accounting	
Salaries	100 K
Overhead	50 K
Supplies	25 K
Other cost	10 K
Total	185 K

ABM	
Work planning	20 K
Work request processing	100 K
Valves repair	25 K
Pump repair	25 K
Pipe fabrication	15 K
Total	185 K

Figure 31.10—Typical versus activity-based management for maintenance services.

Current Behavior	Target Behavior
❖ Disruptive scheduling, coordination	➢ Job planning, Controlled scheduling process
❖ Immediate response / failure focus	➢ Predictive / preventive vs corrective
❖ Only use maintenance when necessary	➢ Maintenance as business partner
❖ Use outsiders when possible	➢ Service provider of choice
❖ Victim mentality	➢ Proactive
❖ No control	➢ In control
❖ Allocation of maintenance cost	➢ Charge for services rendered
❖ Buffer spare parts industry	➢ Optimal parts inventory
❖ Buffer hourly staffing	➢ Optimal hourly staffing

Figure 31.11—Typical and target behavior shift with support of ABM.

product sold. Overall, the unit supervisor will have, through activity-based costing, better tools in his hands to balance between quality control cost and product give-away. He may evaluate the need for on-stream analyzers if he is forced to control quality as often as once per shift or more. In addition, the advanced process control application may require real-time quality information to operate closer to the product specification. The activity-based cost analysis provides information for true incentive calculations.

Overall, one of the successful management tools to optimize the cost is ABM. Its use helps costs to become more transparent and useful as part of the planning optimizers.

31.8.4 Information and Knowledge Management

31.8.4.1 INTRODUCTION

A competitive refinery requires an information system that

- Integrates business processes and technology to improve manufacturing productivity, profitability, and assets.
- Enables make-to-order and shortens fulfillment time from demand-driven production planning.
- Connects to e-marketplace and based on collaboration.
- Increases customer satisfaction through Web-enabled visibility and transparency of the plant's capability to promise and deliver product(s).
- Synchronizes with ERP (enterprise resource planning) and provides access to information throughout the supply chain.

Such a system will enable excellence in refinery operations and provides a sustainable competitive advantage in the marketplace.

Over the past three decades, refineries have implemented many applications as driven by the individual divisions. In the early stages of computing, it began with laboratory automation. Later, the maintenance work order systems were added and then the data from DCS collected frequently into unique databases, called a real-time database or a historian for the process data used by the technical personnel. Many small applications were added (bolt-on), justified by local immediate need, without a strategy or a master plan. As a result, the proliferation of applications was high, and IT personnel had to deal with many systems. Management was dissatisfied with the results.

31.8.4.2 MANAGEMENT SYSTEMS

One reason for dissatisfactory IT systems at refineries is often the lack of adequate management or governance systems. IT Governance is *"a framework for the leadership, organizational structures and business processes, standards and compliance to these standards, which ensure that the organization's IT supports and enables the achievement of its strategies and objectives"* [6].

In particular, IT governance defines the following topics:

- What type of IT governance decisions have to be taken? (Scope)
- Who has the final decision for which type of decision? (Roles and Responsibilities)
- Which mechanisms have to be followed to come to these decisions? (Control)

IT governance is a critical component of corporate and refinery governance.

31.8.4.3 GOVERNANCE – SCOPE

The impact on the business of an organization's IT is high and continuously increasing. Recognizing this, business functions are rightly demanding the participation in key IT decisions. At the same time, IT is emerging as a key business function. IT organizations should be proactive in identifying new IT opportunities to provide a competitive edge to the business through more effective execution of differentiating business processes. No longer the reactive supporting department, IT management positions are increasingly being viewed as key board-level appointments, alongside the business unit managers they support.

In an ideal situation, IT management is being aligned directly to the board to proactively facilitate and implement the needs of the business functions. An effective IT governance structure can realize some of the benefits of this ideal situation. Refinery IT groups are functionally linked to company IT management and take advantage of the management systems related to infrastructure and some applications. The company IT organizations must ensure that the refinery technical type applications are of a high standard. This is more likely to happen if the refinery has an IT group that has a clear charter and strong support from management. The governance portfolio must reflect this.

31.8.4.4 ROLES AND RESPONSIBILITIES

The IT function must assume the role of a reliable utility provider who supports the refining operations. It does not matter where the role and responsibilities are located in either the headquarters or in the plant. This is often dependent on the size of the company and the refinery.

The IT function's role is to:

- Promote, standardize, and support technology, license agreements, and operating system decisions. This includes infrastructure elements, tools, and applications to standardize hardware/software equipment.
- Provide IT service management.
- Provide knowledge management, including guardianship of the company's intellectual capital.
- Establish and maintain project governance principles.
- Conduct risk analysis and provide risk/security management.
- Ensure business continuity and disaster recovery.
- Maintain regulatory compliance.

While remaining the responsibility of the IT function, all of these roles are carried out in a highly interdependent relationship with the users. For this reason, the actions to be taken to fulfill the governance requirements can be neither entirely that of IT, nor of the user, but will be dependent on individual situations.

Some will be readily apparent, such as that the responsibility for all IT hardware and base software should rest within the IT function, as should the responsibility for information security. Other areas are less clear, such as that the IT function might have responsibility for an application's development and support, but not necessarily for its operations. The responsibility for applications might rest within the business function, for example:

- HR application system (HR)
- Finance application system (finance)
- Refinery information system (refinery)
- Maintenance application system (refinery)

Service agreements should be developed to clarify the responsibilities related to all systems in sufficient detail such that there is no scope for misunderstanding.

For this reason, it is essential that the requirements and responsibilities are laid out clearly in Policies and Procedures, which can be established and then monitored by an IT Governance structure. These are both described below.

Policies

Policies are high-level documents developed by management to transmit its guiding strategy and philosophy to employees. They define, detail, and specify what is expected from employees and how management intends to meet the needs of customers, employees, and stakeholders. Policies can be developed internally, or can be based on international standards such as Common Criteria or ISO.

An example of one specific type of policy is the organization's security policy. Another would be the organization's policy on procurement and standardization of individual user PCs.

Procedures

Procedures are somewhat like children—they are detailed documents built from the parent policy. They require more frequent changes to stay relevant to business processes and the technological environment. Procedures are detailed documents tied to specific technologies and devices. Procedures change when equipment changes. For this reason, the prime concern of a refinery is related to procedures that need to be updated with the updated IT strategies and the implementation of larger projects such as workflow and refinery information system (RIS).

Policies and procedures should describe the specific responsibilities for all areas covered by the IT function.

31.8.4.5 CONTROLS

The company has to meet two specific goals:

- Align the goals of IT to the goals of the company—both must be focused on and working for the common good of the company.
- Establish accountability—accountability requires that individuals be held responsible for their actions.

Accountability can be seen as a pyramid of responsibility that starts with the lowest level of employees and builds itself up to top management. It is, however, best described from the top down, and this top-down structure of committees, each with defined accountabilities for defining, monitoring, and reporting compliance, is an essential requirement of IT governance.

31.8.4.5.1 Company IT Steering Committee

The overall IT governance of a company is directed through an IT steering committee with members that are accountable for all policies and procedures covering all IT service provision, but paying particular attention to the larger business applications.

The committee is responsible for reviewing the steady-state performance of IT support at the sites, and of the IT function and major IT projects, budgets, and plans. These duties and responsibilities should be defined in a formal charter. The charter gives the committee the power to provide strategic guidance. The committee should not be involved in the day-to-day activities of the IT function.

Use of the balanced scorecard at the organizational level is a good method for the steering committee to measure performance and align business strategy with IT objectives. It can be used to foster consensus among different organizational departments and groups. The information gathered by using the balanced scorecard should be passed down the organizational structure to supervisors, teams, and employees (Figure 31.12). Managers can use the information to further align employees' performance plans with organizational goals.

31.8.4.5.2 Site Steering Committees

The steering committee by refinery is responsible for:

- IT planning
- Site development and implementation of projects and applications
- Operation and maintenance of site-owned systems and networks
- Management of site-owned data, practices, and procedures
- Review of performance on a frequent basis.

The plant's performance is highly impacted by IT. Each Site IT steering committee should contain a representative from the headquarters IT function to ensure common standards across sites, sharing of development activities, and shared services to minimize cost.

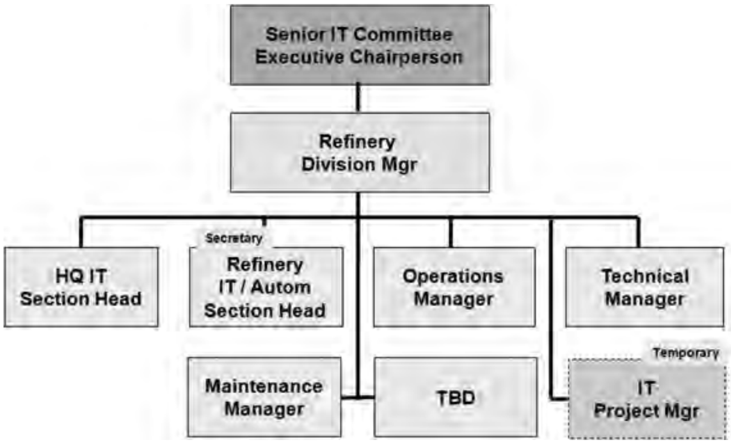


Figure 31.12—Refinery IT steering committee example.

31.8.4.5.3 IT Governance in a Major Project

It is necessary to set up a project team for a large single project such as RIS or maintenance work order management system, which will ensure that the implementation meets the business objectives. This will necessarily operate outside of the usual IT Steering Committee structure until it is fully implemented and handed over to the responsible sites in steady state.

31.8.5 Skill Levels and Training

The refinery is a complex technical manufacturing site and needs high (technical) skills at all levels of the organization. Typically, management systems assist in selecting personnel according to their leadership potential and less to their professional knowledge. As a result, some professional personnel may consider seeking other opportunities where their skills are more valued. Skill levels and lack of a transparent skill development framework are serious issues for the future growth of refineries.

It is mandatory to establish and communicate a career (skill development) system that provides advancement for all professionals. Successful career development frameworks are implemented that reflect the needs.

Broad development of professional knowledge and its recognition should be developed together with clearly defined role statements and mentorship relations. Both the clients (for example, production leaders) and the service persons (technical professionals) must share expectations and performances based on a structure that could be expressed in the form of a detailed skill matrix.

If the technical person does not see a career in the technical field, he will not try to develop himself to his maximum professional potential. This may be one reason for insufficient plant reliability.

ACKNOWLEDGEMENTS

Steve Price, Executive Director, European Institute for Industrial Leadership (www.eiil.net)

31.9 APPENDICES

31.9.1 Refinery Business Processes

Typically, about 40 to 50 main business processes or business functions are needed to manage a refinery of medium complexity (10 to 20 units). Each of these functions includes 5 to 10 major activities. These can be represented on a BPM, a diagram of each of these major functions and activities. A generic model (see below) can be used to explain the management challenges and improvement opportunities faced by a typical refinery management.

Firstly, we should differentiate between a BPM and organization chart. Organization structures at a site may look similar to the BPM, but they are highly dependent for their detail on, for example, the local situation, desired business focus, skill availability, and complexity of production. A BPM, however, will differ less between refineries since it always describes the functions in a company without the duplication of an organization chart. For example, a refinery with 20 units has 20 unit supervisors on an organization chart, but in a BPM it would say *supervise unit*. As a subset, the activities would be defined to operate the units. There is then no difference between a unit that produces a gasoline component and one that extracts hydrogen from fuel gas. The BPM view is on the process and not on the content within the process.

Details of those refinery functions within the responsibility of the refining organization are further explored in Figure 31.13.

31.9.2 Business Process Descriptions

In the following descriptions, we'll use the business process descriptions used in the generic BPM.

31.9.2.1 MAKE QUALITY PRODUCTS

This includes all production functions from feedstock receipt to product delivery.

31.9.2.1.1 Operations Management

Operations management represents the natural clustering of all functions and entities that physically operate the facilities and produce the products. Included are those functions and entities that are required to plan, operate, move, store, and dispatch feed and products. Also included are the direct processes technical and support services (e.g., process engineering and quality assurance).

Feed and product planning and scheduling, develop feed and product plans

Feed: The activities needed to plan, select and allocate feedstock (for example, crude) within the site, for both the short

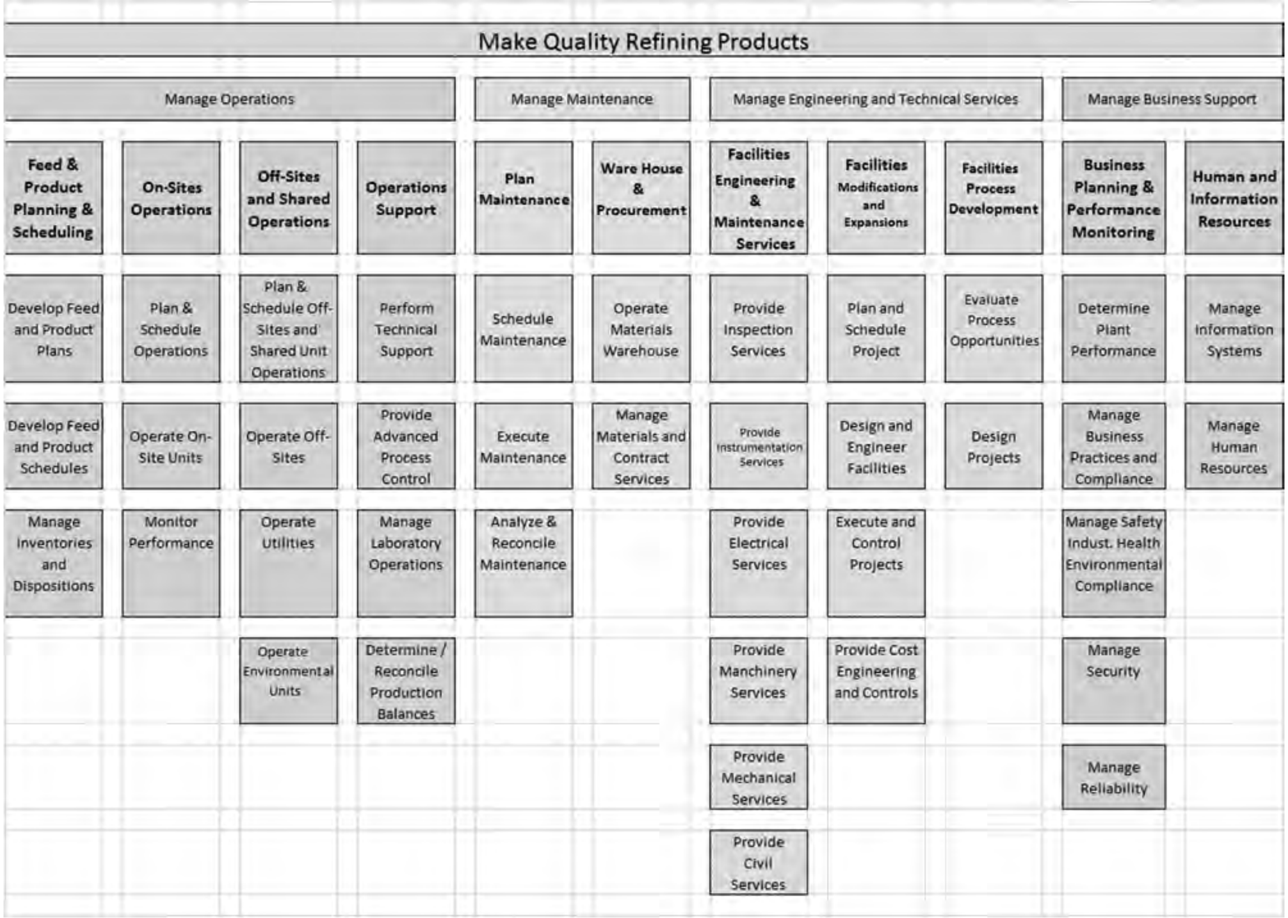


Figure 31.13—Refinery BPM.

and longer term. This includes interaction with corporate functions.

Products: The activities needed to meet the customer requirements in product volume, quality, and time. The Operations and Technical functions provide sufficient data and models of the facilities for optimizing feedstock selection and production targets.

Develop feed and production schedules

Feed includes the activities needed to schedule feed and products for individual units within the plant. This schedule includes the calculation and definition of operations targets to generate optimum margins. The operations and technical functions provide sufficient data and models of the facilities for optimizing the production schedule.

Manage inventories and dispositions

This function ensures that there is a balanced inventory plan of raw materials and products meeting quality and shipping requirements.

31.9.2.1.2 On-Sites Operation

Plan and schedule operations

Plan/Schedule: The function comprises the activities needed to plan/schedule the individual unit operations on the basis of the plant-wide operation schedules. Those schedules cover, for example, feedstock changes, regenerations, turn-arounds and major repairs.

Operate on-site units

The on-sites function is responsible for execution of the actual operation of the units according to agreed targets. It includes keeping the production processes under control and also the delivery of the products according to specifications in quantity and quality at competitive cost at the required time.

Monitor performance

This function captures all activities required to monitor process performance that is to compare actual and historical data (hourly, daily, monthly averages) with targets. These data will include, for example, quality give-aways, utility consumptions, capacity utilization, efficiencies of equipment, and fouling trends. Data reconciliation is performed on the actual plant data as required to ensure that the results of the comparisons are accurate. Deviations from plan and violation of physical and/or technical constraints are highlighted for corrective action. Equipment performance and historical data are available to take corrective actions.

31.9.2.1.3 Off-Sites and Shared Operations

Plan/schedule off-sites and shared unit operations

The plant-wide daily scheduling application function provides the main targets for blending optimization, movements, inventory, and shipments.

Operate off-sites

Blending: This function operates the blending facilities for all products that require blending to specifications. This includes the selection of components from unit run-down lines or tankage and forwarding the products to shipment or tankage.

Feed and product movements: This function operates the movements that are necessary between on-site units and shipment.

Loading and shipment: This function schedules and executes the actual movements of all feed and product entering and leaving the plant via ships, trucks, rail cars, and pipeline facilities. This includes the participation in the development of the plan for pier, station, and tank movements.

The function is responsible for the administration of all activities related to the receipt, dispatch, and storage of feed and products. This includes the documents for suppliers, customers, shipment, and authorities.

31.9.2.1.4 Operate Utilities

This function is responsible for execution of the actual operation of the utility units (e.g., steam, power, air, inert gas, hydrogen purification units or facilities) according to agreed targets. It includes keeping the production process under control and delivering the utilities to required specifications as needed and at competitive cost. This includes scheduling and coordinating the supporting resources such as maintenance and technical for trouble shooting and repair.

Operate environmental units

This function is responsible for monitoring of the environmental units (e.g., waste water treatment) and their operation to agreed targets to meet regulatory requirements.

31.9.2.1.5 Operations Support

Perform technical support

This includes both the determination and guidance functions for all operations improvements.

Determine: This function monitors all production processes to derive an overall performance measure of the operation of the units. It also includes analyzing production performance, losses, quality, give-away for the assessment of utilization and deviation reporting.

Guide: This function is responsible for all activities pertaining to the analysis and the troubleshooting of the production process by anticipating and reacting to process status and events. These activities finally result in guiding and recommending technical settings for the production processes.

Provide advanced process control

This function develops advanced process controls (APC), trains the operators, and maintains any APC applications. This function includes the monitoring of application cost/benefits and the support of the console operator for assisting him in achieving safe and optimum production **results.**

Manage laboratory operations

This function operates the laboratory facilities for the purpose of tracking and analyzing samples to support operations and quality assurance functions. It includes management of the resources within the lab, the scheduling, transportation, receipt and disposal of the samples, and the assistance in monitoring quality assurance.

Determine/reconcile production and energy balances

This function, called in some plants "product accounting," monitors the production and energy consumption and prepares material balances to come to an overall calculation of the energy consumption, and oil/material accounts and any losses. This includes reconciliation and preparation of data for accounting and stewardship purposes. Performance indicators are available for comparison to targets and plans.

31.9.2.1.6 Manage Maintenance

Plan maintenance

Plan maintenance comprises the development of resource plans to ensure the integrity of the facilities and equipment over their planned life cycle based on requirements of operating plans (T/A, regenerations, etc.), equipment inspection, and preventive maintenance needs. Part of this function is the development of maintenance budgets and overall control, issuing and maintaining up-to-date maintenance guidelines and manuals, and training of the personnel on any changes. The systems will permit prioritization and sufficient input to perform work scheduling as the next step of work preparations.

The planning frequency is continuous but has formal planning outputs at monthly, quarterly, and yearly intervals. Turnaround planning is part of this function.

Schedule maintenance

Schedule maintenance comprises all activities pertaining to the scheduling of resources for maintenance jobs including in-house personnel, contractors, material, documentation for repairs, and the equipment and tools to execute the job. It also includes reconciliation after completion to ensure continuous improvement of scheduling.

Execute and control maintenance

The execute and control maintenance function comprises the physical execution and control of tasks outlined in the maintenance schedules. This includes scheduling of daily activities and taking corrective action on backlog of jobs. The function ensures that documentation, material, and tools provided as part of the scheduling activities is correct before use. Finally, the function is responsible for recording of tasks performed, materials used, and services and man-hours consumed for later analysis by the individual equipment such as the pump, the exchanger, and the system of piping.

Analyze and reconcile maintenance

This function consists of monitoring the maintenance activities and cost to come to an overall assessment of the maintenance services provided. This includes analyzing efficiency and effectiveness using indicators for comparison to plans and analyzing backlog of work and the effectiveness of preventive and predictive maintenance.

31.9.2.1.7 Warehouse and Procurement

Operate materials warehouse

This function ensures that there are sufficient parts and tools available at optimum cost to satisfy the refinery's (maintenance) requirements. It includes:

1. Materials cataloging
2. Movement tracking
3. Procurement as an integral part of warehousing management

The function makes required information accessible at plant technician level around the clock. Plant personnel can access materials information, request materials to be routed to work locations, and initiate reorders for larger repair work (turnaround). Reserved stock material information is available to those who are planning, scheduling, and performing work at the plant site. This function also includes the analysis and optimization of warehouse stock levels and reorder frequency.

Manage materials and contract services

This function includes all activities required to develop a legal agreement between the supplier and the plant on services and materials which will allow the various plant departments to purchase services and equipment from the supplier. This includes processing purchase requests, bid development, evaluation, contract negotiations, contract documentation, and approval.

31.9.2.1.8 Manage Engineering and Technical Services

Engineering and technical services management comprises all functions and entities that develop and implement projects and provide technical service and expertise on facilities to operations, maintenance and project functions.

Facilities engineering and maintenance services

Provide inspection services:

This includes all activities that are needed for carrying out quality assurance of all facilities in operation and also those at the design and implementation stage. It includes the translation of statutory regulations into preventive maintenance services and operational constraints.

Provide instrumentation services:

The instrumentation service function concerns all activities related to instrumentation, analyzer, and control systems. This covers the activities over the full life cycle (design, engineering, maintenance) of equipment and software.

Provide electrical services:

The electrical service function comprises all activities related to the electrical equipment and supply of electricity to the plant over its life cycle.

Provide machinery services:

The machinery (rotating equipment) services function includes all activities related to machinery (rotating equipment) over its life cycle. This includes monitoring of the performance of the equipment, the planning, design, and implementation of replacements and new projects.

Mechanical services:

The mechanical services function is responsible for all activities related to the refinery's mechanical equipment over its full life cycle. This includes monitoring of the performance of the equipment and the planning, design, and implementation of replacements and new projects.

Provide civil services:

This function comprises all activities related to the buildings, roads, and similar base infrastructure installations. This includes monitoring the adequacy of those in place and the planning, design, and implementation of replacements and new projects.

31.9.2.1.9 Facilities Modification and Expansions

Plan and schedule projects

The project planning and scheduling function includes all activities pertaining to the planning and scheduling of overall resource allocations for the projects within the plant. It includes the consideration of constraints, synergies, and priorities. Additionally, the detailed project planning and scheduling for each project is covered by this function.

Design and engineer facilities

The facilities design and engineering function supports the design, engineering, and estimating of facilities.

Execute and control projects

The project execution and control function comprises all activities needed to make the facilities physically available and acceptable to the operating functions. Part of this function is the requisitioning and purchasing of goods and services, the control of costs, the coordination of quality assurance of equipment received, the installation, the scheduling of daily activities, and the taking corrective actions on backlogs of jobs.

Provide cost estimating and controls

The cost estimating and controls function includes all activities needed to support the project management from inception to completion.

Cost estimating is performed at an early stage of project planning to understand the cost implications. Cost estimating will be updated as the project develops. Cost control will be performed to ensure the project is on budget and plans.

Facilities process development/evaluate process opportunities

This function comprises all activities that have the objective to evaluate opportunities to improve plant performance through modifications to the existing process and plant. Among others, it includes surveying new technologies, technical and economic feasibilities, and preparing design proposals.

Design projects

The function is responsible for all design and engineering activities needed for the reviews of appropriations and proposals.

31.9.2.1.10 Manage Business Support

Some of the business support processes below are functionally linked to the headquarters processes (business practices) and are needed to focus on meeting functional strategies (e.g., reliability).

Business planning/performance monitoring/consolidate and reconcile business plans

Business planning involves the preparation of medium and longer term plans, including major investments, and the budgeting for capital expenditures, expenses, and costs. Finally, it includes the activities that are needed to effectively measure business performance and to adjust business targets where needed. Business planning is performed at the plant level and will, therefore, impact every organizational unit in the complex.

Determine plant performance

This function evaluates how the plant has performed by comparing planned versus actual business characteristics and identifying reasons for discrepancies both internal and external to the plant.

Manage business practices/compliance

This function translates the corporate goals and governmental rules into a working set of policies, guidelines, and standards. This includes, for example, the business controls, ethics requirements, and engineering standards. Each business function has its own details that relate to the plant master set.

Perform target management

Target management translates the business goals (including balanced scorecards management) and objectives into a working set of policies, guidelines, and standards. This includes the planning, implementation, and control of achievements against these goals and objectives.

Manage safety

Safety management comprises the development and implementation of programs designed to prevent the occurrence of incidents that would adversely affect the plant business assets, human resources, and the public. This includes the effective and efficient implementation of action plans to control incidents.

Manage security

Security management is the development and implementation of programs designed to ensure plant access control and asset control and to perform some investigative tasks to prevent the occurrence of incidents and losses that would adversely affect the plant business assets, human resources, and the public. Regulations and plant management have to know which people are on site at any time. The security task includes the effective and efficient implementation of action plans to control incidents

Manage environmental activities

This function includes the development and implementation of programs designed to ensure compliance with environmental regulations, those determined both internally and externally to the site or company. This includes the effective and efficient implementation of action plans to avoid or to control environmental incidents. Furthermore, the control of waste handling is included in case it is not covered by the operating unit.

Manage industrial hygiene

The function covers the development and implementation of programs designed to comply with industrial hygiene practices and procedures.

Manage information systems

Manage Information Architectures: planning, developing, implementing and maintaining the three architectures of information, systems, and technology.

Manage information applications: Managing the technology which provides the required views of the refinery's information. This includes developing, integrating, and maintaining information applications.

Manage library and data stores: Operating and maintaining the storehouse of information that the company requires to function.

Manage reliability

The function develops and monitors programs designed to improve the integrity and reliability of equipment and processes. This includes the effective and efficient implementation of action plans to avoid equipment failure or process malfunctions and related incidents. This function may act as a consulting service to maintenance, process operations, engineering services, and management.

Manage human resources

Plan: Development of an all-encompassing human resource plan that will provide the right people for the site. It includes managing position planning, the appraisal program, and organizational redesign programs.

Acquire employees: Managing the process which will legally obtain employees for the refinery including recruitment, selection, and orientation of new employees.

Provide employee services: Maintenance of the contractual relationship between the employee and the company including areas of compensation, benefits, transfers, service awards, and retirement.

Manage employee development: Developing and implementing the plan which will continuously balance the variables of employee interests and needs, employee skills and abilities, and the company's needs. This includes management of the employee career development program.

Manage external relations

Interpret government relations: Accumulating, interpreting, and complying with the laws and regulations set forth by all forms of government which may have an impact on the operations of the refinery.

Manage public relations: The management of all activities whereby the refinery interfaces with the general public including the interpretation of public opinion, providing public relations advice on external communications, and enhancing the refinery's public image.

REFERENCES

[1] Birol, F., "Challenges Facing the Global Refinery Industry," *Oil Gas Process*, Rev., 2006, http://www.touchbriefings.com/pdf/1713/Birol.pdf.

[2] Herlyn, F. J., and Starr, S., "The Six Significant Steps in Moving Towards a More Profitable Operating Environment," *NPRA Plant Automation*, NPRA, San Antonio, TX, 2003.

[3] Keese, G., Apple, J. E., and Herlyn, F. J., "Benchmarking Information Systems," *Chem Eng.*, June, 1998.

[4] Herlyn, F. J., *Plant Best Practices*, http://www.herlyn.com/index.php?option=com_content&task=view&id=5&Itemid=9 (accessed on August 16, 2008).

[5] Herlyn, F. J., "A Roadmap to Best Performance Indicators," *Hydrocarbon Eng.*, Vol. 5, July, 2000.

[6] The CALDER-MOIR IT Governance Framework, http://www.itgovernance.co.uk/calder_moir.aspx: http://www.itgovernance.co.uk/calder_moir.aspx (accessed on August 25, 2008).

[7] CSB Investigation Information Page, http://www.csb.gov/index.cfm?folder=completed_investigations&page=info&INV_ID=52 (accessed August 19, 2008).

32

Biofuels and Biorefineries

José Baro Calle[1]

ACRONYMS

A/F	Air-fuel rate
BOB	Blendstock for oxygen blending
BTL	Biomass to liquid
CCS	Carbon capture and sequestration
CDM	Clean development mechanism
CFPP	Cold filter plugging point
CONCAWE	Conservation of Clean Air and Water in Europe
CTL	Coal to liquid
DME	Dimethyl ether
DOE	U.S. Department of Energy
EISA	Energy Independence and Security Act
ETBE	Ethyl terc butyl ether
EtOH	Ethanol
EUCAR	European Council for Automotive R & D
FAEE	Fatty acid ethyl ester
FAME	Fatty acid methyl ester
FT	Fischer-Tropsch
GHG	Greenhouse gases
GMO	Genetically modified organism
GTL	Gas to liquid
HDS	Hydrodesulfurization
HV	Heating value
HVO	Hydrogenated vegetable oil
IEA	International Energy Agency
JRC	Joint Research Centre
LCA	Life cycle analysis
LCFS	Low carbon fuel standard
LHV	Low heating value
LPG	Liquefied petroleum gas
MON	Motor octane number
NOx	Nitrogen oxides
PVO	Pure vegetable oils
R&D	Research and development
RON	Research octane number
SOS	Security of supply
SRA	Strategic research agenda
VP	Vapour pressure
WTL	Waste to liquid
XTL	Something to liquid
WTW	Well to wheel

NOMENCLATURE

Gtoe	Giga tons of equivalent oil
BG	Billion gallons

32.1 INTRODUCTION

Karl Benz built the first automobile in 1885. Since then, the automobile industry has undergone constant technological evolution, involving improvements in a wide variety of areas. Fuels, lubricants, and the processes associated with their production have always been one of the main focuses for technology development.

The continuous demand for innovation implies the existence of future unsolved technological needs. The automobile industry has constantly raced against time to solve these technological issues successfully. For instance, the oil industry has supplied sulfur-free fuels to satisfy environmental regulations, and this change also needs low-sulfur lubricants or gasoline with redesigned volatility. These technology solutions need to be also economically competitive to become widely accepted by the industry.

The evolution of the automobile industry is continuing with no signs of slowing down. Moreover, it is currently facing probable revolutionary changes in the vehicle concept. The most important current challenge for the industry is to increase the energy efficiency of transportation without increasing the associated pollutant emissions, including greenhouse gas (GHG) emissions.

Fossil fuel reserves are finite and not fully available to all market economy countries. The estimated global oil reserves are 335 Gtoe (equivalent to about 70 years at current rate of consumption), and the estimated natural gas reserves are similar. At a glance, fossil fuels were formed over millions of years but have been largely consumed in only one century. This massive consumption of fossil fuels has altered the carbon equilibrium on our planet by releasing large amounts of carbon dioxide (CO_2) into the atmosphere. CO_2 is considered one of the most important GHGs and has direct implications in environmental regulations related to climate change.

These supply and environmental drivers are forcing a change in the conventional distribution of energy sources, as discussed in Chapter 3, and increasing the share of renewable sources in the production of fuels for transportation.

32.2 THE NEED OF BIOFUELS FOR TRANSPORTATION

Over the past decades, scientists around the world have foreseen serious threats for human life in the near future and have identified sustainable energy as a target for the 21st century. However, what exactly does sustainable energy mean? Sustainable energy must fully satisfy global energy demands, produced at the same rate at which it is consumed, and with an economic cost that guarantees availability in every country and social strata. Although this might be considered a utopia, the need is evident and has been one of the main legislation focuses in different world areas during the last decades.

---

[1] Repsol S.A., Madrid, Spain

In 2000, the European Commission released a "Green Paper" proposing a European strategy for the security of energy supply [1]. This Green Paper highlighted and provided evidences on Europe's dependence on energy supply and the narrow available margins, anticipating the challenges to accomplish the targets mandated by the Kyoto Protocol and starting to consider the use of more biofuels for transport. This concern was further developed by a White Paper on a common transport policy [2], suggesting an action plan with a target of substituting 20 % of fossil fuels consumed in transportation with alternative fuels in 2020. This approach should provide:

- Improvement in security of energy supply (SOS) by source diversification
- Reduction of GHG emissions

In November 2001, the Commission presented a communication on alternative fuels for road transportation [3], identifying biofuels, natural gas, and hydrogen as possible future energy sources for transport. Each of these options was proposed to potentially cover at least 5 % of total transportation fuel consumption in 2020 and to be implemented in the following order: biofuels for the short term, natural gas for the medium term, and hydrogen for the long term. In the same document, the Commission presented proposals for directives on the promotion of the use of biofuels for transport and opening the possibility for the state members to introduce reduced tax duties on mixtures of biofuels with mineral oils.

This approach was confirmed by a stakeholder Contact Group on Alternative Fuels, established by the Commission, which presented a comprehensive report outlining a detailed strategy on market development for these alternative fuels [4]. The report confirmed the technical feasibility of reaching the 20 % market share target defined by the Commission for 2020 and was mainly based on a well-to-wheel (WTW) analysis for the different alternative fuels.

In 2003 the European Union adopted Directive 2003/30 EC [5] on the promotion of the use of biofuels and other renewable fuels for transport. Under this biofuels directive, the European Union established the goal for member states to set indicative targets for a minimum proportion of biofuels to be placed on the market of 2 % in 2005 and 5.75 % in 2010. Due to the difference in prices with conventional fuels, the European Union allowed member states to apply a total or partial tax exemption for biofuels, as competitiveness was identified as one of the major barriers [6].

During 2007, the European Union proposed a new energy strategy with several improvements to be attained by 2020. An updated roadmap [7] demonstrated that a target of 20 % for overall share of renewable energies and a 10 % target in transport would be feasible objectives. These targets, together with improvement in energy efficiency, were endorsed by the European Council and by the European Parliament [8] and included in the updated and broader Directive 2009/28/EC [9] on the use of energy from renewable sources. The confirmed targets included 20 % reduction in GHG emissions (versus 1990), 20 % of the total energy from renewable sources (10 % in transport), and 20 % reduction in primary energy consumption.

At the beginning of 2009, a revision of the Fuel Directive (Directive 2009/30/EC, [10]) was approved, allowing the addition of ethanol (EtOH) to gasoline up to 10 % and the addition of fatty acid methyl ester (FAME) (biodiesel) to diesel up to 7 %. The directive also sets targets to reduce fuel's life cycle GHG emissions, placing the responsibility of reducing these emissions on fuel suppliers. The most important commitment is the reduction of GHG emissions to 90 % of the 2010 level by 2020. The targets, which could be reviewed in 2014, include:

- A mandatory reduction of fuel GHG emissions of 6 % by 2020. Member states may increase this reduction up to 10 % and establish intermediate targets (2 % by 2014 and 4 % by 2017).
- An indicative 2 % target subject to a Commission assessment by the end of 2012 to be delivered through alternative vehicles (e.g., electric or hydrogen vehicles, etc.) and the application of carbon capture and sequestration (CCS).
- An indicative 2 % target by 2020 to be achieved by the purchase of credits through clean development mechanism (CDM) under the Kyoto Protocol.

The main current consequence from these regulations related to biofuels is that the European transport sector is required to source 10 % of its energy needs from renewable energies, including sustainable biofuels and others.

While these steps were given in Europe, regulation activities related to biofuels were also taking place in the United States. Legislations like the Clean Air Act Amendments (1990) and the Energy Policy Act of 1992 opened possibilities for alternative fuels that could be produced from internal resources. Although the main biofuels focus was EtOH from corn, activities were also starting in bioethanol from other sources and biodiesel [11].

In 2007, the U.S. Government introduced the Energy Independence and Security Act (EISA) [12], increasing and expanding the Energy Policy Act of 2005 with the objective to improve vehicle fuel economy and reduce U.S. dependence on petroleum. EISA proposed a target to replace 30 % of transportation fuel consumption with alternative fuels by 2030. This reduction should be obtained through an increase of the percentage of renewable fuel blended with conventional fuels for transportation. The new regulation defined seven categories of "advanced biofuels" (other than corn-derived EtOH) that could be grouped in:

- Cellulosic biofuels, including EtOH derived from cellulose, hemicellulose or lignin
- Biomass-based biodiesel
- Other advanced biofuels: EtOH from sugar, non-corn starch or waste material; biogas, butanol and other alcohols from renewable biomass

This legislation proposed a calendar of renewable volume obligations (RVO). Some of the targets proposed for different biofuels with significant GHG emissions reduction include:

- Renewable fuels: 9 billion gallons (BG) in 2008, rising to 36 BG in 2022
- Advanced biofuels: 0.6 BG in 2009 to 21 BG in 2022
- Cellulosic biofuels: 0.1 BG in 2010 to 16 BG in 2022
- Biomass-based biodiesel: 0.5 BG in 2009 to 1 BG in 2012

In another initiative, California issued the executive order S-01-07 [13], which proposed the development of "Low Carbon Fuel Standard" (LCFS), which aims to reduce the GHG footprint of transportation fuels by at least 20 % in 2020. This target would be met largely by the introduction of biofuels, mainly through the addition of EtOH to gasoline at a rate beyond the federal mandate (possibly requiring a 50 to 100 % higher penetration of biofuels by 2020).

Similar legislations have appeared in other areas around the world, including countries like Brazil, Argentina, South Africa, Thailand, India, and China. Taking into account these actions, the market for biofuels seems to be enormous, at least until 2020.

The International Energy Agency (IEA) [14] has forecasted in the reference scenario that biofuel use will continue rising until 2030. After a strong increase from 2006–2008, mainly in North America and Europe, reaching 1.7 % of total road-transport fuels, economic downturn and concerns about effects on food prices related to crop dedication to biofuels reduced the growth rate. However, the projected scenario for 2030 (Figure 32.1) considers a significant growth in all world areas in 2030, when it will meet about 5 % of worldwide transportation fuel consumption. Nearly one quarter of this increase is expected to be produced using second generation technologies.

However, even with current exceptionally high fossil fuel prices, biofuels remain expensive to produce and are generally noncompetitive. Thus, the question remains about the reason why biofuels have received major interest as alternative renewable fuels. Probably the simplest answer would be "because they are here" (quoting Mallory, the mythic mountain climber), meaning that biofuels are the only renewable alternative for transportation fuels that is commercially available. However, simply being here is not enough. Public support schemes must justify the financial resources invested in biofuels. The assumed benefits of biofuels are that they contribute to SOS and reduce GHG emissions. Other benefits might include the reduction of crude oil consumption, and hence a slower depletion of proved reserves, and the support of rural areas, particularly in developing countries, preventing an exodus of the rural population as demonstrated in Brazil.

Depending on the objective and local resources, several biofuels and raw materials could be suitable. However, although any biofuel may be a good response to GHG concerns, the selection between producing biofuels of bioenergy (biomass dedicated to generate electricity or heat) might be uncertain from the savings in GHG emissions point of view [15].

32.3 THE KEY CONCEPT: SUSTAINABILITY

Plants use solar energy to convert CO_2 and water into organic molecules, composed by carbon and hydrogen, allowing them to store energy through this process. During the natural cycle of plant life, these organic molecules formed during crop growth are degraded, releasing CO_2 back into the atmosphere. Therefore, plants can be used not only as food but also to produce energy. In this alternative application, CO_2 returns to the atmosphere when biomass is burned, and the CO_2 is captured again after a limited period of time that may range, depending on the plan, from 1 year in oleaginous or cereal crops to decades for woods.

Under this concept, energy from biomass is renewable. However, the level at which biomass can be considered a renewable energy source is determined by its energy content minus the necessary fossil energy required (if required) for its production. In other words, not 100 % of the energy content in biomass is renewable, and therefore, only some of the CO_2 emitted during biomass combustion is renewable. There are other renewable energy sources (solar, wind, tides, etc.), but energy from biomass is unique in the sense that it is stored in molecules, making possible the conversion to other usable forms of energy or the production of chemicals.

In the past, an energy source only needed to be renewable to obtain social acceptance, but today renewable is an insufficient label, and it must be also sustainable. The sustainability concept implies more than SOS or environmental concerns, and includes the global social impact. It is not just *"what"* needs to be done but *"how"* it is done. Conceptually, sustainable energy refers to energy that can be generated for long periods of time without compromising potential resources for future generations.

Climate change and its relationship with anthropogenic GHG emission promoted interest in sustainability certification. Transportation is presumed to be the main contributor to GHG emissions, and transportation-related emissions will continue increasing over the next decades. For this reason, the transportation sector was a pioneer in GHG control, and proposed some of the first rigorous WTW studies [16].

However, after these analyses were carried out, it was already evident that this approach was insufficient. In 2007, large-scale biofuel development started to raise concerns regarding competition with food and pressure on land resources [17,18]. In some cases, it was even

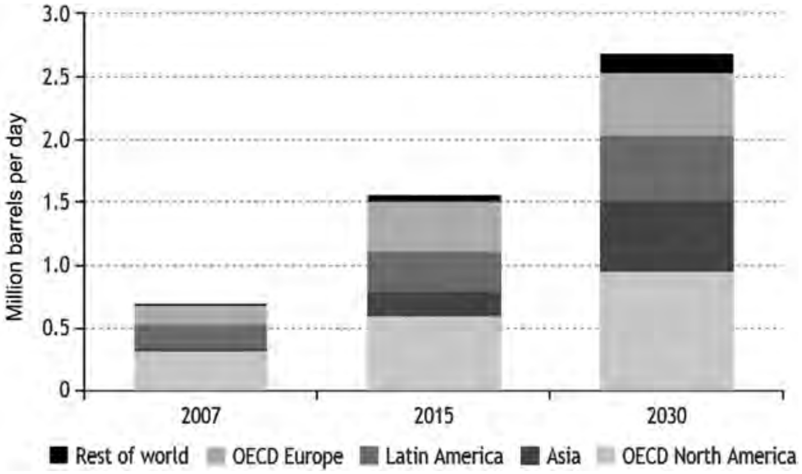


Figure 32.1—Forecast on biofuels demand for transportation. *Source:* IEA [14]. *Note:* On an energy-equivalent basis.

feared that plowing land with high carbon content could produce enough additional CO_2 emissions to negate any GHG emission benefits for several decades. Society needs to be confident that the benefits of biofuels vastly exceed any undesirable effects. Thus, the biofuel industry needs to apply an internationally recognized and accepted sustainability certification scheme and avoid a proliferation of local schemes, which would challenge the survival of a global market.

The scientific community has been working since that moment to define parameters and to create mechanisms to measure these parameters in a transparent and nonautocratic way. The demands for the energy industry should also be comparable with other industries to maintain equilibrium in all economic activities. The criteria for sustainability represent a very complex subject that requires not only technical knowledge but ethical and political aspects. Figure 32.2 represents some of the main groups of sustainability pillars as proposed by IEA [19].

There are currently several initiatives that have built some certification schemes for biofuels with certain degree of international recognition that cover the different sustainability legislations, mainly in Europe and the United States. These schemes consider most of the following sustainability criteria, organized under these main pillar groups:

- *Environmental pillars*: lifecycle GHG, soil quality, soil degradation, harvest levels, emission of non-GHG air pollutants, water use and efficiency, water quality, biological diversity, forest preservation, land use, and land use change
- *Social pillars*: allocation and occupation of land, human food competition, local wealth, jobs in biofuels sector, access to modern energy services, human rights, worker rights, and indicators related to diseases, injuries, and mortality
- *Economic pillars*: productivity, net energy balance, gross value, change in consumption of fossil fuels, workforce training, energy diversity, infrastructure, and logistics, capacity, and flexibility of bioenergy use

IEA [19] identified near 70 worldwide initiatives to develop sustainability criteria and standards, including public and private initiatives. Some of the most advanced international activities for sustainability criteria standards include:

- ISO/TC 248, Sustainability Criteria for Bioenergy (international standard on preparation)
- The European Standard EN 16214 from European Committee for Standardisation CEN/TC 383 on sustainably produced biomass for energy applications [20]
- The Global Bioenergy Partnership (GEBP) Indicators [21]
- Roundtable on Sustainable Biofuels (RSB), open and multi-stakeholder process that has developed certification systems recognized by the European Union under the Renewable Energy Directive [22]
- The International Sustainability and Carbon Certification System (ISCC), with the first internationally recognized certification system for biomass

Some of the main criteria from the previous standard proposals will be covered in this section. It is expected that after biofuels, the certification scheme will be extended to include energetic biomass and, potentially, to other energy sources that could be certified under similar schemes, specifically adapted to each source.

Regarding land use change for biofuels, some theoretical calculations estimate that dedicating a small percentage of arable land (<5 %) would be sufficient to meet the needs for biofuel development. Land use could be the most important issue for biofuel business development because the possibility of extending the available arable land is difficult when considering other sustainability criteria, mainly forest and unaltered land preservation.

A very effective certification system is necessary to ensure that biofuels do not come from land with high carbon stock. Preventing the consequences of indirect land changes is a very challenging problem, beginning with the difficulty of calculating the total negative effects and, in particular, the GHG emissions associated with land use change. The GHG balance seems to be related to the production chain, but it has recently been realized that converting land from natural or man-made forest or grassland to agricultural land can release substantial quantities of carbon through reduction of both the above-ground biomass and the soil carbon content. This land use change effect can be very large and negate the GHG benefits of any energy crop for many years.

The most productive land is already in use for food production or industrial applications. Thus, even under the most optimistic scenarios, the fraction of total biomass that could be used for energy is relatively small, and changes in expected agricultural yields or food production requirements can make a large difference in biomass availability forecasts. This consideration has led the European Biofuels Technology Platform to conclude in their Strategic Research Agenda [23, 24] that research and development (R&D) related to biofuel feedstocks should be focused on areas such as:

- Developing new high-yield and low-input agricultural and forest systems with breeding of crops and trees optimized for biofuel production
- Developing efficient biomass logistic systems (harvesting/collection/storage) for different conversion concepts at different scales

Figure 32.2—Environmental, social, and economic aspects of biofuels and bioenergy production. *Source:* IEA [19].

- Developing second generation biofuels through alternative feedstocks like algae and other aquatic biomass

Several sources estimate that an average 7 % of the world's energy could be covered by biomass by 2030 without generating undue competition with food production and other uses. As previously stated, the degree of uncertainty in such figures is quite high. Competition with food crops raises ethical issues, and public opinion is very sensitive to these issues. The extensive debate of recent years has not yet concluded. It seems evident that large-scale development of biofuels will inevitably impact agricultural commodity markets (e.g., vegetable oil or cereals) and will potentially increase both price level and volatility [25]. However, large-scale development of biofuels will also promote positive impacts in rural areas, particularly in developing countries.

Water availability and biodiversity protection are also serious concerns. However, biofuels are supposed to induce benefits in rural areas (local wealth and social impact), a positive impact on air quality by reducing pollutants from older vehicles, and especially a strong reduction in GHG emissions. This reduction in GHG emissions is the main driver for the introduction of biofuels. Fuel GHG emissions must be considered globally as a chain that begins with the fuel production and ends with the fuel consumption by a vehicle. There are fuel technologies that are efficient in vehicles but inefficient in production, with the result of an overall negative effect. Therefore, to establish the real GHG emissions of a fuel or a biofuel, it is necessary to perform a complete analysis of the production and use cycle, known as a life cycle analysis (LCA). In the case of road fuels, this type of analysis is also called WTW (in reference to oil wells and vehicles).

The energy content of a fuel is measured as its heating value. However, the real energy required to provide a unit of energy to the end user is the sum of the energy employed during fuel production, transport, and distribution. In the case of fossil fuels, providing 1 unit of energy to the end user (the wheel) requires approximately 1.15 units of energy at the beginning of the chain (the well). In the case of biofuels, the required initial energy is significantly larger (e.g., 1.5 units at the well). As the energy contained in a fuel (fossil or bio) comes from its carbon and hydrogen content, the total energy balance is closely related to the GHG content. As previously stated, biofuel carbon originates from biomass and therefore from the CO_2 fixation by green plants. In our example of 1.5 units of energy, only 1 unit is really biofuel and therefore "carbon-neutral." The remaining 0.5 units may be fossil fuel, though the share of fossil fuel in this amount depends on the production chain. In the worst scenario, assuming that all of this required energy comes from fossil fuels, the final biofuel will produce approximately 45 % of the emissions compared with fossil fuels.

This example is largely simplified and performed through a very general approach, as there are many additional variables affecting sustainability to consider. For example, CH_4 and N_2O are more active than CO_2 in greenhouse effects (23 and 300 times more, respectively). N_2O is emitted from fertilizers and thus directly related to agriculture and biofuels. Relatively small volumes of nitrogen oxides (NOx) may drastically change the calculated balance. Another example is the type of energy consumed during the production process. Electricity from wind or from nuclear plants is nearly "carbon neutral," while electricity from coal plants increases the GHG emissions of the associated product, significantly affecting the final GHG balance.

In general, biofuels can potentially reduce the net GHG emissions produced by transportation, although different biofuels produce very different reductions in GHG emissions. Figure 32.3 summarizes JEC (JRC//EUCAR/CONCAWE) WTW report for automotive fuels [16], comparing GHG emissions from biofuels with conventional fossil fuels. For example, EtOH savings range from 0 % to over 80 % compared to fossil gasoline, depending primarily on the crop and type of energy used in the manufacturing process. The European Fuel Directive defines typical and default GHG saving values for biofuels if produced with no net

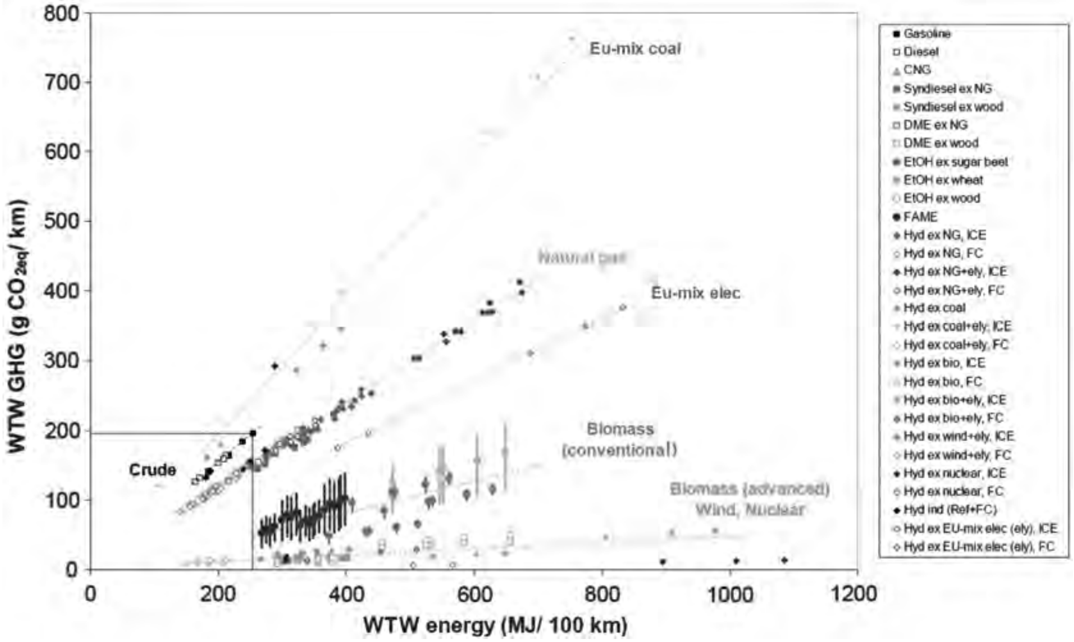


Figure 32.3—WTW energy and GHG emissions. *Source:* JRC/EUCAR/CONCAWE [16].

TABLE 32.1—Typical and Default GHG Savings for Some of the Most Common Biofuels (Selected Data from 2009/28/EC European Directive [9])

	Typical GHG Saving (%)	Default GHG Saving (%)
EtOH from sugar beet	61	52
EtOH from wheat (fuel: lignite in CHP plant)	32	16
EtOH from wheat (fuel: natural gas in CHP plant)	53	47
EtOH from wheat (fuel: straw in CHP plant)	69	69
EtOH from sugar cane	71	71
Biodiesel from rapeseed	45	38
Biodiesel from sunflower	58	51
Biodiesel from waste vegetable or animal oil	88	83
HVO from rapeseed	51	47
HVO from sunflower	65	62

carbon emissions from land use change, and provides rules for calculating GHG impact. Table 32.1 summarizes values for some of the most common biofuels.

As a final summary, sustainability will impact the availability of biofuels. Some principles that are being imposed by world organizations enacting international certification schemes include:

- Land availability, land use, and the management of water are key problems around the world. It is widely accepted that the most productive land must be dedicated to produce food for people. Industrial crops must be grown on degraded land, land that has been set aside, or low-quality land
- Competition between biofuel and food crops is unacceptable
- Crops for biofuels could be an opportunity for developing countries
- International rules must restrict the production of industrial crops in countries suffering from food shortages
- Biotechnology provides hope for reduced GHG emissions and is expected to contribute to the development of new crops able to grow in arid fields
- Industrial use of biomass has to be optimized (biofuel, bioheat, biopower, biomaterials)
- The use of wastes as raw material for biofuels or bioenergy must be an international target

32.4 CATEGORIES OF BIOFUELS FOR TRANSPORTATION

“Biofuel” is a generic term designating fuels produced from raw biological material. Although it can apply to any fuel, in this chapter the term “biofuel” will specifically refer to transportation fuels substituting gasoline or diesel. Although biogas should also be considered, energy density is a critical fuel property related to space and weight limitations in transportation (particularly in private cars), and liquid fuels are favored over gaseous fuels.

Synthetic liquid biofuels can be produced from a wide range of biomass feedstocks and different processes. The alternatives that received more interest during the last decades include:

- EtOH is the main biofuel, produced through the fermentation of a wide variety of feedstocks, mainly corn and sugar cane, but also from other feedstocks like cereals and lignocellulosic materials. Biobutanol may also be produced from similar processes.
- Biodiesels are diesel fuels obtained by reacting vegetable oils with alcohols. The transesterification reaction produces FAME when methanol is the alcohol used or fatty acid ethyl ester (FAEE) when EtOH is used, with properties very similar for both esters. Different vegetable oils used as feedstocks include rapeseed oil (canola), soybean oil, palm oil, and recently jatropha oil, but a wide variety of alternative oils are feasible: castor oil, sunflower oil, tallow, and even used cooking oils and animal fats.
- Pure vegetables oils (PVOs) could be used directly in diesel engines with significant changes in the design of some parts of the engine, but the automobile industry is strongly opposed to this possibility.
- Hydrogenated vegetable oil (HVO) is another alternative to produce fuel from vegetable oils or animal fats. HVO is produced through a hydrotreatment process followed by an isomerization step. HVO has similar properties to fossil diesel, with high cetane numbers and low aromatic contents.
- Synthetic diesel from biomass to liquid (BTL) is produced through a biomass gasification process to carbon monoxide (CO) and H_2 (syngas), followed by oligomerization processes. The process is similar to those currently used to produce liquid fuels from natural gas and coal.
- Other compounds suitable for use as transport fuels can be produced from bio-syngas, such as methanol, dimethylether (DME), and synthetic naphtha. Biomass can also be transformed to biocrude (pyrolysis) and theoretically mixed into the crude basket in conventional refineries.

The previous list includes most of the potential liquid biofuels, although some of them are only considered from the theoretical point of view. For example, biomethanol, PVOs, DME, and biocrudes are currently not suitable fuels. There are no industrial facilities to produce methanol from biomass today, and there are no project plans for them, as the use of biomethanol offers no advantages compared to other biofuels (e.g., EtOH) and has serious issues in comparison with EtOH (less energy content by mass or by volume, higher heat of vaporization and high toxicity). PVO does not reach the minimum quality required for diesel fuel and would require special dedicated engines, and bio-DME also requires dedicated engines or serious modifications to standard diesel engines. Biocrudes are still far from being an industrial reality.

With these practical considerations, the two most common types of biofuels with worldwide use today are bioethanol and biodiesel, and they will be the main focus of the chapter. However, other real alternative biofuels to be considered include butanol, HVO, and BTL, which will also be covered in other sections.

There are several biofuel classifications according to different criteria. One of the most common approaches to categorize biofuels is related to the substituted fuel or to the type of engine fed by each one of the biofuels. EtOH and other alcohols and ethers may substitute gasoline in spark engines, while biodiesels such as FAME, PVO, HVO, BTL, and DME are suitable for use in compression engines substituting diesel fuel. Figure 32.4 shows the substitutability of various biofuels for common fossil-derived fuels [26].

Another classification for liquid biofuels that has become popular during the last years includes the generation, and refers to "first-generation" and "second-generation" biofuels. There are no strict technical definitions for this categorization. In most of the references, the term "first-generation" is widely used to describe current biofuels, made from part of the plant through relatively simple processes and generating large amounts of by-products or residues that may or may not be used for energy. "Second-generation" refers to biofuels made using full plants and maximizing biofuel production per hectare of land, through more complex processes and from a wider range of vegetal feedstocks with rapid growth, including also marine crops, algae, cyanobacteria, and waste material such as straw or agriculture residues.

In other references, the term "first-generation" is used for those current commercial biofuels, produced primarily from food crops, while "second-generation" is used for noncommercial biofuels, to be mainly developed from non-food biomass. A scheme about the routes for several current and future biofuels is summarized in Figure 32.5 [27].

Some authors have even proposed the term "third-generation" to refer to biofuels whose raw materials will be generated from genetically designed plants, algae, or cyanobacteria, some of the most challenging R&D activities, not expected to become commercial in the near future.

32.5 DISCUSSION OF BIOFUELS FOR TRANSPORTATION

A full review of current and future biofuels would be a subject for a complete handbook, and it would be out of the scope of this chapter. In this section, the most common types of biofuels with will be discussed, with criteria based on current worldwide use for first-generation and potential for second-generation biofuels. The discussion will be focused on their production processes and three main aspects:

a) Biofuel properties
The suitability of blending biofuels to be used as automotive fuel is currently an outdated topic. Biofuels have been blended in automotive fuels at low percentages for decades and have been demonstrated to be suitable components for automotive fuels without market problems. In the beginning, biofuels were very extensively tested. Analytical characterization and vehicle performance tests were performed in most of the countries involved in biofuel development, and these studies are available from official organizations (U.S. Department of Energy [DOE], Biofuels Association, etc.). It is important to note that studies were performed both by organizations supporting and opposing biofuels, which represents a very sensitive subject in this field. Several initial national standards were released, and the resulting market was difficult for vehicle manufacturers, requested to guarantee the vehicles they produce and requiring unified and universally accepted fuel standards. Since the 1990s, standards were developed by national institutes of standardization such as ISO, ASTM in the United States, and CEN in the European Union, resulting in the availability of international standards for most of the existing biofuels, and the update of conventional fuel standards to allow biofuel blends.

b) Biofuel handling
Biofuels must be integrated into existing infrastructures and be compatible with existing vehicle fleets and refueling networks. Therefore, biofuels must be blended with hydrocarbons at refineries (or terminal plants) to maintain the primary property of conventional fuels: fungibility. Fungible fuels have common use, commingled distribution, specifications, and quality control that guarantee their substitution for each other without problems [28]. Biofuels could also be commercialized

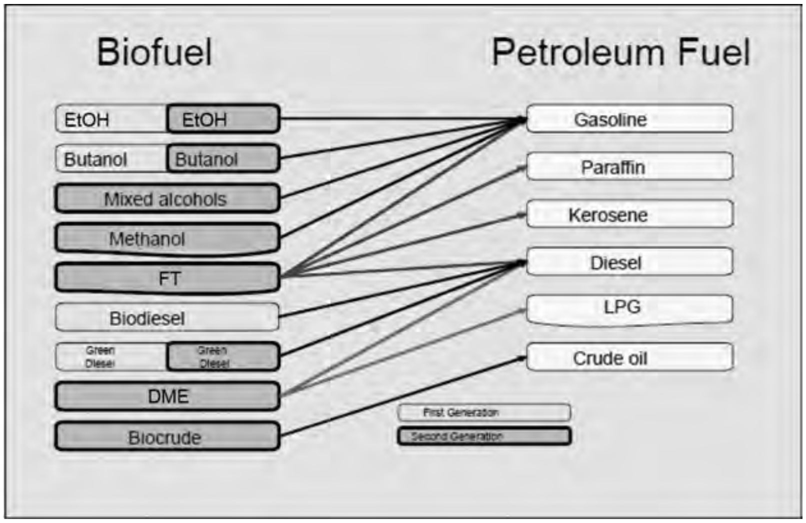


Figure 32.4—Substitutability of biofuels with common petroleum-derived fuels. *Source:* United Nations [26]. LPG, liquid petroleum gas; FT, Fischer Tropsch.

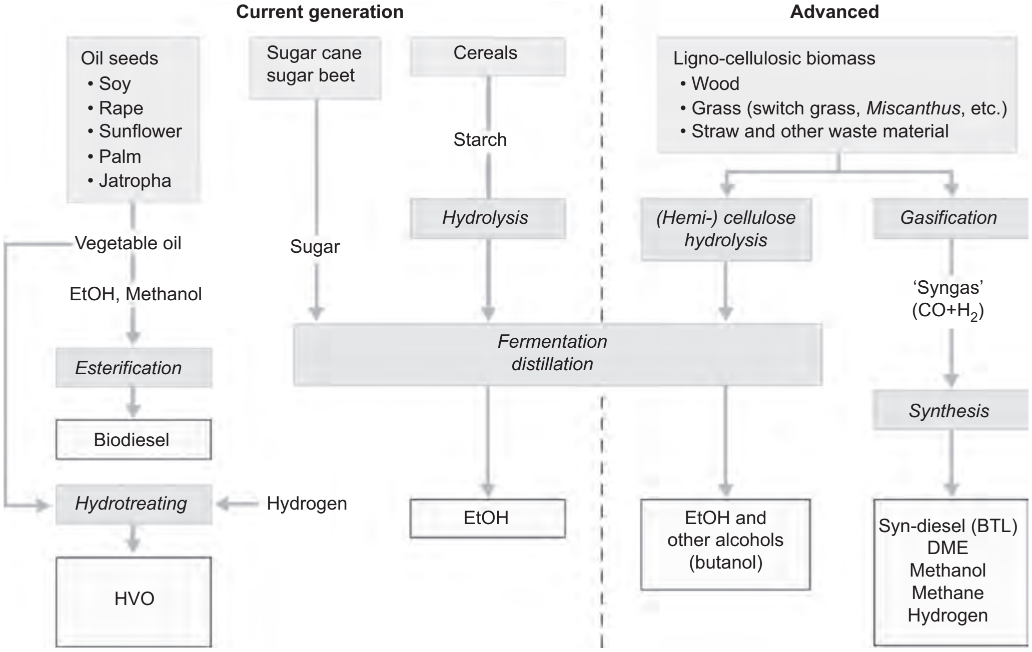


Figure 32.5—Overview of the different routes to biofuels production. *Source:* IPIECA [27].

in special markets for dedicated engines or vehicles, but this niche market is a very small share of the total market.

There are two alternative methods for blending biofuels: splash blending or banalization. Splash blending essentially involves adding biofuels to conventional fuel at the filling station. This practice is not recommended by the oil and automobile industries because the uncontrolled blending of biofuels and conventional fuels can lead to vehicle performance problems. Banalization involves mixing systems in tanks or lines before the loading rack facilities and can be carried out at the refinery or at the terminal. When possible, refinery blending is recommended, and either tank mixing or line blending may be preferred depending on the biofuel handled.

c) Biofuel end use

Biofuels are generally considered to reduce pollutants at the exhaust pipe, but in truth, the reduction occurs before the catalyzer. After the catalyzer, pollutant emissions do not depend on biofuel content. The most important factor in vehicle performance is vehicle technology. Biofuels (or conventional fuels) are not required to improve performance, but they must not be detrimental. Other performance aspects, such as startability, driveability, or the emission of nonregulated pollutants, vary from biofuel to biofuel and will be discussed later.

32.5.1 Bioethanol

32.5.1.1 NATURE AND PRODUCTION PROCESS

Bioethanol is by far the most widely used biofuel for transportation purposes. Although it has been used for decades in countries like Brazil, the beginning of this century saw the worldwide expansion of this biofuel as substitute for gasoline, with a well-established industry because of the availability of a wide range of feedstocks and production processes with well-established technologies.

EtOH is currently produced primarily by the fermentation of sugars produced by plants (sugar cane, sugar beet, etc.), or starches (corn, barley, sorghum). Ethyl alcohol from cellulosic feedstocks (such as wood) is expected to become increasingly important. Although research on the use of cellulosic feedstocks, including paper, wood, and other fibrous plant material, dates back to the early 20th century, only recently are large-scale demonstrating plants coming into production.

Roughly 48 % of world EtOH production is from sugar cane and sugar beet. Most of the remainder comes from grain, with corn playing a dominant role. Brazil is the largest sugar EtOH producer in the world, and the United States and Canada are the largest starch EtOH producers. EtOH is widely used in Brazil and in the United States, and the two countries were responsible for 88 % of the world's EtOH fuel production in 2009, as shown in Figure 32.6 [29].

The traditional biological routes to produce bioethanol are well established. The production from sugar cane, or more properly from molasses (waste from the sugar industry), involves the use of a microorganism named *Saccharomyces cerevisiae*. Since ancient times, EtOH has been made by fermenting sugars and recovering EtOH by distillation. Simple sugars are the basic raw material for fermentation but are not always readily available and alternative feedstocks from starch crops may be used.

When starch crops are used as raw material, the conversion process is similar but includes an additional step to hydrolyze the starch into fermentable sugars. This process, called "saccharification," uses acid hydrolysis or starch-hydrolyzing amylase enzymes. Two types of commercial enzymes are required to completely convert starch into the fermentable sugar glucose: α-amylase and amyloglucosidase. Acid hydrolysis is also possible but requires expensive acid-resistant equipment and is less efficient than enzymatic hydrolysis. After this hydrolysis step, the fermentation process is similar to that of sugar cane, as shown in Figure 32.7.

The saccharification process has changed significantly in the last 15 years. The two best known and most widely used processes for starchy materials are wet and dry milling.

Country	Production (Ml / %)	
United States	40.130	54.3%
Brazil	24.900	33.7%
China	2.050	2.8%
Canada	1.348	1.8%
France	1.250	1.7%
Germany	750	1.0%
Spain	465	0.6%
Thailand	401	0.5%
India	350	0.5%
Colombia	310	0.4%
Australia	220	0.3%
Austria	180	0.2%
Sweden	175	0.2%
Poland	166	0.2%
Hungary	150	0.2%
Others	1.110	1.5%
	73.954	100.0%

Figure 32.6—World EtOH production by selected countries in 2009. *Source:* Data from Biofuels Platform [29].

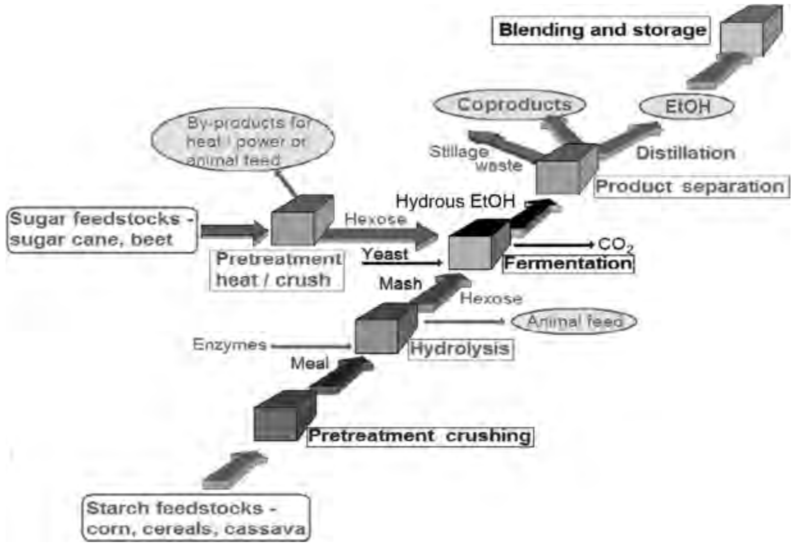


Figure 32.7—Conversion routes for sugar or starch feedstocks to EtOH. *Source:* IEA [30].

The differences between the two processes are in the pretreatment of the grain prior to hydrolysis. In the wet milling process, the corn is first steeped in a solution of water and sulfur dioxide for 24–48 h at 50 °C and then passed through mills to loosen the germ and the hull fibers. Next, the germ is removed from the kernel, and corn oil (a valuable byproduct) is extracted from the germ. The remaining germ meal is added to the hulls and fiber to form the corn gluten feed stream.

In the dry milling process, the grain is first crushed to the smallest possible particle size to facilitate subsequent penetration of water in the process. In both technologies, the final step is the EtOH distillation to remove water. Wet milling industrial plants are larger than dry milling plants, and the decision between the two technologies is driven by the investment and expected product cost.

Although these routes for sugar cane or starch processes may improve in the near future, both methods cannot compete with fossil fuels because of the high cost of feedstocks. Low-cost raw material is critical to develop a profitable EtOH pathway. Using biomass as a raw material (straw, farm residues, forest residues, biomass crops, or industrial and municipal wastes) seems to be one of the most promising approaches in this direction.

Cellulosic materials contain lignin and hemicelluloses, and hence they are sometimes termed as lignocellulosic feedstocks. One of the primary functions of lignin is to provide structural support for the plant. Unfortunately, lignin, which contains no sugars, encloses the cellulose and hemicellulose molecules, making them difficult to reach. Cellulose molecules contain long-chain glucose molecules, comparable to starch molecules, but with a different structural configuration. These structural features and the encapsulation by lignin make cellulosic materials more difficult to hydrolyze than starch feedstocks.

Hemicellulose also contains long chains of sugar molecules, but with pentoses (5-carbon sugars, C_5 sugar) in addition to glucose (6-carbon or hexose sugar, C_6 sugar). As an additional complication, the exact sugar compositions of hemicelluloses can vary depending on the type of plant. As C_5 sugars represent a high fraction of the available sugars, the efficiency and economics of the process depend on the ability to extract and ferment these sugars. There are three basic types of cellulose-to-EtOH processes—acid hydrolysis, enzymatic hydrolysis, and thermochemical—with variations of each one. The most common treatment is acid hydrolysis, which tends to destroy some of the useful products, particularly cellulose and hemicelluloses. Alternative approaches to the separation of lignocelluloses include steam explosion, treatment with EtOH/water mixtures (the "Organosolv" process), treatment with alkalis, and enzymatic separation.

In 2006, the U.S. government announced a new Advanced Energy Initiative to help overcome dependence on foreign sources on energy, with a target for biofuels to become cost-competitive in 2012 and displacing up to 30 % of the nation gasoline's use by 2030. In June 2006, the DOE released a Strategic Research Agenda focused on developing cellulosic EtOH (Figure 32.8). The DOE expects to complete the tasks within 5–15 years, and the R&D agenda requests advances in a number of areas, including collecting and transporting biomass to plants, pretreatment, enzymatic saccharification, and fermentation, to obtain significant cost reductions and reach the target for bioethanol to become cost competitive.

Figure 32.8—Phased development of bioenergy systems. *Source:* Biological and Environmental Research Information System, Oak Ridge National Laboratory; sponsored by the U.S. Department of Energy Biological and Environmental Research Program [31].

32.5.1.2 PROPERTIES

Over the last decades, the most important world gasoline specifications (ASTM and EN) have allowed the formulation of gasoline containing oxygenated compounds, including EtOH. The Worldwide Fuel Charter Committee (World Car Manufacturers Association), in their EtOH Guidelines [32] established a recommended limit of 10 % volume of anhydrous EtOH in blends with petroleum-based gasoline used in vehicles with spark ignition engines. Additionally, there are specifications to establish the quality of EtOH for automotive use, such as ASTM D4806) [33] and the equivalent European specification EN 15376 [34].

The fuel properties of EtOH compared to those of gasoline are summarized in Table 32.2. The addition of EtOH to gasoline raises three main concerns:

- Effect of EtOH on fuel volatility (vapor pressure and distillation)
- Effect of EtOH on fuel octane
- Hygroscopic nature of EtOH

In addition, there are other nonnegligible challenges to consider:

- Removal of solid contaminants, such as dirt or rust
- Material compatibility
- Minor contaminants such as sulfates in the EtOH

Although pure EtOH, as shown in Table 32.3, has a much lower vapor pressure (15–20 kPa) than gasoline, the addition of EtOH increases the vapor pressure of the EtOH/gasoline blend, with a maximum increase low concentrations (1-5 % v/v) of EtOH in the blend. Addition of only 2 % of EtOH can increase the vapor pressure by 6-8 kPa, as shown in Figure 32.9, potentially leading to noncompliance with fuel specifications [35,36].

EtOH also influences the distillation characteristics of the fuel, primarily the evaporated fraction at 70 °C (E70) and 100 °C (E100). E70 increases by up to 18 % volume for a 10 % EtOH blend and E100 by about 5 % volume for the same blends as shown in Figure 32.10.

Another important issue is the effect of EtOH in octane numbers. The octane blending index of EtOH can vary

TABLE 32.2—Fuel Property Comparison for Gasoline and Several Biofuels

	Gasoline[a]	EtOH[a]	ETBE	n-Butanol
RON	90–100	108	118	96
MON	81–90	92	101	78
Boiling range, °C	27–225	78	70	118
Density at 15 °C (kg/m^3)	720–780	792	742	810
Reid vapor pressure, kPa (pure)	50–100	15–17	30	2.2
LHV (MJ/kg)	41.8–44.0	28.9	36.3	33.1
LHV (MJ/l)	31.1–33.5	23.0	27.0	26.8
Stoichiometric air/fuel, weight	14.5–14.7	8.9–9.0	68.7	11.2

ETBE, ethyl terc butyl ether; LHV, low heating value; MON, motor octane number; RON, research octane number.

[a] Data compilation from several sources.

TABLE 32.3—Average Fatty Acid Composition (wt %) of Different FAME (Source: [40])

FAME	Lauric	Mystic	Palmitic	Stearic	Palmitoleic	Oleic	Linoleic	Linolenic
Soybean	0.00	0.06	10.64	3.88	0.14	32.38	46.36	5.53
Sunflower	0.00	0.01	6.48	4.25	0.00	18.97	69.07	0.26
Peanut	0.29	0.87	43.08	4.31	0.12	40.55	9.64	0.32
Tallow	0.08	1.30	23.88	17.88	0.00	45.25	2.85	0.53
Cottonseed	0.02	0.32	22.05	2.17	0.13	16.13	55.72	0.25
Palm Oil	0.00	0.00	11.10	4.22	0.00	47.23	32.14	0.68
Lard	0.07	1.00	26.03	15.00	0.00	45.43	9.87	0.50
Rapeseed	0.00	0.02	4.06	1.20	0.04	63.12	21.28	8.63

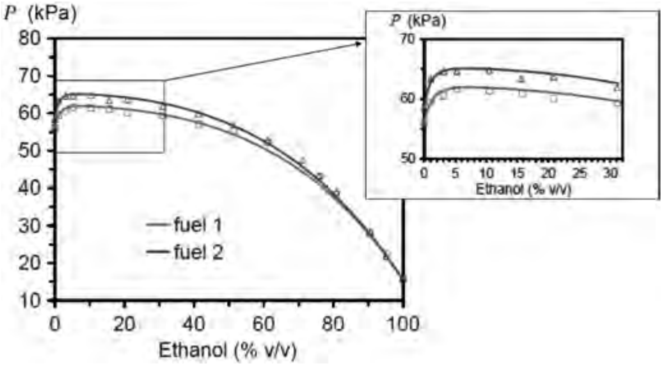


Figure 32.9—Vapor pressures of mixtures of unleaded gasoline and EtOH. *Source:* CONCAWE [35].

from 120–130 (for RON) and 98–103 (for MON), values significantly higher than pure EtOH (Table 32.3). EtOH improves the octane of the gasoline base stock as shown in Figure 32.11, and the increase depends on the gasoline base stock. Typical values for E10 (10 % EtOH blend) are +2 RON units and +1.5 MON units, and these values increase as the base gasoline octane number decreases.

EtOH has a strong affinity for water due to its hygroscopic nature. As a result, EtOH absorbs existing water in distribution, storage, and vehicle fuel systems, which can result in phase separation. When this occurs, the gasoline in the upper phase contains a reduced EtOH concentration and may fail to meet specifications for octane or other key characteristics such as vapor pressure and distillation. Higher EtOH content in gasoline creates a greater capacity to absorb water (Figure 32.12) but does not increase the risk of phase separation because the amount of water needed to cause phase separation is very large and less probable at higher EtOH contents.

The solvent nature of EtOH is well known. For this reason, EtOH blends may remove sediment and sludge from tanks and filling lines due to the solvency of the blend. Special care should be taken in the distribution system, as discussed in the handling section, with filters to prevent the arrival of those sediments to the vehicle.

With respect to compatibility of EtOH blends with materials from various components in fuel distribution systems and vehicles, there are differences from normal hydrocarbon fuels. EtOH is different from other fuel hydrocarbons in aspects such as the presence of polar groups, a relatively smaller size, and higher conductivity. These properties

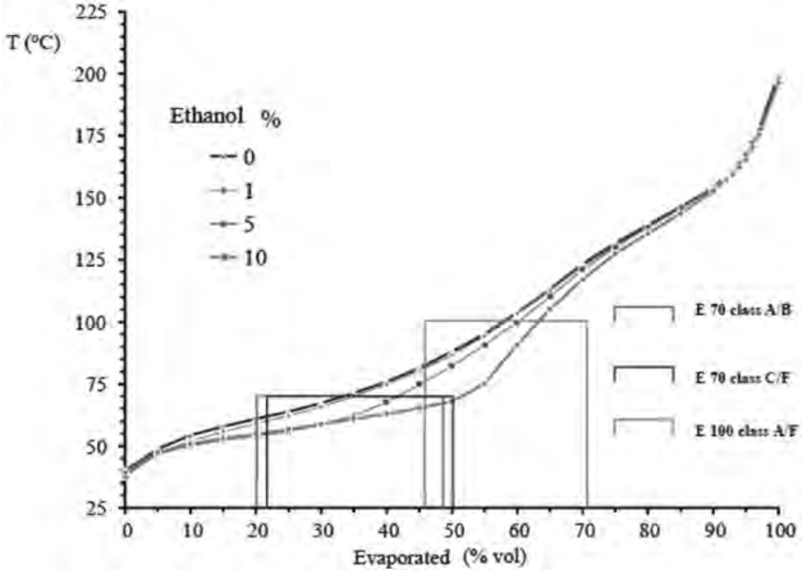


Figure 32.10—Changes in distillation curve for motor gasoline as a function of EtOH content. *Source:* CONCAWE [35].

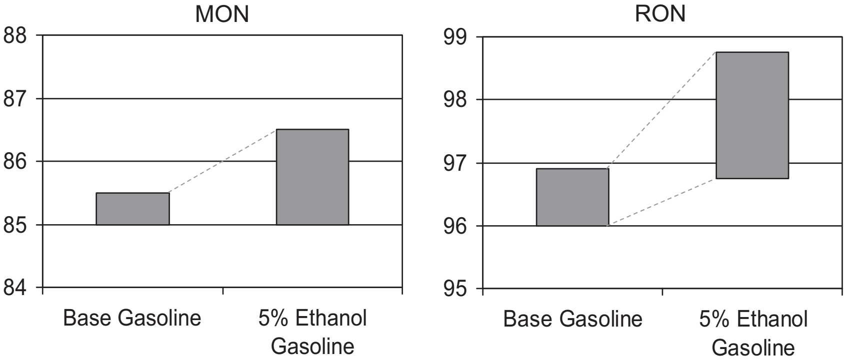


Figure 32.11—Octane numbers of 5 % EtOH mixtures with base gasolines.

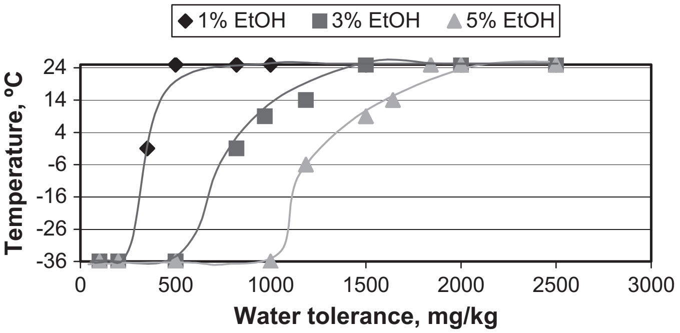


Figure 32.12—Effect of EtOH content on blend water tolerance.

may create problems with the integrity of some polymers used in different parts of the supply and distribution chain and EtOH diffusion through polymers, increasing volatile organic compound emissions [35]. EtOH can also contribute to corrosion and wear of various metal components.

Other issues reported are related to the presence of minor amounts of sulfates in EtOH/gasoline blends. These sulfates are believed to originate from sulfates carried over during the manufacturing process, and should be minimized through proper fuel specifications to avoid plugging problems in vehicle filters and injectors.

32.5.1.3 HANDLING

The concerns related to the use of gasoline formulated with EtOH usually increase with EtOH concentration. The main potential complications related to handling EtOH blends are related to water content, vapor pressure, and energy content.

EtOH distribution is rather difficult because of its affinity with water and its solvent properties, which allow it to dissolve substances insoluble in gasoline. This solvent capability allows the dissolution of material accumulated in pipelines, storage tanks, and other parts of the distribution system and thereby introduce impurities into the fuel. The affinity of EtOH for water can also result in phase separation of blended alcohol/gasoline fuels. If phase separation occurs, the quality of the remaining gasoline phase will change and is not likely to meet specifications. The water-rich phase has no value and contains hydrocarbons, which makes it a waste to be treated with special handling according to local regulations. Phase separation is a function of water and EtOH content, temperature, and gasoline properties.

To minimize potential phase separation problems, the EtOH-fuel blend should be made as far down the chain as possible, maintaining the quality control that guarantees that the fuel meets standards. Distribution of EtOH-blended gasoline via multiproduct pipelines is usually not recommended, due to concerns about water content and the serious potential risk of jet fuel contamination. Loading racks at terminals appear as convenient places for blending facilities. Bioethanol is usually blended in distribution networks by mixing with special gasoline basestock (blendstock for oxygenate blending [BOB]) (matched blends) or with conventional gasoline (splash blends). A BOB is a base fuel formulated at the refinery with specifications already adjusted to account for the changes caused by EtOH. To prevent the fuel from failing to fulfill volatility specifications, some countries tolerate extended limits for EtOH blends (volatility waiver). At terminals, pure EtOH can be stored in fixed roof tanks with or without internal floating decks. Tanks with external floating decks are not recommended given the hygroscopic nature of the product. If no additional measures are taken, the vapor concentration above the liquid EtOH will generally be flammable, so adequate safety measures must be implemented.

Special attention should be taken when EtOH-blended gasoline is introduced to filling stations for the first time to account for the risks of phase separation and sediments (rust particles, etc.) dissolving into the fuel. It is recommended to install filters (preferably those resistant to water) in the fuel dispensers. Additionally, when EtOH blends are first introduced, the compatibility of existing materials should be reviewed because some materials (elastomers, hoses, nozzles, etc.) commonly used in distribution systems are affected more strongly by EtOH blends than by hydrocarbon fuels. Some metallic components can also be susceptible to the corrosion caused by adding EtOH, but this effect can be controlled with anti-corrosion additives.

The introduction of pure EtOH or EtOH blends into the market requires proper handling and refueling practices. In the United States, safety protocols for handling EtOH have been edited for several years. In Europe, the CEN TC19 (European Standardization Committee) has more recently approved a protocol based primarily on CONCAWE reports including guidelines for blending and handling fuels containing EtOH [35].

32.5.1.4 END USE

Ethyl alcohol has long been used as an automotive fuel in two different ways: hydrous alcohol, which can completely replace gasoline in dedicated internal combustion engines, and anhydrous alcohol, as an effective "octane booster" when mixed with gasoline. EtOH is an appropriate biofuel for Otto engines because of its high octane number and compatible volatility.

As previously stated, EtOH is the most widely used biofuel in the world [37]. The most common blends range from E10 (10 % v/v EtOH) to E22 (22 % v/v EtOH). Most vehicle engines can consume low-percentage EtOH blends without any inconvenience, although the European Car Industry Association published a list of noncompatible E10 vehicles. However, the feasibility to use higher EtOH blends is an issue still under discussion. New vehicle technologies (flexible fuel vehicles) have been developed that can use blends up to 85 % v/v EtOH (known as E85), based on Brazilian experience. The possibility to use these blends in conventional vehicles without modifications depends on variables like the age of the vehicle, the vehicle manufacture and emission control type [38].

Automotive EtOH has been supported through extensive studies by worldwide institutions, mainly in the United States and Europe. The use of EtOH introduces new challenges not just to refineries and distribution logistics, but also to the performance of vehicle engines and fuel systems:

- As the heating value of EtOH is lower than that of gasoline, both in mass and volumetric terms, the fuel consumption is higher—that is, the fuel economy is lower—when an engine consumes EtOH (approximately 3.5 % less distance per litre in the case of E10).
- Although engines can theoretically be designed to use the high octane number of EtOH to achieve better performance, this is not usually the case in practice, particularly due to the need to revert to gasoline when EtOH is not available.
- Startability in cold conditions could also be worse because of the high heat of vaporization of EtOH. On the other hand, the higher volatilities of EtOH blends, already discussed in this section, slightly increase the evaporative emissions in older vehicles. However, modern vehicles with active coal canisters and new refueling facilities will practically eliminate this increase in emissions. Other exhaust emissions, particularly CO emissions, are improved in older vehicles.
- Water phase separation in case of problems through the distribution system could cause engine damage or poor vehicle performance.

EtOH has been used in diesel engines, but this application has strong barriers, primarily the stability (EtOH is not soluble with diesel at low temperatures) and bad ignition quality (cetane number) of diesel-EtOH blends.

A special and less controversial way to blend EtOH in gasoline is ETBE. ETBE is produced at refineries through reactions with isobutene. ETBE can be blended with gasoline to percentages defined by oxygen content legislation without any technical problem in vehicle performance. Physical properties of ETBE are also summarized in Table 32.2.

32.5.2 Biobutanol

Butyl alcohol is a 4-carbon alcohol that can be obtained from the same agricultural feedstocks as EtOH through the use of different microorganisms during the fermentation process. Although there have been many attempts to improve butanol production in conventional fermentation processes, the productivity is still relatively low, but new approaches provide promising results [39]. The companies BP and Dupont have updated the biobutanol production process, announcing the construction of an industrial plant in the UK through a promising Genetically Modified Organism (GMO).

Future final target would be the production of butanol from lignocelluloses, profiting from the advances of second-generation EtOH-derived processes, as the first step generating sugars from lignocelluloses is common to both processes. It is expected that the biobutanol process may require better biomass pretreatment, improvements in biotechnology, and reduced energy consumption during the purification process.

Biobutanol is claimed to offer a number of advantages over EtOH-based biofuels:

- It can be blended at higher concentrations than bioethanol for use in standard vehicles and current technologies without further modifications.
- Biobutanol has lower problems in terms of volatility, due to its low vapor pressure, and can be adapted to current distribution systems. It also has better material compatibility than EtOH.
- Energy density of butanol is closer to gasoline, with impact in fuel consumption compared to EtOH. However, the octane number of butanol is lower than that of EtOH, as summarized in Table 32.2.
- Biobutanol is less susceptible to suffer from water separation problems, as its affinity towards water is significantly reduced compared to EtOH.

As a summary, butanol is expected to become a more suitable biofuel than EtOH from the point of view of the end user, and in terms of WTW analysis of GHG emissions, it also seems to be comparable to EtOH. The future expansion of butanol-based biofuels will depend on its economic competitiveness with EtOH, especially with second-generation processes from lignocellulosic feedstocks from fast-growing crops or agricultural by products.

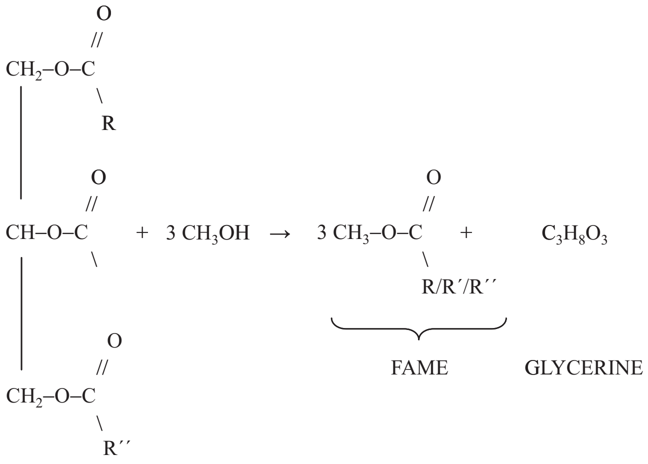
32.5.3 FAME (Biodiesel)

32.5.3.1 NATURE AND PRODUCTION PROCESS

FAME, also commonly known as biodiesel, is the most common biofuel used in diesel engines. FAME is not a single molecule like EtOH, but a mixture of several methylic esters of different fatty acids, depending on the original vegetable (or animal) oil used in the production process. Vegetable oils are primarily composed of triglycerides (glycerol esters of fatty acids). Theoretically, PVOs can be used in diesel engines but are strongly disapproved by the most important car and fuel injection equipment manufacturers for several reasons, among them the presence of very high molecular weight compounds (e.g., sterol glucosides), which can induce severe deposit problems. Therefore, using vegetable oils in vehicles requires transforming triglycerides into more engine-friendly molecules. Vegetable oils are trans-esterified with light alcohols; if the reaction is carried out with methanol FAME is obtained, while FAEE is the product if the alcohol is EtOH.

The production of biodiesel is more geographically dispersed than EtOH. Germany leads the world production (primarily from rapeseed and sunflower) with nearly 16 % of world biodiesel production, closely followed by France. In the United States, biodiesel production, mainly from soybeans, was close to 2 billion litres in 2009. World biodiesel production in selected countries is shown in Figure 32.13 [29].

The esterification process for biodiesel manufacture is relatively simple and takes place at normal pressure and ambient temperature, through the following reaction, with glycerol obtained as a coproduct of the transesterification process.



$$\begin{array}{l} CH_2\text{–}O\text{–}C(=O)\text{–}R \\ | \\ CH\text{–}O\text{–}C(=O)\text{–}R' \\ | \\ CH_2\text{–}O\text{–}C(=O)\text{–}R'' \end{array} + 3\,CH_3OH \rightarrow \underbrace{3\,CH_3\text{–}O\text{–}C(=O)\text{–}R/R'/R''}_{\text{FAME}} + \underset{\text{GLYCERINE}}{C_3H_8O_3}$$

The radicals R, R′, and R″ represent the different fatty acids involved. The composition of these fatty acids depends on the feedstock plant and range from 14 to 24 atoms of carbon. FAME may be produced from raw vegetable oils derived from soybean, palm, canola, rapeseed, or sunflower, as well as animal fats and used cooking oil. Table 32.3 compares the average compositions of biodiesel products from the most common feedstocks [40].

Figure 32.14 shows the different steps in the biodiesel production process. The reaction to produce FAME is in fact a set of three reactions: from triglycerides to diglycerides, from diglycerides to monoglycerides, and a final step to convert monoglycerides to FAME. Catalysts are used to improve reaction rate and yield. Basic homogenous catalysis is the most common technology employed in FAME plants, but there are also commercially available heterogeneous catalysis processes working at higher pressures and temperatures, but requiring very dry reactants. Although there are currently few or no biodiesel plants using heterogeneous catalysts, potential advantages of this technology would include:

- No acids are required for neutralization
- There are no waste soaps
- There are no catalysts consumed in the reaction
- Increased conversion yields (> 99 %)
- Easier purification
- The coproduct is pure glycerine

FAME is mainly produced from rapeseed (canola), palm, soybean and sunflower oils feedstocks. Jatropha oil has also recently entered the market. There is also research into using other plants (brassica carinata, crambe abyssinica, camelina, jojoba, etc.). It is also possible to use used cooking oil and animal fats, and research on lipids originating from algae is currently underway.

Methanol could be replaced by other alcohols, such as EtOH or butanol. The same reaction using EtOH produces FAEE. However, as EtOH is usually more expensive than methanol and plant investment and operational costs are higher, FAEE is commercially nonexistent.

32.5.3.2 PROPERTIES

As previously stated, FAME is a complex mix of compounds, and its specifications must regulate characteristics to ensure correct engine behavior (cetane number, cold filter plugging point [CFPP] or oxidation stability for example). There are two specifications for FAME (EN 14214 [41] in Europe and ASTM D6751 [42] in the United States), which do not relate fuel properties to the origin of the fuel (except for the Iodine Index in EN 14214) but do depend on the production process (content of monoglycerides, diglycerides, triglycerides, and total glycerine). Table 32.4

Country	Production (Ml / %)	
Germany	2.859	15.9%
France	2.206	12.3%
United States	2.060	11.5%
Brazil	1.535	8.6%
Argentina	1.340	7.5%
Spain	967	5.4%
Italy	830	4.6%
Thailand	610	3.4%
Belgium	468	2.6%
Poland	374	2.1%
Netherlands	364	2.0%
Austria	349	1.9%
China	338	1.9%
Colombia	330	1.8%
South Korea	300	1.7%
Others	2.998	16.7%
	17.929	100.0%

Figure 32.13—World biodiesel production by selected countries in 2009. *Source:* Data from Biofuels Platform [29].

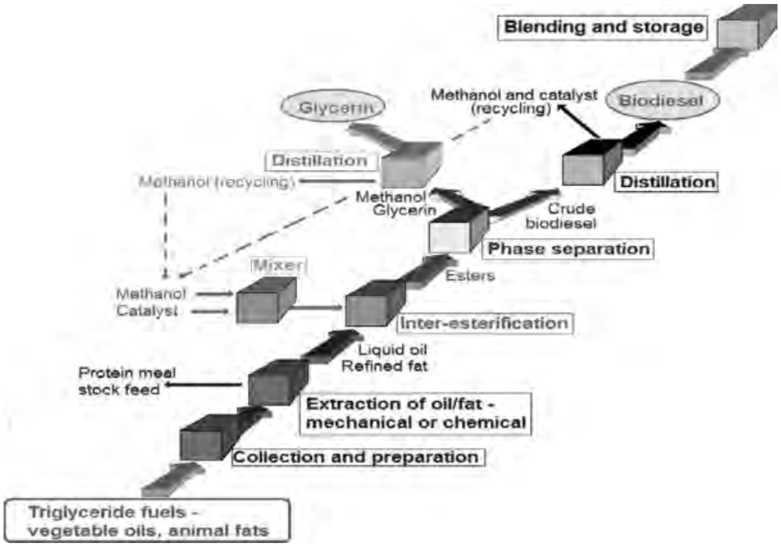


Figure 32.14—Conversion routes for biodiesel. *Source:* IEA [30].

compares European FAME and diesel specifications. FAME is fully soluble and compatible with diesel oil.

The implementation of these standards has been a key element for market penetration of biodiesel, leading to its acceptance by vehicle manufacturers as a reliable fuel. Modern diesel engines are expected to provide very high performance and efficiency but require advanced fuels, manufactured to very fine tolerances. Biodiesel is produced from many different sources and feedstocks, and constant quality is an issue even with batch quality control. Small differences in the fatty acid distribution may led to differences in heating value, viscosity, and lubricity, without

TABLE 32.4—Comparison of European Diesel and FAME Specifications

		Diesel A EN 590		Biodiesel EN 14214	
Property	**Units**	**min**	**max**	**min**	**max**
Cetane number	–	51.0		51.0	
Cetane index	–	46.0			
Density @ 15°C	kg/m^3	820	845	860	900
Aromatic PCAs	% (m/m)		11		
Sulfur content	mg/kg		50		10
Kinematic viscosity @ 40 °C	mm^2/s	2.0	4.5	3.5	5.0
Flash point	°C	55		120	
Cold filter plugging point					
Winter (Oct 1st – Mar 31st)	°C		–10		–10
Summer (Apr 1st – Sep 20th)	°C		0		0
Carbon residue	% (m/m)		0.30		0.30
Lubricity (corrected wsd 1.4) @ 60 °C	µm		460		
Water content	mg/kg		200		50
Solid particles	mg/kg		24		24
Ash content	% (m/m)		0.01		0.02
Acidity	mg KOH/g				0.5
Oxidation stability	g/m^3		25		
Oxidation stability @ 110 °C	hours			6	

TABLE 32.5—Fuel Property Comparison for Diesel and Several Biofuels[a]

	Diesel EN-590	FAME	HVO	BTL
Cetane number	>51	51	80–99	70–80
Density at 15 °C (kg/m^3)	820–845	885	775–785	700–800
LHV (MJ/kg)	42.0–43.0	37.5	44.0	43–45
LHV (MJ/l)	35.3–36.4	33.2	34.4	33.1–34.3
Viscosity 40 °C (mm^2/s)	2.0–4.5	4.5	2.5–3.5	–
Distillation range (°C)	180–360	350–370	180–320	–

[a] Data compilation from several sources: EN 590 summer diesel; FAME from rapeseed.

taking into account contaminations from different part of the process. As an example of this specification complexity, EN 14214 has more than 30 criteria and limits to guarantee fuel quality [29].

The properties of FAME compared with conventional diesel are summarized in Table 32.5. The main differences between FAME and diesel oil are:

- Lower heating value (equivalent to less energetic density)
- Low temperature operability
- Lower stability

As it happened with bioethanol, the heating value of biodiesel is lower than conventional diesel. The difference in density creates a difference between the two products of about 8 % in volume and 12.5 % less energy per weight unit. This difference creates higher fuel consumption, which depends on the percentage of FAME in the fuel.

Distillation properties have also been identified as an issue with FAME. The higher distillation profile (biodiesel exhibits a distillation range more than a distillation curve) and some evidences of dilution because of the appearance of biodiesel in the lubricant are considered an issue.

Low-temperature properties of biodiesel are also a critical specification. Individual FAME products have different properties, related to their composition and impurities from the production process, but typically with higher pour point, cloud point, and CFPP, and more difficult to predict. Table 32.6 summarizes cold properties from different feedstocks. Saturated chains increase the oil's tendency to block filters in cold conditions [43]. Concerns on cold properties are related to handling and operability, as discussed later in those sections.

Stability is related to the fuel's tendency to form deposits that could induce filter blocking or foul injector nozzles in vehicles, and also if the product can be stored during long periods. Stability depends on the original vegetable oil, which impacts the type of seed used for the raw material. Oils with more unsaturated fatty acid chains produces less stable FAME, and antioxidants must be added. Although additives may solve this technical barrier, additive response depends on the feedstock, with FAME from sunflower oil being the most difficult to treat.

TABLE 32.6—Typical Properties for FAME Manufactured from Different Feedstocks [43]

Feedstock	Cloud Point (°C)	CFPP (°C)	Viscosity (mm^2/s at 40°C)
Rapeseed	–5	–18 to –12	5.0
Sunflower	–1 to +3	–7 to –3	4.4
Soybean	–7 to +3	–6 to –2	4.0
Coconut	+9 to +12	8	4.8
Palm	+13 to +16	+5 to +11	4.3 – 5.0
Tallow	+10 to +20	+9 to +14	4.8

In addition, the presence of metals increases the amount of insoluble deposits formed. In a vehicle it is very difficult to avoid the presence of trace copper or zinc, and therefore antioxidant additives may not be enough. When metals are present, FAME blends require stabilizing additives, and some reports strongly recommend the use of metal-deactivating additives in modern engine injection systems (small hole injectors, small tolerances, and extremely high working pressures). The tendency to form deposits (and more specifically, to block filters) is a very complex problem. Other factors aside from stability are now being considered, and there are proposals to specify a lower limit for monoglyceride content or to introduce limits on the saturated mono-glyceride and sterol-glucoside contents in future specifications.

FAEE has not been widely studied in vehicles, but it is expected to behave similar to FAME. Although there are no industrial plants producing and commercializing FAEE, the European Committee for standardization has created a group to specify the characteristics of FAEE. The properties of FAEE are very similar to those of FAME, but FAEE does have some advantages:

- Slightly higher LHV
- Better cetane number
- Better properties in cold conditions
- Better GHG savings

32.5.3.3 HANDLING

FAME is usually blended with diesel fuel at refineries because FAME-diesel blends are compatible with delivery networks. Nevertheless, transportation of FAME blends in multi-product pipelines is highly restricted to prevent cross-contamination in the supply chain between diesel and other fuels that may only accept FAME traces, such as jet fuels, heating oil, and marine gasoil [43]. Tests are currently being performed by international organizations regulating aviation fuels to establish an acceptable limit for FAME content and to define final specifications on this issue.

Due to its hygroscopic nature, FAME blends may contain more water than hydrocarbon fuels. As water separation is more difficult, proper water management is essential at the refineries and the terminals when FAME is handled.

Procedures to control water buildup (regular water bottom checks and facilities to drain water when required) should be established. Because water exposure facilitates biological growth, particularly when FAME is present, tanks containing FAME and FAME-diesel blends should also be checked periodically for the presence of microbiological contamination.

FAME has very good solvent capacity. Biodiesel may dissolve accumulated sediments in storage tanks, which may lead to later injector and filter plugging [44]. In addition, FAME also exhibits compatibility problems with some polymers (polyethylene, polypropylene) and rubbers (natural and nitrile rubbers). Some metallic components may also be affected by biodiesel blends.

32.5.3.4 END USE

FAME is currently blended at low percentages (up to 7 %) with fossil diesel in Europe. Some vehicle manufacturers are opposed to exceeding this amount, but other vehicle manufacturers have proposed up to 30 %. Vehicle manufacturers and injection equipment manufacturers do have some concerns regarding FAME use in modern diesel vehicles, particularly in engines with common rail injection systems. Problems with dilution of FAME into lubricants have been also noted in vehicles with particulate traps in the exhaust pipe. In the United States, B20 (20 % FAME) is the most commonly used biodiesel [44]. Higher blends are possible but may require equipment or engine modifications. It is possible to use pure FAME in dedicated engines.

FAME performs very similarly to conventional diesel in engines when all of the appropriate specifications (such as ASTM or EN) are observed. No problems with driveability or startability have been described. However, because the heating value of FAME is less than that of diesel fuel (92 % of energy content from conventional diesel in a volumetric basis), fuel consumption increases (fuel economy decreases) when the engine consumes FAME (approximately 1 % less distance per litre in the case of B10).

Modern diesel vehicles are more sensitive to water and sediment in the fuel due to the very fine tolerances required by their high-pressure fuel injection systems. The previous section described measures that can be taken in the fuel supply system to contribute to the cleanliness of fuels delivered to the vehicles. However, even after clean, dry fuel has been delivered, vehicle factors must also be considered to achieve problem-free operation. Because FAME is more aggressive to elastomers, its compatibility with certain materials must also be checked.

In general, regulated exhaust emissions decrease except for emissions of NOx, which increase slightly. Particulate matter emissions decrease even when compared with low-aromatic, nonsulfur (S<10 ppm) diesel.

32.5.4 HVO

HVO, also referred to as “green diesel,” “hydrobiodiesel,” or “renewable diesel fuel,” is a biofuel produced by hydrogenation of vegetable oil, used oil, or animal fats. This biofuel is chemically comparable to fossil fuels, as it is a mixture of saturated hydrocarbons derived from triglycerides. While FAME quality is strongly dependent on the feedstock used, HVOs can be produced from many oils without compromising fuel quality.

HVO is produced in dedicated hydrogenation units at oil refineries or in existing hydrodesulfurization (HDS) units by coprocessing vegetables oils with diesel. The resulting product is HVO, with propane (bio-propane) as a coproduct that can be blended with conventional LPG. Compared to existing units, dedicated units make possible reaction optimization routes to maximize HVO production and quality with minimum hydrogen consumption. This optimization can be achieved with proper catalyst selection and operating conditions, but requires a large investment. Additionally, the hydrogenated product obtained from a dedicated unit has unsuitable properties under cold conditions and thus requires an additional isomerization step. The Finnish Company NESTE OIL is most likely the most active HVO producer and uses its own NExBTL process [45].

Coprocessing of vegetable oil in an existing HDS unit at refineries is the least expensive way to obtain biofuels with a low investment as only minor modifications are required. The amount of vegetable oil that can be coprocessed depends on hydrogen availability, compressor capacity, and required cold properties for the product. In most cases the isomerization step is unnecessary because cold properties are adequate, though this may depend on the season and country.

The obtained product exhibits improved properties, including density and cetane number, in diesel blends. Table 32.5 compares the characteristics of HVO with FAME and conventional diesel. HVO exhibits properties similar to gas-to-liquid (GTL) and BTL fuels. HVO is also reported to have benefits in term of reduced NOx and smoke emissions.

Because HVOs are hydrocarbons, they do not need to comply with biodiesel specifications, but to conventional diesel fuel requirements (EN 590 and ASTM D975). HVO has no harmful effects in vehicle motors due to its similar chemical properties to conventional diesel, which is an advantage over FAME, and can be blended to conventional diesel at any percentage. In addition, the low density of HVO allows it to extend diesel production by including heavier fractions such as LCO, a possibility very interesting for the European oil industry.

HVO production is currently more expensive than FAME production because of the price of vegetable oil and hydrogen consumption. HVO production is expected to use nonconventional vegetable oils and treated greases, considered as residues, thus improving the economy of the process. From the end use point of view, vehicle manufacturers prefer HVO to FAME.

32.5.5 Synthetic Fuels (BTL)

During the first half of the 20th century, coal was transformed into liquid fuels by the FT reaction. In a first reaction step coal is transformed into syngas (a mixture of CO and H_2), which later reacts in the presence of a cobalt or iron catalyst to produce a mixture of long-chain liquid hydrocarbons. The process takes place at high temperature and pressures. This process, using coal as the raw material, is called CTL (coal to liquids).

Later developments focused on natural gas as preferred raw material, and the process was renamed as GTL. The natural gas industry considers this process to be an economic option for remote or small size gas field development by converting them into liquids, and commercial GTL plants are already in operation.

Even more recently, biomass has also been proposed as a suitable raw material for the FT process. When biomass is the raw material, the process is known as BTL or "biomass to liquids." Waste products could also be used as the raw material (WTL [waste to liquids]). However, although it is possible to gasify organic residues into syngas, it does not seem economically feasible to invest in a plant dedicated exclusively to waste processing and most probably, waste would be processed in a mixture with biomass in BTL plants.

The products obtained in a something to liquid (XTL) process (term used to refer to this group of thermochemical processes independently from the feedstock) need further hydrocracking, hydrogenation, and fractionation to produce the final products, which range from naphtha to solid paraffins. However, the most interesting products are middle distillates (diesel fuel and kerosene) and lubricants.

FT technologies are not readily available for companies wishing to invest in XTL plants. There are only a few companies with strong position on this technology that could be open access to FT technology for BTL projects, but not for GTL or CTL. In the case of BTL, the gasification technology is also critical and depends on the type of biomass available. Considering the considerable investment necessary to build a BTL plant, it is critical to guarantee a homogenous supply of biomass, and that the quality of the generated gases is acceptable for the rest of the conversion process.

Currently, there are no commercial, large-scale BTL production plants. There are some demonstration projects, and one of the most promising technologies is the so-called "Carbo-V" process from Choren Industries Ltd. However, the development is still in progress and far from competitive. The production costs of BTL products are higher than those of conventional products or alternative biofuels, but the quality of FT diesel fuel is also the highest. Therefore, there is a significant support for this type of biofuels from vehicle manufacturers, particularly the German manufacturers Daimler, Volkswagen, and Bosch.

The products of BTL (or XTL) processes are biohydrocarbons that are nearly chemically identical to fossil fuels. The main differences are the absence of sulfur and aromatics and the structural form of the hydrocarbon chains, which are more linear than those of conventional fuels. These properties make BTL synthetic diesel the ideal product to feed compression ignition engines. Table 32.5 compares the main properties of BTL with HVO, FAME, and conventional diesel.

Synthetic biofuels are suitable for use in conventional engines as they are similar hydrocarbons to those obtained from crude oil, with excellent engine properties and low sulfur content. However, some car manufacturers have publically communicated that dedicated XTL engines would exceed the performance of conventional engines, although this theoretical statement should be confirmed.

The production of BTL has a more favorable energy balance than other biofuels. In general, all regulated exhaust emissions decrease when engines are fed with XTL diesel, including NOx and particulates. GTL and CTL have poor GHG balances, but BTL and WTL have very positive balances.

32.5.6 Others: Methanol, DME, Bio-Crudes

There are other synthetic products that are suitable as transportation fuels and can be obtained from biomaterials. Most of them are in the group of second-generation biofuels—new alternative processes based on non-food biomass, biomass byproducts or residua—mainly through thermal conversion processes.

- Methanol can be produced from biomass via syngas processing. Methanol was proposed in the 1980s as an octane improver when lead-based antiknock was forbidden. The use of methanol was unsuccessful, and it was abandoned in practice because of its harmful effects (including toxicity) and its very low heating value.
- Another future promising option is DME. DME can be produced from the dehydration of methanol or directly from syngas ($CO+H_2$). When biomass is the raw material in the syngas production process, the product can be considered bio-DME. Although the physical properties are suitable to substitute or blend LPG, DME is also an excellent diesel fuel due to its high cetane number (55) and very high autoignition temperature (350 ºC). In addition, its toxicity is low and its GHG balance is very good when lignocellulose is the raw material. DME is acknowledged as one of the best diesel fuels in terms of burning cleanliness, pollutant emissions, and fuel economy. However, it is not feasible to blend DME with conventional diesel fuel in existing engines because it must be stored under mild pressure to maintain a liquid state. The vapor pressure of DME at 25 ºC is 610 kPa, so it is gaseous at ambient conditions and requires a dedicated distribution infrastructure. Other disadvantages of DME as a diesel fuel include its low viscosity, very bad lubricity, and material compatibility. As a consequence, vehicles using DME must be dedicated or undergo serious modifications: fuel tank, fuel injection system, etc. Additionally, bio-DME is very expensive and is not yet produced for fuel applications. Although DME is still considered to be a possible niche fuel (for instance, for fleets), it is a much more difficult proposal as a mainstream fuel.
- Another option is the thermal treatment of biomass (pyrolysis) to produce a liquid "bio-crude," which could be included in the crude basket at conventional refineries after adequate pretreatment. The combined process is also known as thermal fepolymerization. The product can be used as heating fuel or can be further converted to other biofuels.

32.6 ECONOMICS

In the introduction of this chapter, it was discussed how different countries were supporting the inclusion of biofuels blends in the mixture of transportation fuels. The economics of biofuels are far less efficient than those of fossil fuels, and it will not be easy for first-generation biofuels to achieve fossil fuel prices. This justifies government actions creating differential tax systems to minimize this price gap with conventional fossil fuels. EtOH from sugar cane seems to be the only economic option, but even in that case Brazilian EtOH is the only biofuel currently commercialized at competitive prices with fossil fuels. However, the Brazilian experience is unlikely to be reproduced in other countries, and even the most efficient producers cannot compete without subsidizing production costs, as shown in Figure 32.15 for EtOH from corn. With respect to biodiesel, any product from vegetable oil is also far from competitive compared to conventional diesel fuels.

For first generation biofuels, the cost of the raw materials is by far the most important factor in biofuel prices,

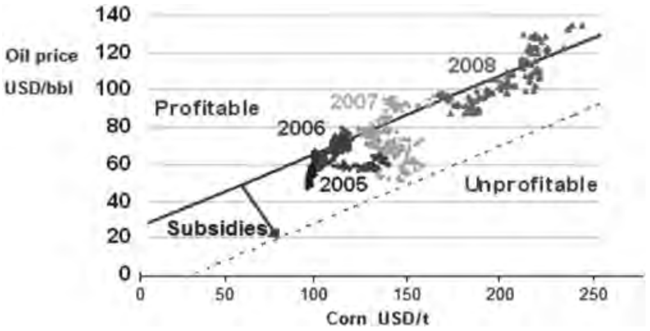


Figure 32.15—Corn EtOH profitability and subsidies, *Source:* IEA [30]. USD, U.S. dollar.

which may account for 50–70 % of total production costs. Despite high oil prices, feedstock prices have risen in some cases even more strongly, creating doubts about current and future profitability of biofuel plants. As an example, vegetable oil prices are compared to diesel oil prices from 1997 to 2012 in Figure 32.16. The figure shows strong variations in raw material prices, and also energy price variations, indexed to the price of oil. However, these energy price variations also affect production costs, so feedstock prices are not totally independent.

In addition, the claim that biofuels feedstock needs have driven up food prices and some question marks about environmental benefits with full-life-cycle GHG analysis have led many countries to modify planned regulation, subsidies, or taxation benefits. Direct comparison with fossil fuels and even with biofuels from different countries is very challenging, as the cost of diesel fuel includes taxes, which are different in different countries. With current production costs, FAME blending in Germany could have been a good business with tax exemptions in several years, and very bad in others, while in other countries, over the same period of time, blending FAME would not have been economical even with de-taxation.

Independently from the price of crude oil, it is expected that the increase in demand for biofuels will contribute to increasing prices for feedstock, especially for oil seeds. The need of new non-food feedstock crops is based on reducing the social alarm caused by the price increases in food crops, and improving the efficiency of second-generation biofuel processes, in which the feedstock represents a smaller cost factor (25 % to 40 %), plant investment being the first one. This capital investment intensity would favor large size plants to capture scale economy, especially in thermochemical processes versus biochemical processes.

Even assuming that biofuels will be produced from a non-food feedstock in the future, these price uncertainties cannot be dismissed because biomass producers do not follow the practices of long-term contracts usually required by the energy industry. Thus, the market situation may change in relatively short periods and induce large fluctuations, with feedstock availability highly compromised. Strong international biofuel feedstocks trading systems would be required to avoid dependence on domestic productions.

In addition to the political and moral questions that have arisen from the potential effect of first-generation biofuel on food prices, there is an important issue related to land resources. Infrastructure is also a critical factor to consider in several aspects. First, even with advances in plant productivity, the feedstocks are by nature dispersed, and they require adequate transport infrastructure to the processing centers. Second, the limitations to use conventional fuel handling and distribution systems discussed in previous section. Both transports affect the economy of the process, and are closely related to energy costs.

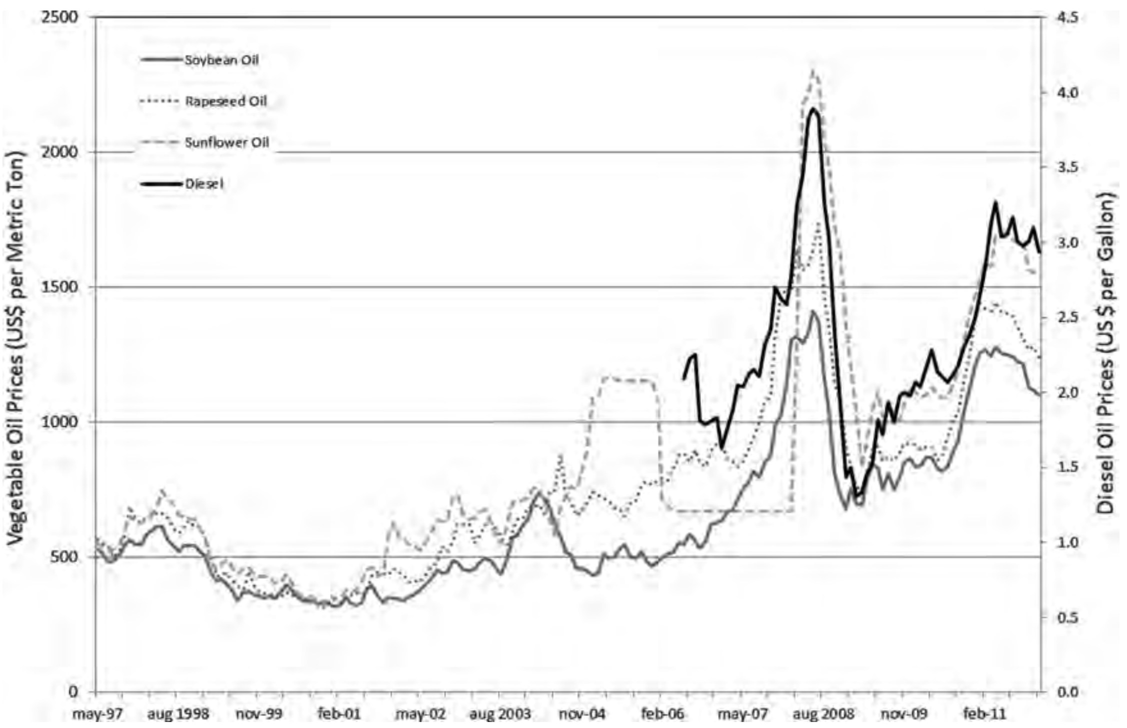


Figure 32.16—Vegetable oil prices versus diesel comparison.

Finally, even in a positive scenario in which advances in second generation biofuels make them economically competitive with conventional fuels, this does not guarantee their consolidation. Current biofuels and biorefineries economics are based on today's engines and markets, and any evolution in vehicle technology (electric car, for example) will affect these scenarios, because feedstock availability could be compromised for increasing land resources dedication to biopower generation and competition with biofuels.

A comprehensive economic evaluation of current and future biofuels is out of the scope of this chapter and has been a subject for many studies during the last years. The main objective of this section was to emphasize the strong relation between feedstock availability and biofuel economics because this is one of the drivers for new second-generation biofuels to overcome this limitation.

32.7 CONCLUSION: LOOKING AT THE FUTURE

Meeting the world's growing demand for energy is an enormous concern. A continuous growth as forecasted will result in energy needs in 2050 doubling current demand, although, as discussed in Chapter 3, there is some uncertainty in these scenarios because of the progressive implementation of laws and carbon policies with a focus on energy efficiency. However, it seems there is a general agreement about a significant increase, and that the driver for this demand will come mainly from developing countries.

A scenario in which this demand is completely covered with sustainable energies is hardly considered, and most likely an energy model combining fossil fuels and low-carbon energy sources would be a reasonable configuration to satisfy this demand. As transportation will grow around the globe, transportation fuel consumption will also increase despite current and future improvements in vehicle efficiency.

To support current working scenarios for future biofuels, there are some assumptions with a reasonable degree of consensus:

- Developed countries will maintain their support for renewable energy, including transportation biofuels and GHG emissions reduction
- Sustainability exigencies will be maintained and increasingly regulated
- Certification schemes will be established and accepted around the world
- Biofuels should be economically competitive, with a decisive element in the price per ton of CO_2 avoided
- The GHG savings of conventional biofuels must improve, or such biofuels are likely to disappear in short to mid term
- To develop renewable energies, some type of carbon tax will be imposed on fossil fuels
- Waste as a raw material will be developed as much as possible as one of the highest priorities in R&D strategies

There are discrepancies among different reports on the availability of biomass. However, even in the most optimistic scenario, biomass will be unable to cover a significant share of the future energy needs. The potential of biofuel production is a controversial issue. In Europe there are some studies suggesting that biofuels will not be able to cover the current target (5.75 % of transport fuel consumption), while others argue that biofuels could potentially cover up to 15 %, and even in very optimistic scenarios biofuels cover up to 40 % of world transportation fuel consumption.

A summary of problems for biofuels development and some potential solutions include:

- Land restriction must be solved by increasing yields. Possible answers include improvement of non-food crops, searching for naturally genetic diversity of non-developed plants such as jatropha, and microorganism farming (microalgae but also other microorganisms). Land availability could also be improved by feasible yields in "waste" (degraded) lands.
- Logistics of biomass must be improved by increasing energy density, meaning to develop "on-site densification," avoiding biomass movement, developing "on-site processing units," or increasing the biomass energy content by developing hydrocarbon producer plants.
- The need of advanced biomass to fuel process could have different approaches:
  - Biological process substituting for thermal ones
  - Improving energy efficiency of the existent processes (for example, extracting dry biomass from aquatic crops)
  - Waste recycling (urban waste to fuel)
  - Reducing concerns on biomass metal content in processes including combustion plants or gas pretreatment
  - Developing a full plant processing concept starting by extracting valuable molecules and ending by processing cellulose

Biofuels need a change of paradigm to improve their forecast. This change may arise particularly, but not only, from alternative feedstocks. Many of the problems from first-generation biofuels could be addressed by the production of biofuels from wood and plant residua, and from non-food feedstocks. Agronomists have named this new paradigm the Agro Energetic Industry, to differentiate it from the food industry. The new Agro Energetic Industry will request new infrastructure to reach target efficiency, in addition to new crops and new water management. It will also involve changes in the mentalities of the current landowners, one of the main barriers.

Some of the targets for this new industry would include:

- Fix the prices of biomass per energy content (€/GJ)
- New biotechnological plants should reduce dependence from uncontrollable variables including biotic attacks (parasites) or abiotic attacks (water scarcity in dry years)
- New crops should be suitable for marginal lands
- Soil erosion must be prevented

The achievement of these targets would boost the Agro Energetic Industry, increasing the yield per hectare without environmental impact. Current R&D efforts address these targets, in addition to a wide range of improvements in the industrial processes to convert biomass into energy, including the thermo-chemical processes. In the short term, these improvements will focus on improving the energy efficiency and GHG balance of the final products. In the long term, multifeedstock biorefineries are expected to be developed. These industrial plants will process a wide variety of biomass in an integrated way to obtain food, feed, chemicals, and energy. As an intermediate step, raw biomaterials could be treated in existing refineries or gasification plants to produce power. Also in the long term, biomass produced through biotechnology, marine algae crops, or salt-resistant plants could be the answer.

Regarding pretreatment technologies, it is important to highlight that one of the main biomass disadvantages is the logistics, as discussed in the economics section. Biomass has a very low energy density per volume, so biomass transportation without any densification process is very inefficient and could damage the GHG balance. Solutions to this problem could be technological (densification of biomass to obtain more weight per volume) or conceptual (such as centralizing production plants) in nature. As an example, it is assumed that the surplus residues of agriculture in Europe could provide more than 800 PJ. Assuming that efficient collection is feasible in a 50-km radius around transformation plants (i.e., a power plant), the available biomass can provide only 200 PJ, so about 75 % is unavailable for economic energy generation. Thus, there are significant opportunities for biomass pretreatment and for decentralized biomass plants.

Finally, it is important to remember land availability as one of the limiting factors. Biofuels have to compete for biomass with other applications that seem more effective in terms of GHG savings (such as converting biomass to power). Directly producing power from biomass avoids energy consumption associated with biofuel production, very intensive in some cases. Some preliminary studies have advanced the possibility that GHG avoidance could improve by 4 to 8 times. In this situation, a new competition emerges: biomass to produce biofuel or biomass to produce power (electricity), which could change completely the energy scenario during the next decades. The key issue could be the vehicle development, because if car manufacturers consider electric car technically and economically interesting, the development of vehicles consuming conventional fuels (and biofuels) could be compromised. If this is not the scenario, thermal engines will be improved and optimized for fuel and biofuels blends. The final conclusion might be that the biofuels future will largely depend on vehicle development.

ACKNOWLEDGMENTS

The coordinating author acknowledges the support in the writing of this chapter of Carlos Díaz and Silvia Martín as well as other colleagues from the Repsol Technology Center: Javier Ariztegui, Diana Cano, Robert Coll, Enrique Espi, Lucía Gonzalez and Rebeca Yuste.

REFERENCES

[1] Commission of the European Communities, "Green Paper—Towards a European Strategy for the Security of Energy Supply," COM(2000) 769, November 29, 2000.

[2] Commission of the European Communities, "White Paper—European Transport Policy for 2010: Time to Decide," COM(2001) 370, September 12, 2001.

[3] Commission of the European Communities, "Communication from the Commission to the European Parliament, the Council, the Economic and Social Committee and the Committee of the Regions on Alternative Fuels for Road Transportation and on a set of Measures to Promote the use of Biofuels," COM(2001) 547, November 7, 2001.

[4] Alternative Fuels Contact Group, "Market Development of Alternative Fuels," December 2003 Report.

[5] "Directive 2003/30/EC of the European Parliament and of the Council of 8 May 2003 on the Promotion of the Use of Biofuels or Other Renewable Fuels for Transport," Official Journal of the European Union, May 17, 2003, L123, pp. 42–46, http://ec.europa.eu/energy/res/legislation/doc/biofuels/en_final.pdf (accessed January 31, 2012).

[6] Matthies, J., Suchy, C., and Belyi, A., "Production Capacity of the Renewable Energies in the European Union," DG Research, Scientific and Technological Options Assessment Series, STOA 115 EN, July 2003, published 02-2004.

[7] Commission of the European Communities, "Communication from the Commission to the Council and the European Parliament on Renewable Energy Roadmap—Renewable Energies in the 21st Century: Building a More Sustainable Future," COM(2006) 1719, January 10, 2007.

[8] Commission of the European Communities, "Proposal for a Directive of the European Parliament and the Council on the Promotion of the Use of Energy from Renewable Sources," COM(2008) 19, January 23, 2008.

[9] "Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the Promotion of the Use of Energy from Renewable Sources and Amending and Subsequently Repealing Directives 2001/77/EC and 2003/30/EC," *Official Journal of the European Union*, June 5, 2009, L140, pp. 16–62, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0016:0062:EN:PDF (accessed January 31, 2012).

[10] "Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 Amending Directive 98/70/EC as Regards the Specifications of Petrol, Diesel and Gas-Oil and Introducing a Mechanism to Monitor and Reduce Greenhouse Gas Emissions and Amending Council Directive 1992/32/EC as Regards the Specification of Fuel Used in Inland Waterway Vessels and Repealing Directive 93/12/EC," *Official Journal of the European Union*, June 5, 2009, L140, pp. 88–113.

[11] Pelkmans, L., "Biofuels in the United States," In: PREMIA WP2: International Activities on Alternative Motor Fuel, December 2005.

[12] U.S. Government, "Energy Independence and Security Act," Public Law 110-140, December 19, 2007, http://www.gpo.gov/fdsys/pkg/PLAW-110publ140/pdf/PLAW-110publ140.pdf (accessed January 31, 2012).

[13] State of California, "Executive Order S-01-07," January 18, 2007, www.arb.ca.gov/fuels/lcfs/eos0107.pdf (accessed January 31, 2012).

[14] IEA, "World Energy Outlook 2009," International Energy Agency, Paris, 2009.

[15] CONCAWE, "Energy and Greenhouse Gas Balance of Biofuels for Europe—An Update," CONCAWE Report 2/02, April 2002.

[16] Joint Research Centre-EUCAR-CONCAWE, "Well-to-Wheels Analysis of Future Automotive Fuels and Powertrains in the European Context," Version 1b, January 2004.

[17] European Environmental Agency, "How Much Bioenergy Can Europe Produce without Harming the Environment?" EEA Report No 7/2006, June 8, 2006, http://www.eea.europa.eu/publications/eea_report_2006_7/at_download/file (accessed January 31, 2012).

[18] Thrän, D., Weber, M., Scheuermann, A., Fröhlich, N., Zeddies, J., Henze, A., Thoroe, C., Schweinle, J., Fritsche, U., Jenseit, W., Rausch, L., and Schmidt, K., "Sustainable Strategies for Biomass Use in the European Context," Institut für Energetik und Umwelt GmbH, 2006.

[19] IEA, "Technology Roadmap: Biofuels for Transport," International Energy Agency, Paris, 2011.

[20] CONCAWE, "EN 16214: A New European Standard for Sustainable Biofuels," *CONCAWE Review*, Vol. 20, No. 2, 2011, pp. 14–15.

[21] Global Bioenergy Partnership (GBEP), "The Global Bioenergy Partnership Sustainability Indicators for Bioenergy," 1st ed., December 2011.

[22] Roundtable on Sustainable Fuels (RSB), "List of Documents," RSB International Standard RSB-DOC-10-001 v2.0, July 14, 2011, http://rsb.epfl.ch/page-67254.html (accessed January 31, 2012).

[23] European Biofuels Technology Platform (EBTB), "Strategic Research Agenda & Strategy Deployment Document," January 2008, http://www.biofuelstp.eu/srasdd/080111_sra_sdd_web_res.pdf (accessed January 31, 2012).

[24] [24] European Biofuels Technology Platform, "Strategic Research Agenda (2010 Update)—Innovation Driving Sustainable Biofuels," July 2010, http://www.biofuelstp.eu/srasdd/SRA_2010_update_web.pdf (accessed January 31, 2012).

[25] Food and Agricultural Policy Research Institute (FAPRI), “U.S. and World Agricultural Outlook,” FAPRI Staff Report 08-FSR 1, January 2008, http://www.fapri.iastate.edu/outlook/2008/text/OutlookPub2008.pdf (accessed January 31, 2012).

[26] Larson, E.D., “Biofuel Production Technologies: Status, Prospects and Implications for Trade and Development,” UNCTAD/DITC/TED/2007/10, United Nations, New York and Geneva, 2008.

[27] IPIECA, “Biofuels, Sustainability and the Petroleum Industry,” February 2009, http://www.ipieca.org/system/files/publications/biofuels.pdf (accessed January 31, 2012).

[28] Bunting, B., Bunce, M., Barone, T. and Storey, J., “Fungible and Compatible Biofuels: Literature Search, Summary and Recommendations,” ORNL/TM-2010/120, Oak Ridge National Laboratory, U.S. Department of Energy, September 30, 2010.

[29] ENERS Energy Concept, “Production of Biofuels in the World in 2009—Geographic Distribution of Bioethanol and Biodiesel Production in the World,” Biofuels Platform, August 30 2010, http://www.biofuels-platform.ch/medias/download.php?get=433 (accessed January 31, 2012).

[30] Sims, R., Taylor, M., Saddler, J., and Mabee, W., “From 1st to 2nd-Generation Biofuel Technologies: An Overview of Current Industry and R&D Activities,” IEA Bioenergy, November 2008, http://www.ieabioenergy.com/MediaItem.aspx?id=6060 (accessed January 31, 2012).

[31] U.S. Department of Energy, Office of Science and Office of Energy Efficiency and Renewable Energy, “Breaking the Biological Barriers to Cellulosic Ethanol: A Joint Research Agenda,” DOE/SC/EE-0095, June 2006.

[32] Worldwide Fuel Charter Committee, “Ethanol Guidelines,” March 2009, http://www.acea.be/images/uploads/files/20090423_E100_Guideline.pdf (accessed January 31, 2012).

[33] ASTM Standard D4806-11a: Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel, *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 2011.

[34] Standard DIN 15376:2011-04: “Automotive Fuels—Ethanol as a Blending Component of Petrol—Requirements and Test Methods,” 2011.

[35] CONCAWE, “Guidelines for Blending and Handling Motor Gasoline Containing up to 10 % v/v Ethanol,” Report 3/08, April 2008.

[36] CONCAWE, “Ethanol/Petrol Blends: Volatility Characterisation in the Range 5–25 vol% Ethanol,” Final Project BEP525 Report, December 31, 2009.

[37] Dogu, T., and Varisli, D., “Alcohols as Alternatives to Petroleum for Environmentally Clean Fuels and Petrochemicals,” *Turk. J. Chem.*, Vol. 31, 2007, pp. 551–567.

[38] Hammel-Smith, Fang, C.J., Powders, M., and Aabakken, J., “Issues Associated with the Use of Higher Ethanol Blends (E17–E24),” NREL/TP-510-32206, National Renewable Energy Laboratory, U.S. Department of Energy, October 2002.

[39] Ramey, D., and Yang, S.T., “Production of Butyric Acid and Butanol from Biomass,” Final Report DE-F-G02-00ER86106, U.S. Department of Energy, 2004.

[40] Bamgboye, A.I., and Hansen, A.C., “Prediction of Cetane Number of Biodiesel Fuel from the Fatty Acid Methyl Ester (FAME) Composition,” *Int. Agrophysics*, Vol. 22, No. 1, 2008, pp. 21–29.

[41] Standard DIN EN 590:2010-05, “Automotive Fuels—Diesel Fuel: Requirements and Test Methods,” 2010.

[42] ASTM Standard D6751-11b: Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 2011.

[43] CONCAWE, “Guidelines for Handling and Blending FAME,” Report 9/09, November 2009.

[44] National Renewable Energy Laboratory, “Biodiesel: Handling and Use Guide,” 4th Ed., Report NREL/TP-540-43672, January 2009.

[45] Aatola, H., Larmi, M., Sarjovaara, T., and Mikkonen, S., “Hydrotreated Vegetable Oil (HVO) as a Renewable Diesel Fuel: Trade-off between NOx, Particulate Emission, and Fuel Consumption of a Heavy Duty Engine,” SAE Technical Paper 2008-01-2500.

33

Future Directions in Petroleum and Natural Gas Refining

Mohan S. Rana[1], Jorge Ancheyta[2], M.R. Riazi[3], and Meena Marafi[1]

33.1 OVERVIEW

Worldwide efforts have recently been intensifying to explore energy sources by using fossil fuel, particularly heavy and extra-heavy crude oils, to provide better technologies for their processing. Heavy oil not only has low API gravity but such a crude also significantly deteriorates the effectiveness and servicing life of the catalysts of subsequent processes that are needed to remove sulfur, nitrogen, and metals from the oils. The demand for petroleum products such as transportation fuels (gasoline and diesel) and petrochemical feedstocks (such as aromatics and olefins) is increasing throughout the world [1,2]. Traditional markets such as North America and Europe are experiencing a moderate increase in demand, whereas emerging Asian markets are exhibiting a rapid surge, as shown in Table 33.1.

Oil prices are finally generating more serious investments into alternative energy such as those described in the subsequent chapters. World energy demand may increase over 50 % from 2008 to 2030, and fossil fuels could grow to 80 % of the primary energy demand [3,4]. The environmental movement might try to close down fossil fuel industries, just as they stopped growth in nuclear energy 30 years ago. Thus, an increasing role of heavy oil is meeting the world's growing energy demand, which could provide a unique pathway to increase supplies of clean-burning fuels to the marketplace. The lack of clean and abundant energy has contributed to social conflicts, environmental problems, and poverty where billions of people (world wide) still rely on traditional biomass for cooking and heating whereas the rest of the world wastes billions of gallons of petroleum in traffic jams annually (hydrocarbon energy). Apart from the large source of energy available, non-nuclear fission and nonfossil fuel at low investment are the most important missions for science and engineering to improve the future. However, on the way to clean energy, hydrogen fuel cell investigation in the European Union, Japan, and the United States may accelerate the development of this alternative. The possible booming economic growth in Asia (China and India) is going to play an increasingly important role in global economic matters and its energy markets. Both countries' energy markets generally depend on coal reserves. In addition, the quality of coal is low, and there are limitations on coal burning because of environmental contemplation. Thus, petroleum plays an important role in the energy scene of the world and self-sufficiency for any country because this major source of energy has always been envisaged as the necessary ingredient of the formula to achieve stable economic growth. Therefore, the development of any country absolutely depends on its energy source and its fulfillment.

Worldwide fossil fuel resources and an estimation of crude oil and natural gas reserve are shown in Figure 33.1, which is being explored every day at approximately 80.5 million barrels per day, including natural gas liquids (NGLs). Most of the crude reserve remains heavy and extra-heavy in nature, which requires huge amounts of processing in order to upgrade and make them useful. This is the reason why refiners or researchers need to place more emphasis on the development of technology to maximize this immense source of energy. Moreover, petroleum oil (liquid oil and natural gas) comes in many forms, which are usually fractionated by a distillation column as shown in Figure 33.2. From here this chapter will focus on gas (natural gas) and liquid oil (crude oil).

A refinery well site that produces crude oil has natural gas as byproduct because light gases come out of liquid as it undergoes pressure reduction from the reservoir to the surface. This gas usually is called "associated gas" to be distinguishable from natural gas produced directly from gas reserves. Thus, associated gas can be a disposal problem at the well site, particularly if there is not a market for it near the well head; otherwise it is practically valueless because it must be piped to the end user. Hence, such unwanted gases are usually burned off at the well site with the consequent environmental concerns; however, because of recent high-energy requirements this practice is becoming less common. As alternative approaches, these gases are pumped back into the reservoir through an injection well for disposal, repressurizing the well–bore, or to export the gas as a liquid [5]. Gas-to-liquid (GTL) is relatively new technology that converts stranded natural gas into synthetic gasoline, diesel, or jet fuel through the Fischer-Tropsch processes developed commercially [6–10], which are given in Table 33.2.

The second part of this compilation is the crude oil, which is more complex than natural gas and contains different fractions, as shown in Table 33.3. The operation of a modern oil refinery is usually very complex because of the nature of a feedstock (crude oil quality), which varies or becomes more difficult day by day in its composition and flow properties. Since the last decade, global production of the light, sweet crude oil that is easiest to refine into high-quality products has been declining whereas the

---

[1] Kuwait Institute for Scientific Research (KISR), Kuwait
[2] Instituto Mexicano del Petróleo, Mexico City, Mexico
[3] Kuwait University, Kuwait

TABLE 33.1—Energy Sources by Regional Considerations

Region	Energy Sources and Their Applications
Africa	• Technical hydropower, geothermal potential, abundant biomass potential, substantial solar potential, and in some countries significant wind potential. • Renewable sources contribute less than 1 %. • Conflict in Nigeria may reduce global energy security.
Asia and Oceania	• China is the second-largest oil consumer, accounting for 40 % of global growth in oil demand in the last 4 years and may go for breakthroughs in renewable energy sources. • China intends to increase its energy efficiency by increasing its nuclear capacity. • Two thirds of China's energy comes from coal. • India is now also beginning dramatic energy growth. However, this country will find it difficult to supply electricity to urbanizing populations. Nuclear energy always remains an option. • Japan and South Korea import nearly all of their energy. • Japan is going to process solar energy in orbit and beam it to electric power grids on Earth. • Japan also has plans for 5 million fuel cell cars by 2020.
Europe	• European wind electricity contribution could increase from 5.5 % in 2010 to 23 % by 2030. • Europe's increasing dependence on Russian energy gives Russia gas tool to Germany, Poland, and even North European countries. • Sweden aims to become a fossil-fuel-free country by 2020 without increasing nuclear power plants.
Latin America	• Brazil is producing ethanol for approximately $1 (U.S.) a gallon, making them the world leader in ethanol production, which now accounts for ~20 % of Brazil's transport fuel market, and ethanol exports are expected to increase in coming years. • Venezuela has announced its heavy-oil reserves because approximately 1.3 trillion bbl are known to exist in the Orinoco Belt. They have announced their plans to build a gas duct to Argentina and Bolivia in order to expand their hydrocarbon fields.
North America	• Mexico is unwilling to have foreign investment develop its natural gas, but it lacks the domestic funds to do so. • The United States and Canada should initiate work-at-home tax incentives; require new vehicles to be plug-in hybrids, gas-ethanol-methanol fuel-capable, electric, or fuel cell; invest in carbon-tolerant alkaline fuel cells that can use methanol as well as hydrogen; and develop low-cost carbon nanotube "molecular sponges" to hold high volumes of hydrogen under relatively low pressure for hydrogen-powered cars. • The United States plans to build a demonstration "zero-emissions" coal-fired power plant and hydrogen production facility with integrated carbon capture and sequestration.

Source: Data taken from various sources.

availability of heavier oils is increasing [1]. However, the price of crude oil or even natural gas is not so simple to explain because their prices have fluctuated more with time, particularly in recent years as shown in Figure 33.3. Moreover, forecasting oil price is utterly confounded because of its volatile behavior. Crude oil and natural gas production along with oil demand variation between 1994 and 2009 is shown in Figure 33.4. The prices in the international markets are unprecedented. The high price of crude oil has been sustained by the increasing global demand for energy and by the ongoing political uncertainties (wars, social conflicts, or political situation) in many countries, particularly oil-producing countries, which significantly alter the price scenario. Moreover, price oscillation in crude oil is not limited to its products but will also affect several industries that depend on transportation; thus, as a result, gamut inflation in the economy is usually observed. The recent worldwide economic crisis is also affected by petroleum prices, which is most likely because of the instability in the crude oil prices (Figure 33.3). We have already seen (May 2008) that the oil price rise has an adverse effect on the world economy. Crude oil prices are mostly affected by the reflection of the United States because they are the third oil producer as well as the first consumers (42 % of the top-ten consumers) and importers (36 % of the top-ten importers) in the world [10]. The top-ten exporter and importer countries are shown along with their place and capacity in Table 33.4. The United States has huge facilities to process heavy crude, which make them more important than any other country, particularly in the North American countries (Mexico, Canada), where they are sending a portion of their crude oil for upgrading or refining and importing back refined products. The wide range of crude oil price variation ($50–$90/bbl) depends on supply and demand, which means if fuel demand increases the crude price will keep on rising. Generally, without prior notice, low supply and high demand increases price, and high supply and low demand decreases price. Thus, the oil market will come under the influence of several issues and rapidly goes from a situation of abundance to a situation of shortage and vice versa. If oil prices stay at $90/bbl or above, it would be impractical to look at these fossil fuel petroleum sources. Apart from another emerging source of competition for existing petrochemicals are the materials coming from renewable resources (e.g., vegetable oils and biofuels), the long-term prospects of which have been considerably brightened by huge hikes in oil prices. Thus, biomass produced fuels are becoming competitive when oil is at or above $70/bbl. In some countries (United States) biodiesel is less expensive than conventional diesel [11].

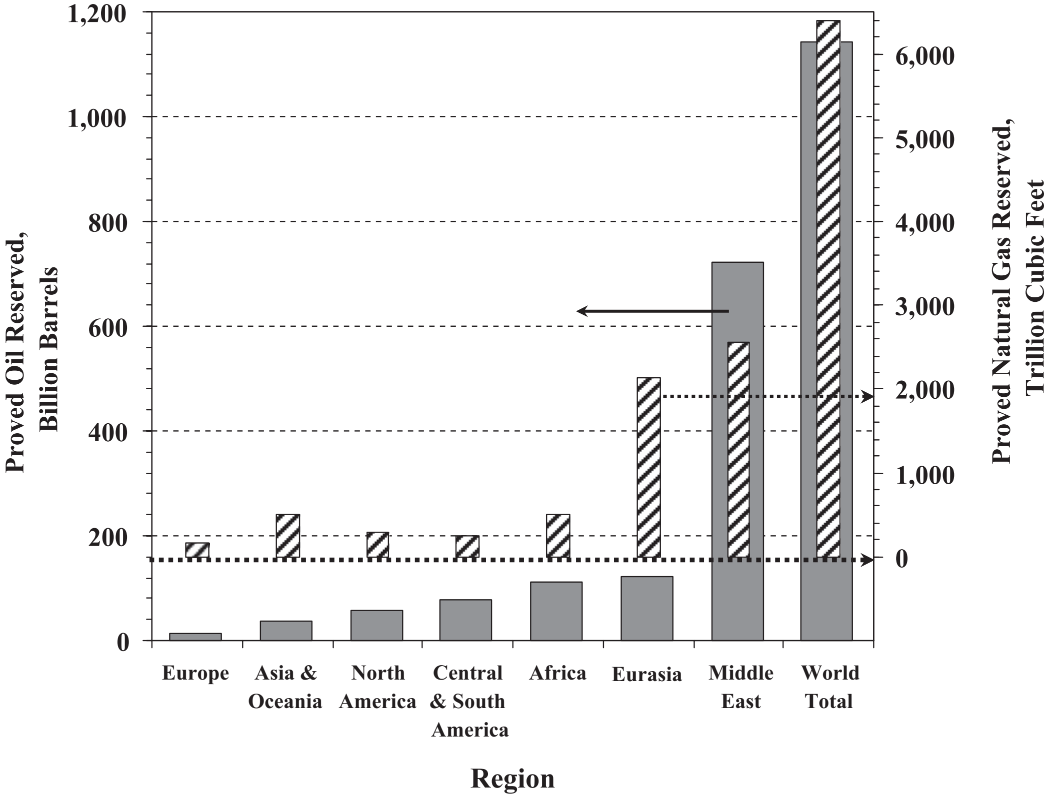


Figure 33.1—World proved reserves of oil and natural gas. On the basis of year-end 2006, the analysis of geologic and engineering data demonstrates with reasonable certainty that these reserves are recoverable under existing economic and operating conditions.

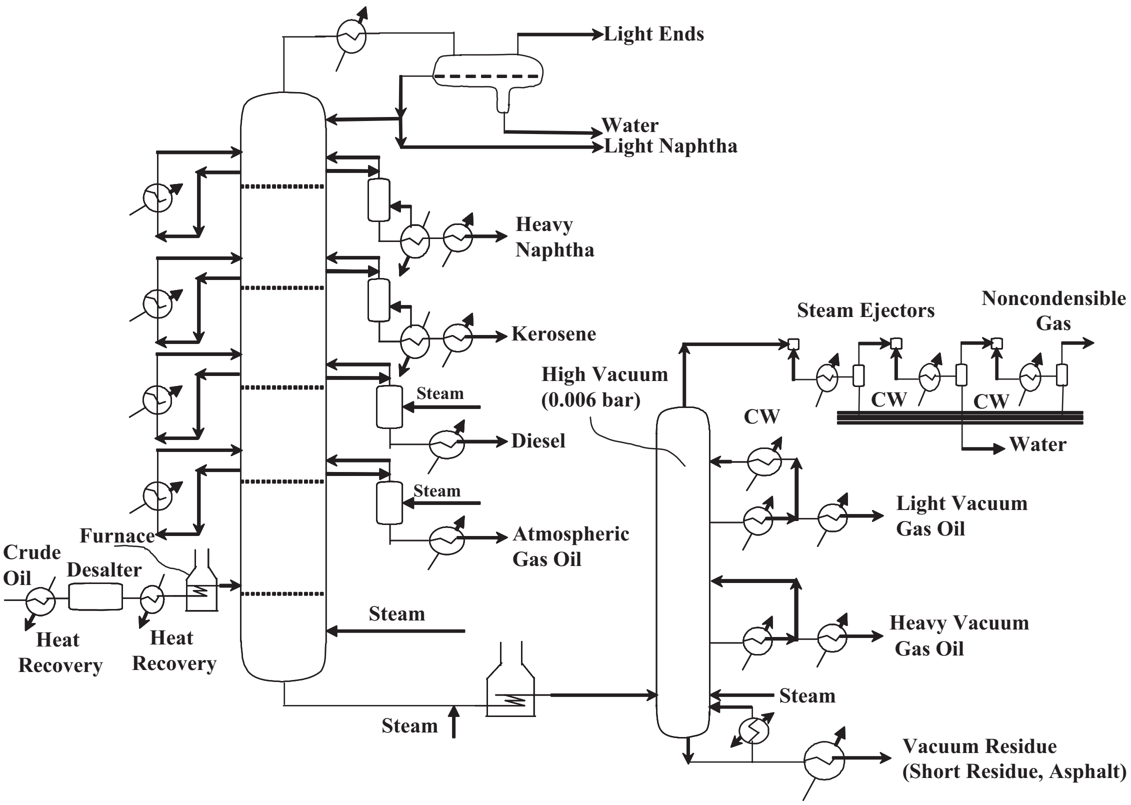


Figure 33.2—Typical complete crude oil distillation.

TABLE 33.2—Commercial Companies and Their Technologies along with Their Main Aim of Product Selectivities

Company	Technology	Product Selectivity
Statoil[a]	Three-phase slurry-type reactor in which syngas is fed to a suspension of catalyst	Middle distillates from natural gas
Sasol[a]	Synfuel technology	Commercialized four reactor types with the slurry phase distillate process
Syntroleum	Low cost because of the redesign of the reactor using an air-based autothermal reforming process	Free from sulfur, aromatics, and metals that can help refiners to meet new guidelines and general environmental standards
Synfuels	Four-step technology: conversion, absorption, hydrogenation, and oligomerization (Synfuels Eclairs Technology)	Production of gasoline from natural gas
Rentech	FT process using molten wax slurry reactor and precipitated iron catalyst	GTL facility producing 800–1000 bbl/day of aromatic-free diesel, naphtha, and petroleum waxes
Shell	Low-temperature FT GTL technology	GTL process, also known as Shell Middle Distillate Synthesis (SMDS), notably kerosene and gas oil
Exxon	Low-cost oxygen-extraction technology process	Synthesize diesel fuel from natural gas
Mobil	Mobil's methanol-to-gasoline (MTG) process based on the ZSM-5 zeolite catalyst	Methanol-based routes to gasoline

[a] Sasol formed a FT technology alliance with Statoil of Norway in 1997 to evaluate the economic conversion of associated gas into synthetic crude oil at the point of production, obviating the need to flare or reinject associated gas.

TABLE 33.3—Common Petroleum Products That Are Manufactured by Petroleum Industry

Class	Description
Gasoline (aliphatic, alicyclic, aromatic) Motor Aviation Other (tractor, marine, etc.)	Gasoline is a mixture of >500 hydrocarbons with 5–12 carbons.
Gas turbine (jet) fuels	Jet fuel is a mixture of many different hydrocarbons.
Kerosene	Paraffin oil and petroleum distillation fraction between 150 and 275°C; a mixture of 12–15 carbons.
Middle distillates (diesel and light fuels)	Petroleum distillation fraction between 250 and 375°C and a mixture of 14- to 20-carbon atom range.
Residual fuel oil (heavy fuel oils)	Type of fuel oil used in ships (bunker fuel) containers, also called navy special fuel oil or simply navy special.
Lubricating oils	Distillation fraction between 340 and 400°C mainly of alkanes (typically 15–40 carbons) and cyclic paraffins.
White oil	White oil is a commercially made insecticide spray.
Greases	Grease is used to describe several semisolid lubricants possessing a higher initial viscosity than oil.
Waxes	Its melting point is above ~45°C.
Asphalts	Highly viscous black liquid or semisolid that is present in most crude petroleum and natural deposits; it is widely used for making asphalt concrete for road surfaces.
Cokes	Petroleum coke is a carbonaceous solid derived from oil refineries.
Carbon blacks	Carbon black is produced by the incomplete combustion of heavy petroleum products.

33.2 HISTORICAL DEVELOPMENTS

Petroleum was first mentioned in the thesis *De Natura Fossilium*, published in 1546 by the German mineralogist Georg Bauer, also known as Georgius Agricola [12], and was reported to be a naturally occurring, flammable liquid found in rock that contains a complex mixture of various molecular hydrocarbons. Petroleum is the most important substance consumed in modern society. It provides not only the transportation fuel and energy but is also used in plastics, paint, fertilizer, insecticides, the medical

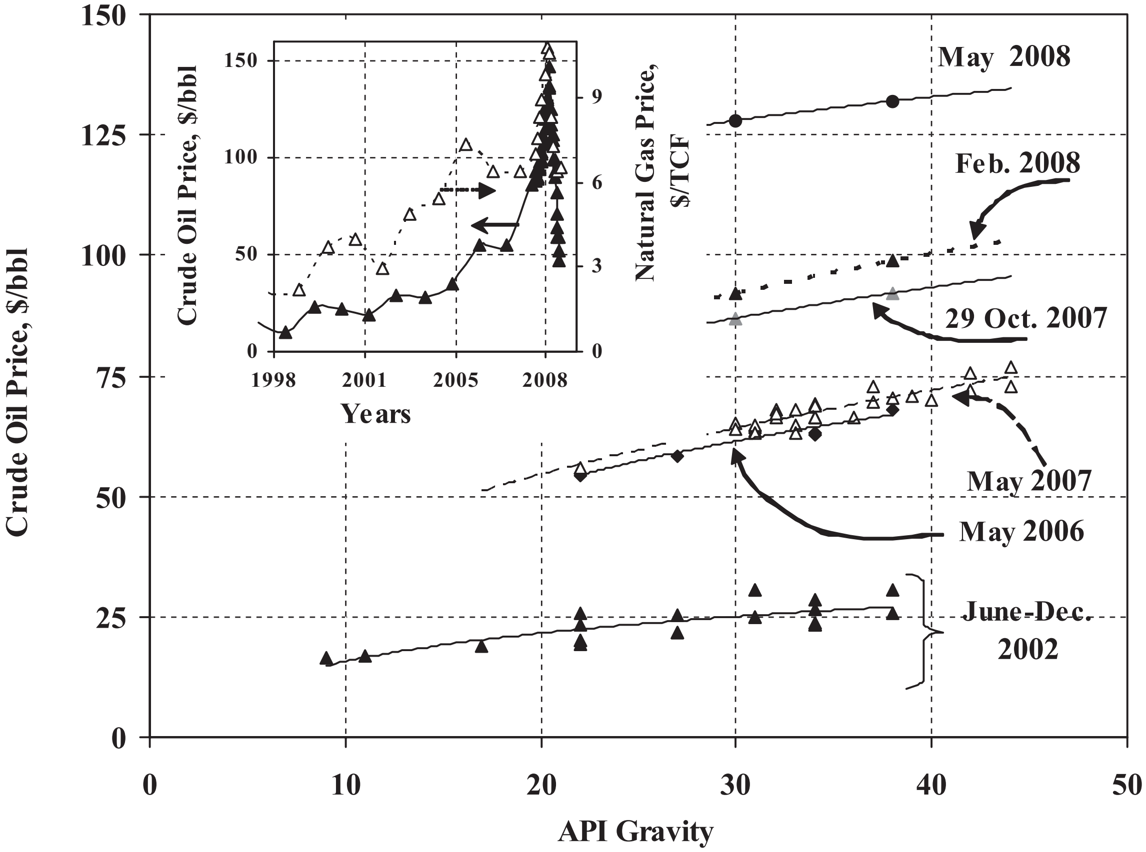


Figure 33.3—Effect of crude oil quality on the price (inset) fluctuation in crude oil and natural gas (well head) prices in the last 10 years. ▲ = crude oil price ($/bbl), Δ = natural gas price ($/thousand cubic feet [TCF]).

industry, etc. The word "petroleum" is derived from the Latin names *petra* and *oleum* and means "rock oil," which refers to the different hydrocarbons such as gas, liquids, and solids. The exact molecular composition varies widely based on the origin of the crude oil (source to source), but the proportion of chemical elements changes over fairly narrow limits with a complex mixture of hydrogen and carbon as the major components and a minor content of sulfur, nitrogen, oxygen, and metals as shown in Table 33.5. The first time petroleum was used was in the streets of Baghdad, which were paved with tar, and petroleum was first distilled by a Persian chemist M.Z. Razi in the 9th century, producing chemicals such as kerosene, which was mainly used for kerosene lamps [13]. The distillation fraction became available in Europe by the end of the 12th century [14].

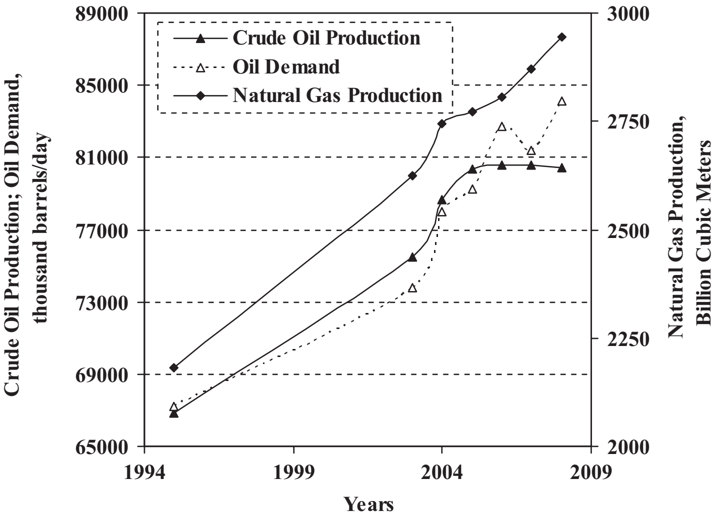


Figure 33.4—Crude oil and natural gas production along with oil demand variation between 1994 and 2009 [10].

TABLE 33.4—Top Ten Import/Export Countries and Their Net Oil Imports Exports in 2007 [10]

Exporters		Net Oil Exports, Million bbl/day	Importers		Net Oil Imports, Million bbl/day
1	Saudi Arabia	8.73	1	United States	11.8
2	Russia	6.67	2	Japan	5.3
3	Norway	2.91	3	China	2.9
4	Iran	2.55	4	Germany	2.5
5	Venezuela	2.36	5	South Korea	2.1
6	United Arab Emirates	2.33	6	France	2
7	Kuwait	2.2	7	Italy	1.7
8	Nigeria	2.19	8	Spain	1.6
9	Mexico	1.8	9	India	1.5
10	Algeria	1.68	10	Taiwan	1

TABLE 33.5—Common Elementary Composition of Crude Oil

Element	Weight Percentage
Carbon	84–87
Hydrogen	11–14
Sulfur	0.5–6
Nitrogen	0.1–2
Oxygen	0.1–0.5
Metals	0–0.1

The modern history of petroleum began in 1846 with the discovery of a process to refine kerosene from coal using Gesner's method. In 1854, Benjamin Silliman, a science professor at Yale University in New Haven, CT, was the first to fractionate petroleum by distillation. These discoveries rapidly spread around the world, and Meerzoeff built the first Russian refinery in the oil fields at Baku in 1861, which was producing at that time approximately 90 % of the world's oil.

On the other hand, the first commercial oil well was drilled in Romania (1857) at Bend, north of Bucharest. In North America the first well was dug by James Miller Williams in Oil Springs, Ontario, Canada (1858), whereas the U.S. petroleum industry began with Edwin Drake drilling an oil well in 1859 near Titusville, PA. The industry grew through the 1800s, driven by the demand for kerosene and oil lamps. It became a major national concern in the early part of the 20th century with the overture of the internal combustion engine to petroleum that endowed a demand that has largely sustained the industry until today.

By 1910, significant oil fields had been discovered in Canada, Iran, Peru, Venezuela, and Mexico and were being developed at an industrial level. Even today petroleum remains the world's foremost control on the economy because from time to time we have energy crises such as in 1973, 1979, and even in 2008, which are usually related to military conflicts between different countries, incidentally most of the time in Middle East countries, which has about 62 % of the world's oil reserves. The reason may be because 80 % of the world's readily accessible petroleum reserves are located in the Middle East, with 62.5 % coming from the Saudi Arabia, the United Arab Emirates, Iraq, Qatar, and Kuwait [3].

33.3 MARKET DRIVERS

Energy requirement for power generation and its demand is strongly linked to gross domestic product (GDP) or gross domestic income (GDI), which is defined as the total market value of all final goods and services produced within the country in a given period of time. The world's economy is precisely run on energy and, in turn, rising prosperity and personal development of individuals. The linkage between electricity demand and economic progress is evident when considering electricity use (kilowatt-hours, kWh) on a per-capita basis relative to GDP per capita in countries around the world. However, people are very concerned about energy and its availability, reliability, cost, and environmental impact. Energy is a complex subject, touching every part of daily life and the overall economy, involving a wide variety of technologies and deeply affecting many aspects of common man [15–17]. An integrated energy market is a collective view of supply, demand, infrastructure, technology, and geopolitics. However, the industry has taken steps to address future issues to analyze oil, gas, and other sources of energy and its role in the economy; to identify the issues that will most likely shape the industry over the next 25 years; and to provide approaches to the resolution of these issues. In general, global primary energy demand could grow by 50 % from 2008 to 2030, raising serious energy security and environmental sustainability concerns. In this regard, global energy-related carbon dioxide (CO_2) emissions show no sign of decline and indicated an approximately 33 % rise between 1990 and 2006 [3,10]. The dramatic fall in energy prices in recent months has helped to provide breathing space for the miserable economy, but it could cause delays in investment in new production, leading to a supply crunch in the medium term as energy demand grows as well as slow progress in energy efficiency and the development of cleaner alternative technologies [15].

The World Energy Outlook 2008 [4] states that there will be no shortage of oil and gas within the next 30 to 40 years, but lack of investment in new infrastructure to explore and process it. First, global energy demand is expected to grow at 1.3 percent per year on average to 2030. Coal will continue as the most prominent source of power, while gas will have the most significant growth. Nuclear power will also expand, primarily in developing countries like India. Therefore, oil will remain essential to meeting transportation demands. In addition, green power marketing renewable sources have emerged in more than a dozen countries around the world; almost two million customers worldwide buy green power today, mostly in Australia, Japan, Canada, US, and in a number of countries in Europe to gain an understanding of consumer demand for electricity generated from renewable sources.

33.3.1 Production of CO_2

There is variation in Earth's temperature because of the atmospheric gases. Earth's temperature depends on the balance of energy entering and leaving the planet's system. If the incoming energy from the Sun is absorbed, Earth warms, and if the Sun's energy is reflected back into space, Earth avoids warming. Thus, when gases like H_2O (vapor), CO_2, CH_4 or synthetic gases such as chloroflorocarbons (CFCs), hydrofluorocarbons (HFCs), etc. absorb energy, which slows or prevents loss of Earth's heat to space, it is called the greenhouse effect.

Burning fossil fuels (gasoline/diesel) releases CO_2 and other greenhouse gases (GHG) into the atmosphere, contributing to global climate change. CO_2 is the most important human-made GHG, and every one liter of gasoline burned by our vehicles releases about five kilos of CO_2 into the atmosphere. Because of the worldwide industrial revolution, the balance between these gases has been disturbed, particularly CO_2, which is believed to further increase the Earth's surface temperature (1.2–5.8°C), which is known as the "anthropogenic green effect" or "global warming." However, production of CO_2 is inescapable by using fossil fuel combustion. The amount of CO_2 emission varies with the variation in fuel as shown in Figure 33.5, whereas world CO_2 production is shown in Figure 33.6, which indicates that the United States and China are the countries producing the most CO_2. If we express CO_2 emission per capita, then India and China are rather small emitters. Indicating its high level of economic development, the United States has the highest level of CO_2 emissions per capita, which is three times higher than China and about ten times higher than India. However, per-capita CO_2 emissions patterns are changing, particularly in the United States and Europe. It

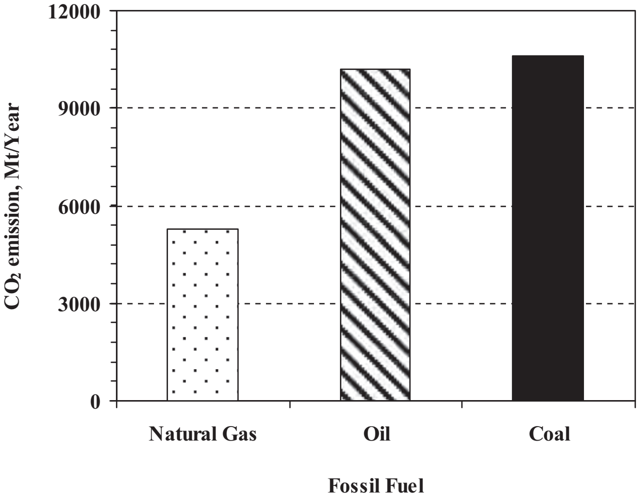


Figure 33.5—Production of CO_2 using fossil fuel. Mt = megatons. *Source:* U.S. Energy Information Administration data, 2008 [10].

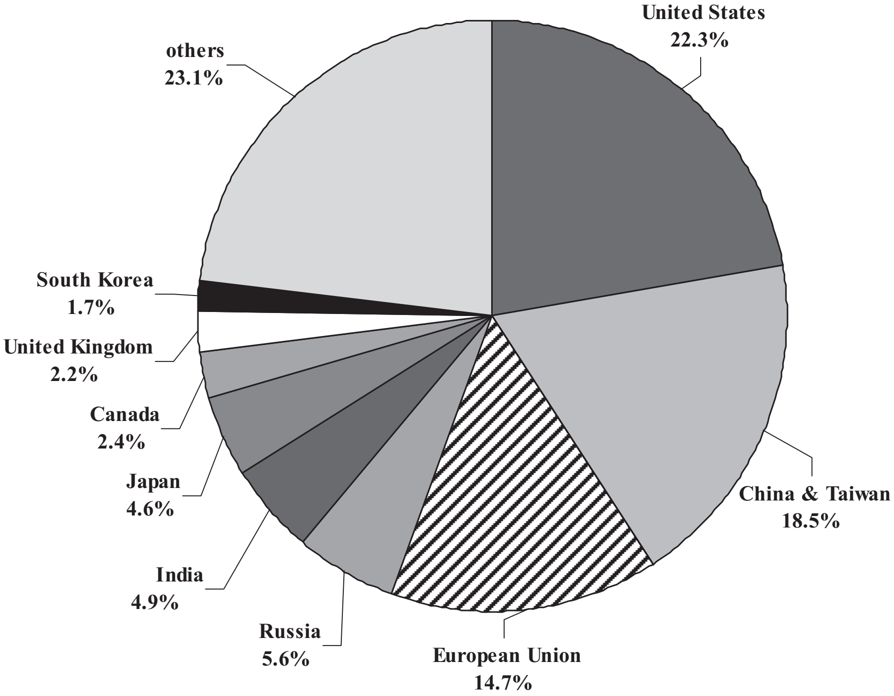


Figure 33.6—Worldwide CO_2 production distribution in 2007 [10].

is expected that the United States will reduce its per capita CO_2 emissions by 40 % over the next 30 years (2040). On the other hand, CO_2 production ensures energy demand, which can be satisfied using alternative sources such as renewable or nuclear sources or both, but these alternative sources are also having their own limitations as given in Table 33.6. Deforestation usually has a negative effect on the environment by enhancing the CO_2 concentration, which takes CO_2 from the air and exchanges fresh oxygen in the atmosphere [18].

33.3.2 Petroleum Market Analysis

Oil and petroleum liquid fuels will remain the world's largest energy source in the future, partially meeting the market demand, but expected to be the slowest growing fuel over the next 30 years. Globally, demand for liquid fuels will rise by almost 30 % over the next 30 years, which is close to an 80 % increase and that will be tied to transportation. Overall, global energy demand for transportation will go up by nearly 45 % from 2010 to 2040. It is expected that heavy-duty vehicles will grow significantly more fuel-efficient over the next 30 years. As a result, by 2030, the world will use more fuel for heavy-duty vehicles. Thus, the gasoline reduction shift will be reflected in the market for transportation fuels. In fact, real per-mile fuel costs in 2007–2008 increased an average of 10 %/year, somewhat less than that in 1979–1980 (increased an average of ~15 %). Nonetheless, highway travel declined by an average of more than 2 %/year, 2 times that of the 1979–1980 decline despite an average GDP growth similar to that of 1979–1980 (annual GDP growth of 1.5 %) [10,19–21]. Demand for popular diesel fuel will increase for heavy-duty vehicles, which is likely to rise by 85 % through 2040, while gasoline demand will fall by about 10 %. Short-term oil market indicators and world economic developments, factors affecting the short-term oil supply/demand balance as well as the latest developments in energy policies, directly affect prices and demand for various petroleum products [22–24]. Thus, the gamut of petroleum prices and GDP were significantly affected by the worldwide recession, which varies with the individual country demand and supply. An average oil price increase in 2010 ($80/bbl) was due to high demand and lack of sufficient supply. Prices were even higher at the end of 2011 ($106/bbl), which is expected to continue increasing in the long term such as $108 or higher per barrel in 2020.

Oil refineries are subject to numerous environmental regulations aimed at reducing pollution from petroleum products and the refineries themselves. The most significant of these in terms of their effect on refinery operations are currently the regulations calling for a large reduction in the sulfur content of gasoline and diesel fuel. These reductions will fundamentally be met through an expansion of hydrotreating units, which are projected to be among the fastest growing areas in refineries. The stepwise specifications for gasoline and diesel fuel phased in Euro fuel are shown in Figure 33.7. Since 2000, it has been demanded that the sulfur content in fuel meets the specification, obviously different for the gasoline and diesel [10]. Apart from the sulfur there are a few other specifications; for instance, very low aromatic content (<1 % by volume) diesel fuel has been made available in the United States, Japan, and a few European countries in commercial markets [4,22,23].

In this regard, several countries have already promoted alternative fuels and decreased their use of fossil fuel as well as energy, particularly commercial vehicles running on compressed natural gas (CNG) fuel. India (Delhi) has the largest number of CNG vehicles running at present. Several countries have also set up a task force for preparing the hydrogen, biofuel, and electric road map. The use of liquefied petroleum gas (LPG) has also been introduced as an automotive fuel, and the oil industry has drawn up plans for setting up of automotive LPG dispensing stations.

TABLE 33.6—Different Energy Sources and Their Advantages and Disadvantages

Energy Source	Advantages	Disadvantages
Fossil Fuel (Hydrocarbon)		
• Natural gas • Oil • Coal	• Huge applicability in the daily lives of human beings	• Contaminated feedstock • Combustion produces pollution
Alternative Energy Sources		
Renewable		
• Hydroelectric • Direct solar heating • Photovoltaic power • Biomass • Solar energy • Geothermal • Air (wind) energy	• Longer life of source • Clean fuel	• Limited commercial applicability • Most of them not proven yet
Nuclear		
• Fission • Fusion	• Large amount of energy can be produced with high care	• Difficult to generate raw material • High price required • Disposal of waste • Resources could be an eventual problem • Difficult to obtain public acceptance

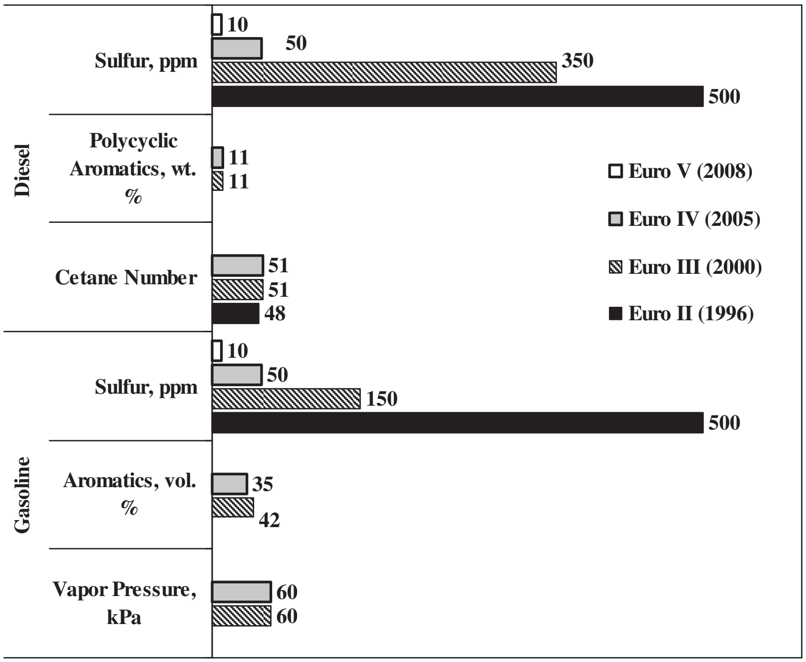


Figure 33.7—Environmental specifications for the transportation fuels.

The specification may not be the only solution to environmental protection but also how and where these fuels are used. The group of such transportation vehicles is known as fleet vehicles. Fleet vehicles are groups of motor vehicles owned or leased by a business or government agency, rather than by an individual or family. Typical examples are vehicles operated by car rental companies, public utilities, public bus companies, and police departments.

Fleet vehicles typically have hard lives. Although the fleet vehicle owner may have a maintenance department, assigning the vehicles to specific mechanics, usually such vehicles are often operated by several drivers, subjecting them to accelerated wear. In addition, drivers often do not exercise the same care for fleet vehicles as they might for their own personal vehicles. Fleet vehicles may also be subjected to unusual conditions such as 24-h use or excessive cargo weights and may be kept in service until they have accumulated hundreds of thousands of miles. Organizations with fleet vehicles are exposed to legal liability, largely because of the actions of their drivers and vehicle maintenance. Thus, collisions and wear and tear are the predominant concerns in this area.

The term “fleet” may be described by its make (automobile manufacturer) in a particular model (year). With time, fleet vehicles will be more prone to pollution. This is usually the case in developing countries where the life of vehicles is longer than expected.

33.4 QUALITY TRENDS IN FEEDSTOCKS OR CRUDE OIL

Fossil fuel remains an important source of energy, and there is much more to do to find better quality and quantity of hydrocarbons. Crude oil usually comes from deep underground, where the remains of plants and animals from millions of years ago have been heated and pressurized over time. Crude oil is blackish in color and has a characteristic odor that comes from the presence of small quantities of chemical compounds containing sulfur, nitrogen, and metals. There are different grades of crude oil, and each one has a specific composition that is determined by the original decomposed source materials as well as the properties of the surrounding soil or rock formations. Since 1997, the global production of the light, sweet crude (low-sulfur) oil, which is easiest to refine into high-quality products, has declined whereas the availability of heavier oils is increasing. Heavy and extra-heavy petroleum feed properties are comparable to the vacuum (VR > 565°C) and atmospheric (AR > 345°C) residua, which are constituted by heavy hydrocarbons and several metals, predominantly in the form of porphyrins [25]. Typical amounts of different impurities and hydrocarbon compositions are shown in Table 33.7. The potential composition of the different products obtained from crude oil is shown in Figure 33.8; of course, the composition may vary with the crude oil API gravity and the origin. Because of the subterranean origin of petroleum it must be extracted by means of wells. Petroleum from a new well will usually come out to the surface under its own pressure; as time passes, the crude oil must be pumped out or forced to the surface by injecting hot water, air, natural gas, etc. Crude oils are normally measured by volume (barrel), and 1 bbl contains 158.9 L (42 gal). The crude oil is usually sent from a well to a refinery by pipelines or tanker ships.

The physical properties and exact chemical composition of crude oil generally vary from one source to another. The hydrocarbon components are separated from each other by the heating or fractionated distillation (Figure 33.2) of petroleum according to boiling points. The lighter fractions, especially gasoline and diesel, are in greatest demand and are used to produce commercial fuels. To provide an idea about the chemical composition of heavy fractions present in crude oils, Table 33.8 reports the results of the saturate, aromatic, resin, and asphaltene (SARA) contents in different samples. The most complex fraction of petroleum is asphalt, which is a brownish-black hydrocarbon natural mixture commonly used in road paving, roofing,

TABLE 33.7—Properties and Amount of Asphaltenes, Resins, and Oils in Light and Heavy Crudes and Residue [33]

					Contaminants		
	API Gravity	Asphaltenes, wt %	Resins, wt %	Oils, wt %	S, wt %	N, wt %	Metals (Ni + V), ppm
Extra light	>50	0 to <2	0.05–3	–	0.02–0.2	0.0–0.01	<10
Light crude	22–32	<0.1–12	3–22	67–97	0.05–4.0	0.02–0.5	10–200
Heavy crude	10–22	10–25	14–39	24–64	0.1–5.0	0.2–0.8	50–500
Extra heavy	<10	15–40	–	–	0.8–6.0	0.1–1.3	200–600
Residue	–	15–30	25–40	<49	–	–	100 to >1000

etc. It varies from a solid to a semisolid, has great tenacity, melts when heated, and when ignited it will leave very little or no ash. Heavy petroleum exhibits a wide range of physical properties, and several relationships can be made between the various physical properties as shown in Figure 33.9. Properties such as the viscosity, density, boiling point, and color of petroleum may vary widely whereas the ultimate or elemental analysis varies over a narrow range for many samples [26]. The relative amounts of these components are also presented as functions of the asphaltene content. Metals have a tendency to concentrate more in the heavier fraction (asphaltene and resin) than in the saturated and aromatic fractions. The higher the asphaltenes in crude oil, the higher the metal content; however, the increase in vanadium concentration is not proportional to that of nickel. The crude oil major hydrocarbon (SARA) component relationship is shown in Figure 33.10, where the aromatic content increases with asphaltene. These results are complementary to the distillation fraction and function of the API gravity of the crude oil as shown in Figure 33.11. If we separate asphaltene and other fractions, then most of the metals go to the asphaltene, as shown in Figure 33.12, which further indicated that asphaltene is the most problematic component of crude oil. Nitrogen and sulfur can be present in only trace amounts in lighter or sweet petroleum, but as the crude oil becomes heavy or extra heavy, the sulfur and nitrogen content also increases as shown in Figure 33.13. Crude oil API gravity is also affected by the excess exploration of wells, which decreases API gravity with time as well as increases the sulfur content as reported in Figure 33.14.

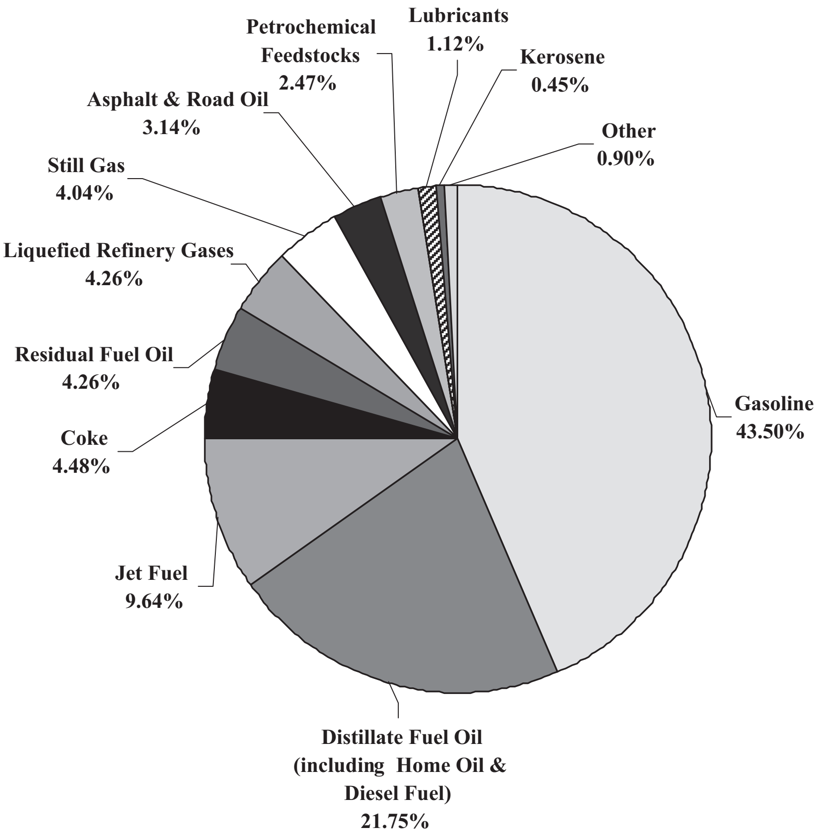


Figure 33.8—Percentage composition of products that a barrel of crude oil can make (exact amounts depend on API gravity of crude oil).

TABLE 33.8—Composition of Crude Oil and Its Physical Properties along with the Separation or Analysis Methods Used for Different Hydrocarbons in Petroleum Fractions

Oil Component		Physical Properties			Analysis Method or Separation Methods	
		Nonpolar	Weight Light	Low Aromaticity		
Saturates (S)	MALTENE	↓	↓	↓	ASTM D4124 ASTM D2007	n-C_7 as solvent in a column packed with alumina n-C_5 as solvent in a column packed with silica/clay
Aromatics (A)					ASTM D4124	Toluene as solvent in a column packed with alumina
Resins (R)					ASTM D4124	Methanol:toluene (1:1) and trichloroethylene in a column packed with alumina
Asphaltenes (A)		Most polar	Weight heavy	High Aromaticity	ASTM D893 ASTM D4124	n-C_5 as solvent at 65 ± 5°C, centrifugation for 20 ± 1 min n-C_7 as solvent at boiling point temperature and stirring 1 h

It appears that asphaltenes are complex polar structures with polyaromatic character containing metals (mostly Ni and V) that cannot be properly defined according to their chemical properties, but they are usually defined according to their solubility. Asphaltenes are soluble in aromatic solvents such as toluene but insoluble in paraffins such as *n*-heptane. Asphaltenes are constituted by condensed aromatic nuclei carrying alkyl groups, alicyclic systems, and heteroelements [27–30]. Asphaltene molecules are grouped together in systems of up to five or six sheets, which are surrounded by the so-called maltenes (all of those structures different from asphaltenes that are soluble in *n*-heptane) and resin.

The fraction and composition of these crudes are quantitatively determined by using true boiling point (TBP) distillation and by other methods as presented in Figure 33.15. The molecular composition of heavy fractions is difficult to analyze, but for lighter fractions (<210°C) it is

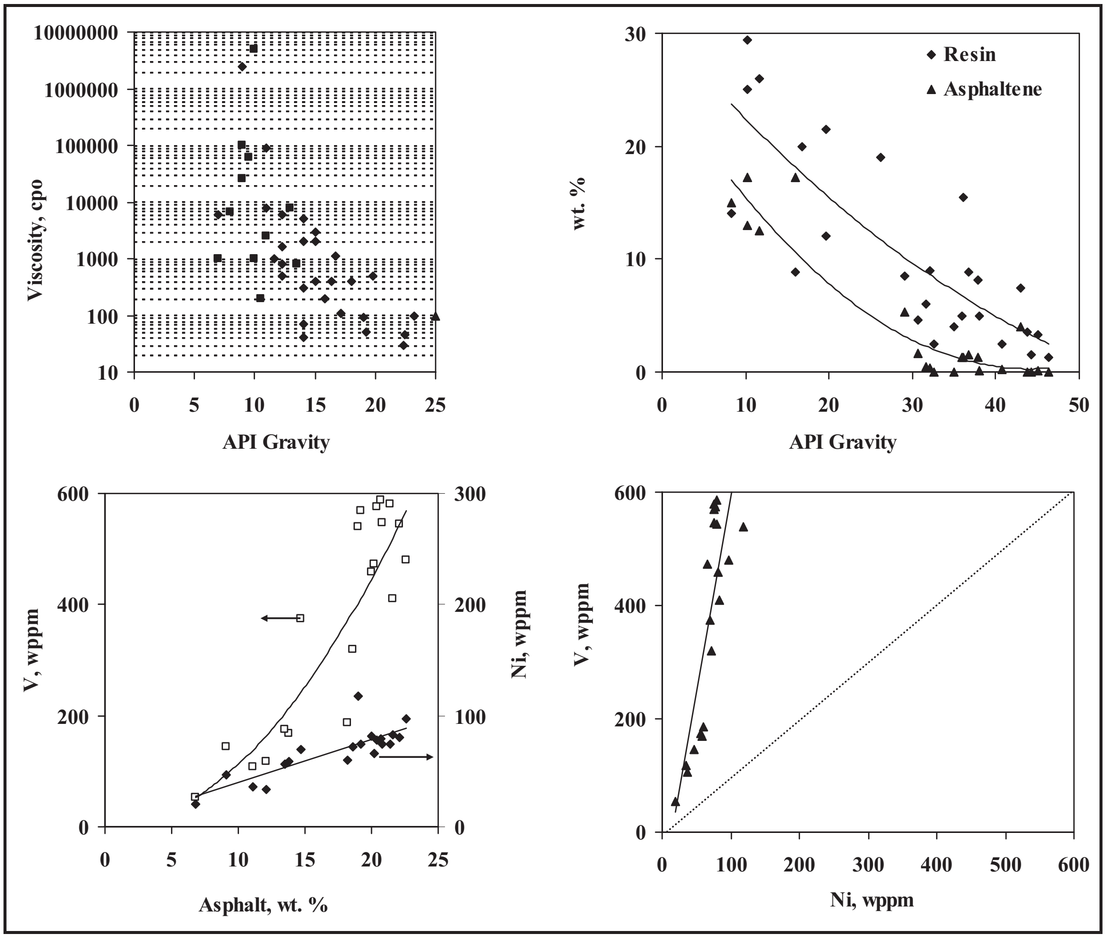


Figure 33.9—Relationship between the different properties and composition of various crude oils.

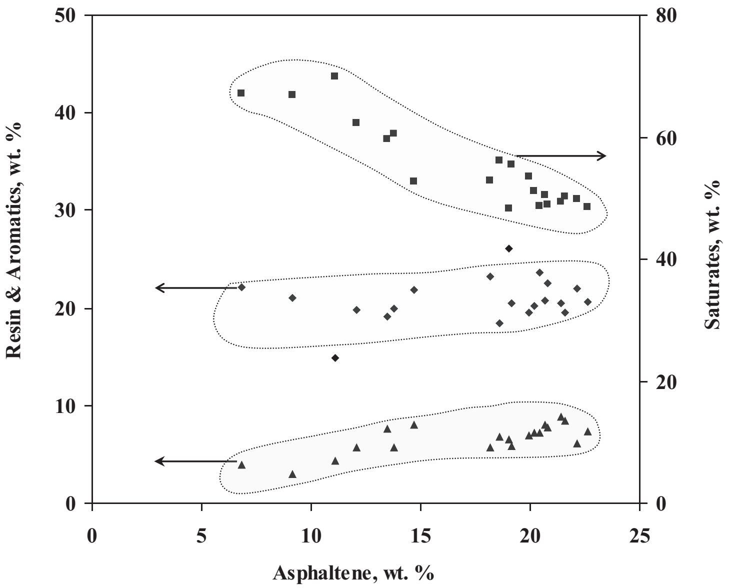


Figure 33.10—Composition of petroleum hydrocarbon heavy oil. ■ = saturates, ◆ = resins, and ▲ = aromatics.

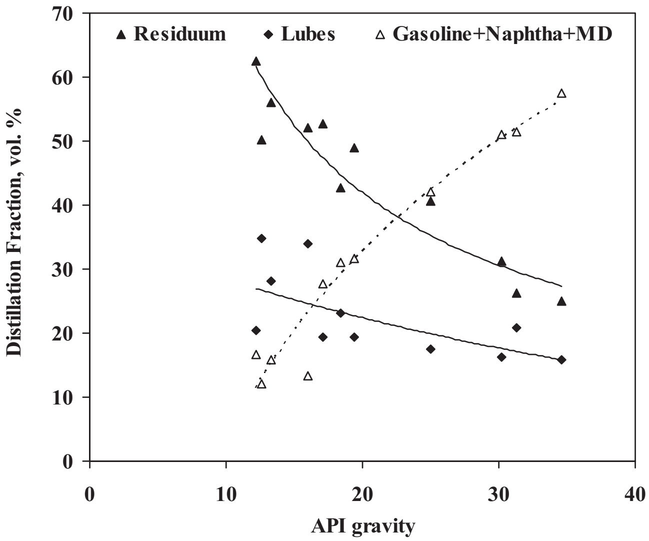


Figure 33.11—Effect of API gravity on the residue and lighter fraction (middle distillate).

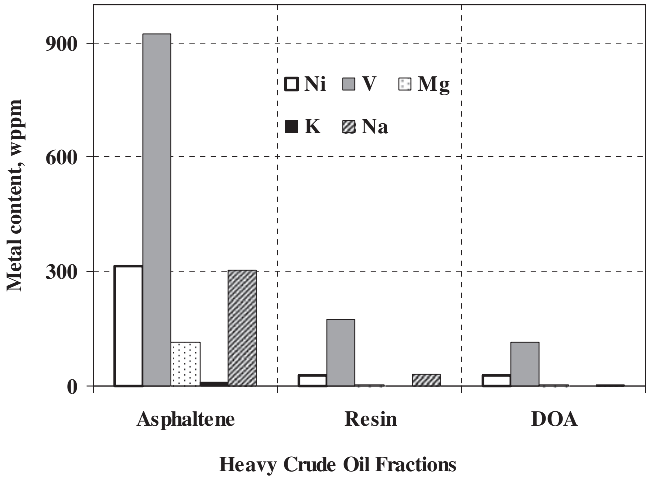


Figure 33.12—Content of metals in different fractions of crude oils.

easier. For instance, characterization of Maya crude fractions was performed by gas chromatography (flame ionization detection, FID) whereas its sulfur component analysis was performed by flame photometric detection (FPD), as shown in Figures 33.16 and 33.17, respectively, in which sulfur molecular size increases with higher boiling point of the petroleum fraction. The composition of distillates presents different groups of sulfur such as mercaptane, thiophene, benzothiophene (BT), dibenzothiophene (DBT), and alkylated DBT particularly 4,6-dimethyldibenzothiophene (4,6, DM DBT). Alkyl-substituted DBTs are difficult to convert into H_2S because of the sterically hindered adsorption of these compounds on the catalyst surface. It appears that more than 50 % of sulfur species are associated into the asphaltene and resin molecules, which is more likely in the form of alkyl-substituted DBTs. Because these sulfur molecules are saturated in the heavy fractions (Table 33.9), the suitable catalyst requires large pore diameter.

33.5 TECHNOLOGY DEVELOPMENTS IN REFINING AS WELL AS GAS CONVERSION

There are two distinct sectors in the crude oil petroleum industry—upstream and downstream—that are explained along with their role in Table 33.10. The midstream sector manages crude oil stores, markets, and transports commodities. The focus on the downstream and upstream sectors may depend on the oil-producing country and the quality of the crude oil. Significant advances have been made in these petroleum sectors over the last few decades. The upstream sector is devoted to the exploration of petroleum whereas downstream refers to all of the refining processes of crude oil. On the other hand, natural gas is the part of the petroleum sector that either comes along with the crude oil origin or it can be separately explored from its own gas wells. The subsequent section will discuss in detail the refining technology development in the area of crude oil upgrading as well as natural gas.

33.5.1 Crude Oil Upgrading

Upgrading technologies are basically performed by means of catalytic and noncatalytic processes. The primary

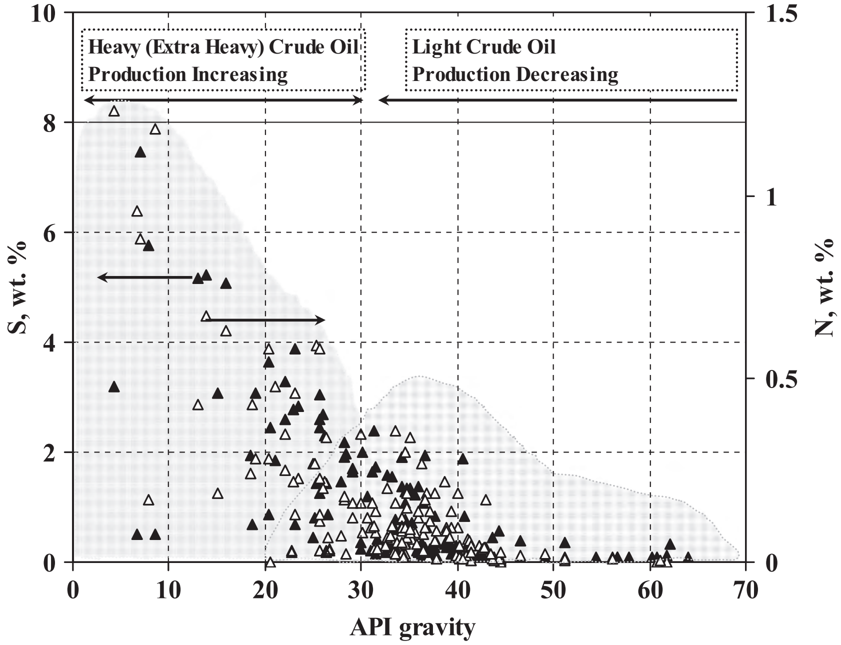


Figure 33.13—Sulfur and nitrogen contents in light, heavy, extra-heavy, and bitumen. ▲ = sulfur and Δ = nitrogen.

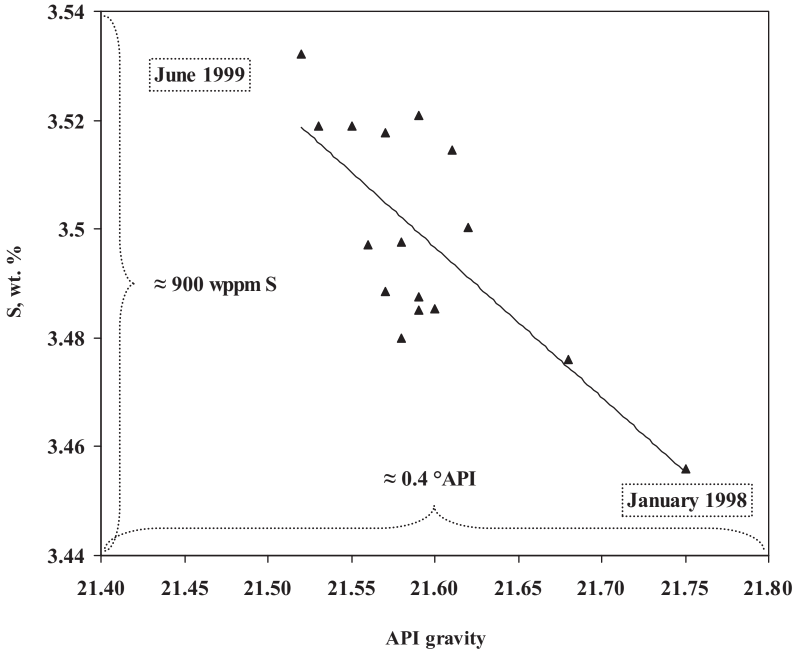


Figure 33.14—Effect of variation in Maya crude oil properties (API gravity and sulfur content) during 1.5 years.

process usually prepares synthetic crude oils that contain a relatively large amount of heteroatoms such as nitrogen and sulfur, which must be removed in secondary processes that are able to produce transport fuels [31–33]. Petroleum prices are not just affecting how far people can drive, they are also affecting where and what they are driving on. In this regard, "what" corresponds to the quality of petroleum and "where" to the quality of roads, which further depends on the quality of asphalt used during construction. As reported before, asphalt is a complex ingredient in crude oil, which prices fluctuate similar to crude oil and have increased approximately 40–50 % in the past few years. An increase in asphalt price mainly affects non-petroleum-producing countries because the development of a country depends on the number and quality of roads or national highways. The higher asphalt costs are forcing planners to scale down the amount of road construction work or to postpone it altogether.

In general, the whole crude oil enters into the refinery through the distillation column (Figure 33.2), which separates different fractions by their volatility either in approximately 345°C+ atmospheric (AR) or 565°C+ vacuum (VR) cut points, yielding nondistillable residues. These nondistilled cuts further concentrate with contaminants. For most of

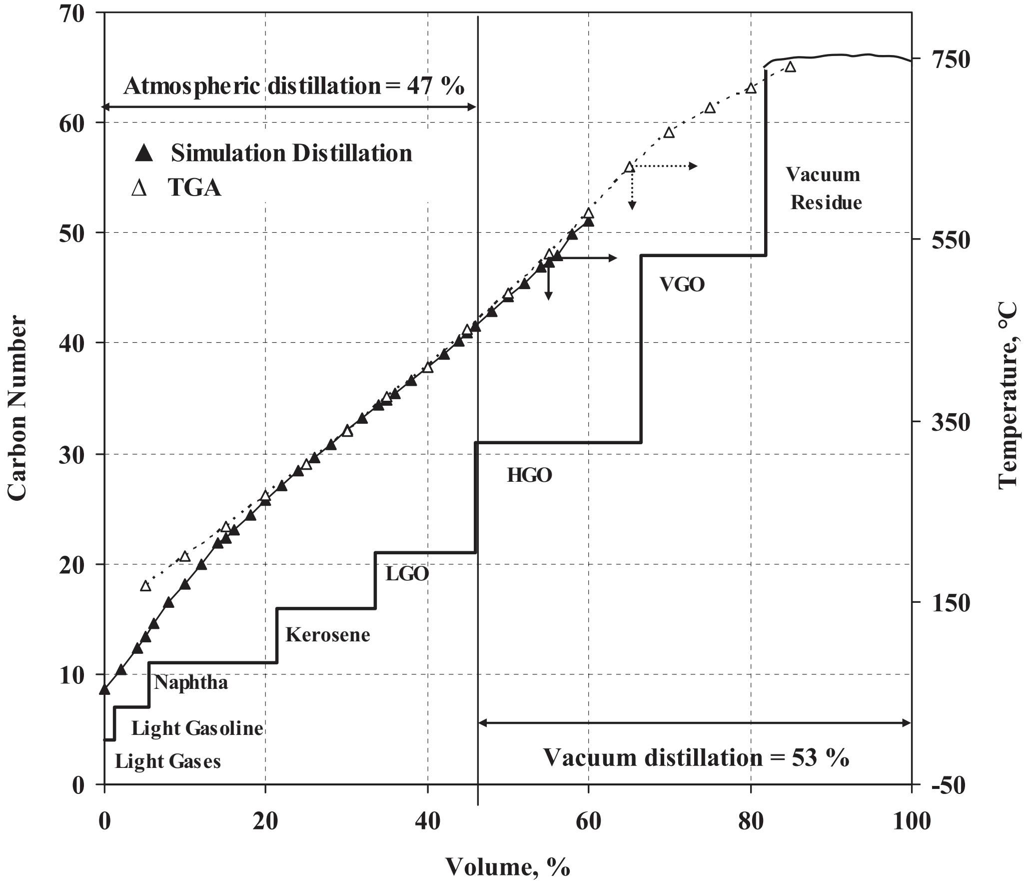


Figure 33.15—Composition of Maya heavy crude oil (API gravity = 22, sulfur = 3.5 wt %, nitrogen = 0.3 wt %, asphaltene = 12.7 wt %) and its variation with temperature. LGO = light gas oil, HGO = heavy gas oil, and VGO = vacuum gas oil.

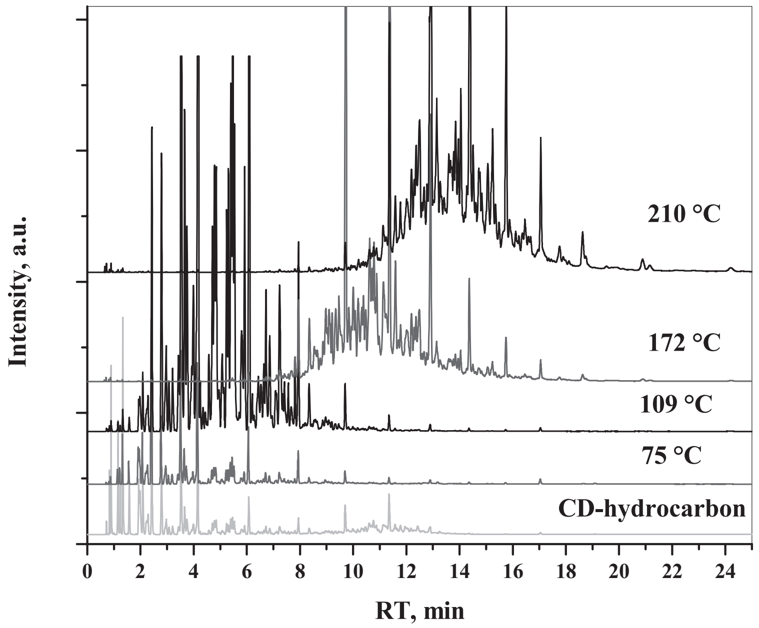


Figure 33.16—Effect of distillation temperature on hydrocarbon composition. CD = condensed hydrocarbon.

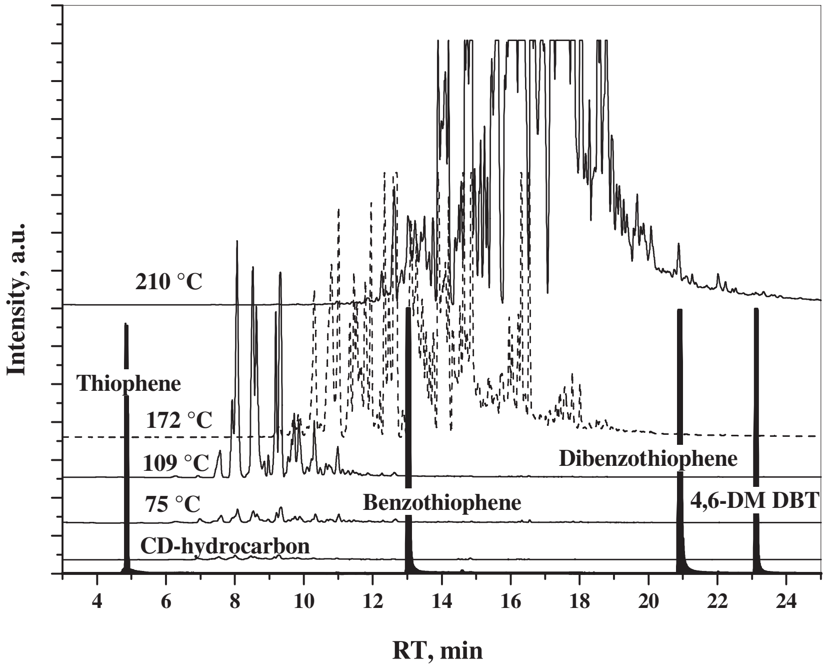


Figure 33.17—FPD gas chromatographic traces showing distribution of the different organosulfur compounds at various distillation temperatures (Maya crude oil). The lower trace represents the feed, and the traces of reference compounds represent a family of organosulfur compounds such as thiophene, benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DM DBT).

TABLE 33.9—Distillation Analysis of Bitumen (Canadian Tar Sand Bitumen)

Equivalent Distillation Range at 1 atm Temperature, °C	Fraction, wt %	Cumulative, wt %	Specific Gravity of Fraction, wt %	Sulfur wt % in Fraction
IBP 200	1.4	1.4	0.816	1.52
200–250	2.2	3.6	0.856	1.02
250–333	9.7	13.3	0.904	1.78
333–418	17.7	31.0	0.955	2.98
418–524	17.5	48.5	0.989	3.8
524	51.5	100.0	1.073	6.39

IBP = initial boiling point.

the heavy crude oils, the content of AR or VR is relatively high; therefore, some of the refiners are considering direct processing of whole crude [34]. Processing of these residues using various technologies is classified into two main routes as shown in Table 33.11. From another point of view, the upgrading technologies can be classified as catalytic (hydrogen addition) and noncatalytic (carbon rejection) as presented in Figure 33.18. The process technologies are principally different on the basis of the feedstock and process conditions (reactor) and the catalyst used by the different licensers. A compilation of residue process technologies throughout the world is given in Table 33.12, which indicates that for the feeds used today, fixed-bed

TABLE 33.10—Principal Petroleum Oil Sectors and Their Role

Upstream Sector (Exploration and Production)
• The focus for this sector includes exploration and development involved in the search of petroleum oils.
• The development includes underground or underwater oil and gas fields and drilling of exploratory wells.
• Principal hydrocarbon analysis:
○ API gravity, viscosity, recovery efficiency, quality, and transport.
○ Flow assurance problems in well bores and topsides including asphaltene or wax precipitation, contaminants, corrosion, slugging, hydrate foaming, and emulsion breaking.
○ Early identification of oil quality issues allows the downstream sector to develop targeted solutions and prepare refineries for upcoming feedstock changes.
Downstream Sector (Refining/Upgrading)
• The focus for this sector covers the oil refineries, product quality, and its distribution.
• It handles consumers through thousands of products such as gasoline, diesel, jet fuel, heating oil, asphalt, lubricants, petrochemicals, or even pharmaceuticals.
• Petroleum product sales focus on wholesale, industrial, and commercial customers.

TABLE 33.11—Classification of Residue Upgrading Processes

Noncatalytic Processes	Catalytic Processes
Solvent deasphalting	Residue fluid catalytic cracking (RFCC)
Thermal (carbon rejection)	*Hydroprocessing (H_2 addition)*
Gasification	Fixed-bed hydrotreating
Delayed coking	Fixed-bed hydrocracking
Fluid coking	Slurry hydrocracking
Flexicoking	Ebullated-bed hydrotreating
Visbreaking	Ebullated-bed hydrocracking

reactor systems are more popular than ebullated beds or slurry systems [35]. The compilation presents only a brief summary of these topics to provide a general idea of the relationship among catalysts, reactors, and processes. The selection of these processes depends on the required product selectivity, which includes the final product and the commercial trade in the market. However, the most important product prices are cited in Figure 33.19, which are clearly increasing with time and could be due to the increase in price of processing. Carbon rejection processes usually promote the gas formation whereas the hydrogen addition processes increase liquid yield, but these processes are expensive [36].

Apart from the aforementioned processes, solvent deasphalting (SDA; extraction process) is recently becoming more eminent because of its easy and low-cost process. The most common method used for asphaltene precipitation is SDA. This process uses a paraffin solvent to separate a crude oil or residue into a deasphalted oil (DAO) and a pitch (asphaltene), which contains most of the impurities of the feedstock. In addition, it only removes the most important problematic elements of asphaltene and significant amounts of sulfur, nitrogen, and metals.

33.5.2 *Natural Gas Processing*

The origin of natural gas is similar to the fossil fuel that remains from plants and animals or microorganisms that lived millions of years ago. Natural gas in these reservoirs is typically under pressure, and it is usually found underneath the Earth surface, which does not allow it to escape from the reservoir on its own. The composition of natural gas is given in Table 33.13. Natural gas is formed primarily of methane; it can also include traces of ethane, propane, butane, and pentane along with inorganic impurities such as H_2S, CO, CO_2, etc. Natural gas has a low density; its pressure will rise toward the surface of the Earth to be able to escape into the atmosphere, shale-type rock, and other material. Most of the time gas (methane) simply rises to the surface and will disperse into the atmosphere. The trapped natural gas under the Earth can be recovered by drilling a hole through the impermeable rock or Earth surface.

33.5.2.1 NATURAL GAS SOURCES

Natural gas is commercially produced from oil fields and natural gas fields. Gas produced from oil wells is called casing-head gas or associated gases. Along with natural gas, these sources produce gases such as sour gas, tight

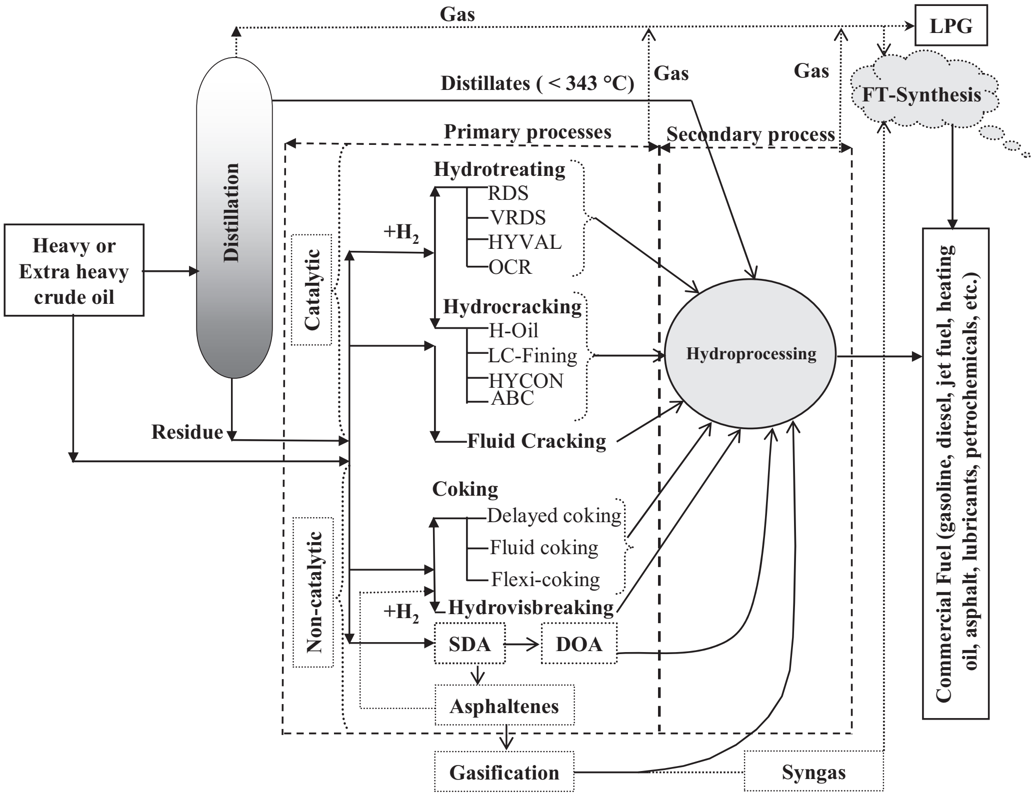


Figure 33.18—A comprehensive schematic flow diagram of typical oil refinery technologies for upgrading heavy and extra-heavy crude oil and residue (catalytic route and noncatalytic routes) and gas produced during the processing.

TABLE 33.12—Residue Commercial Process Technologies in the World[a]

Process Technology	North and South America	Europe and Japan	Others	Total	%[b]
Hydroprocessing					
Fixed bed	12	21	27	60	9
Ebullated	7	4	1	12	2
Slurry	1	0	0	1	0
Total hydroprocessing	20	25	28	73	12
Solvent deasphalting	15	3	6	24	4
Thermal processing	131	155	147	433	69
RFCC	19	26	57	102	16
Total[b]	185	209	238	632	100

[a] Units operating in March 2003. [b] Based on total units. *Source:* Data taken from [33].

TABLE 33.13—Typical Composition of Natural Gas

Compounds	Chemical Formula	Composition (%)
Methane	CH_4	70–90
Ethane	C_2H_6	0–20
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon dioxide	CO_2	0–8
Oxygen	O_2	0–0.2
Nitrogen	N_2	0–5
Hydrogen sulfide	H_2S	0–5
Rare gases	Ar, He, Ne, Xe	Trace

gas, and shale gas as well as coal-bed methane. The world's largest gas field is offshore of Qatar (25 trillion m^3) whereas the second-largest natural gas field is in Iran under the waters of the Persian Gulf. The list of major gas-producing/reserved countries is reported in Figure 33.20. There are several other sources, mainly for methane origin, which are well known by their commercial name such as town gas (produced by treating coal chemically), biogas (produced from organic material), landfill gas (a type of biogas), and hydrates (under sediments in the oceans

33.5.2.2 GAS FIELDS

Similar to oil, natural gas is often found in land-based gas fields as well as underwater in offshore gas fields such as the North Sea, the Corrib Gas Field of Ireland, and the Scotian Shelf near Sable Island. The technology utilized to extract and transport offshore natural gas is different from land-based fields in that a few, very large rigs are usually used because of the cost and logistical difficulties in working over water. Rising gas prices have encouraged drillers to re-examine gas fields that have yet to be explored or were not considered economically viable before. For example, McMoran exploration passed a drilling depth of over 32,000 ft (deepest trial well in the history of gas production) at the Blackbeard site in the Gulf of Mexico. Of course, finding gas reserves is not so simple, and sometimes things go such a way that a drilling company must leave a well after digging. For example, in 2006 Exxon Mobil abandoned a well after drilling 30,000 ft underwater without finding gas [37].

33.5.2.3 NATURAL GAS PROCESSING

Natural gas processing is a purification process technology [38–40] that is basically performed by means of different chemical solvent treatment and catalytic processes. A schematic flow diagram of a typical natural gas processing plant is shown in Figure 33.21. It shows a combination of several processes used to purify raw natural gas into sales gas

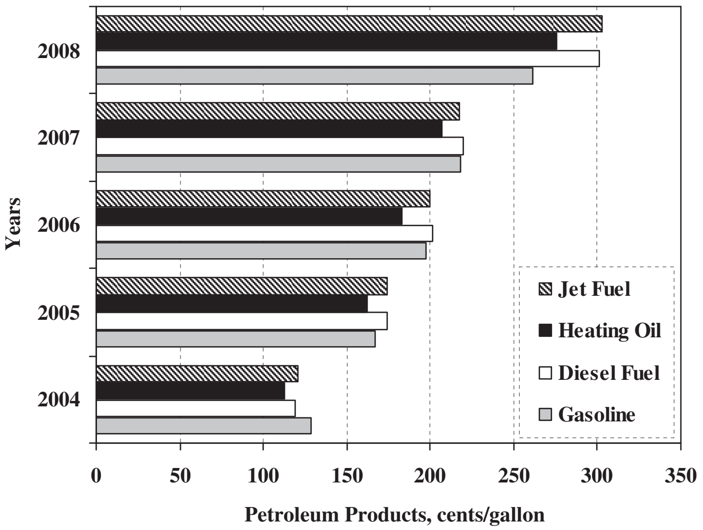


Figure 33.19—Commercial fuel prices for petroleum products of crude oil recovered.

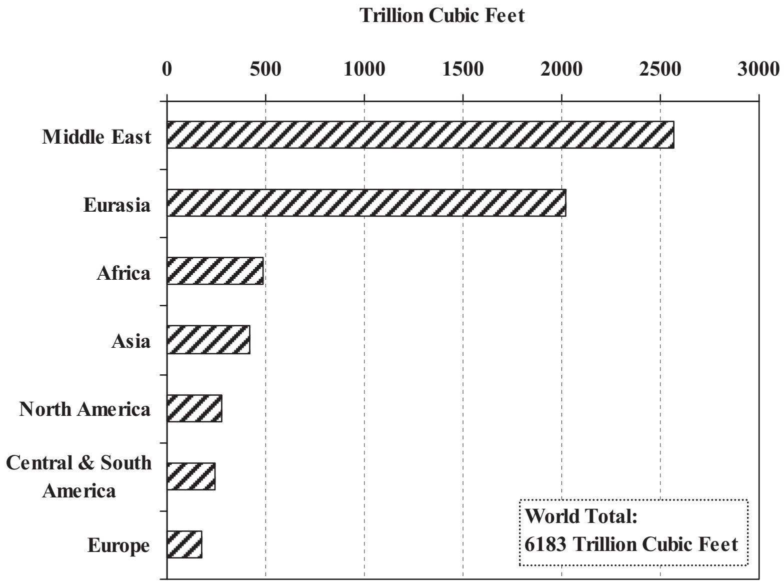


Figure 33.20—World natural gas reserves by region, December 2006. *Source:* U.S. Energy Information Administration, 2007 [11].

pipelined to the end-user markets. The figure also shows how processing of the raw natural gas yields byproducts such as sulfur, ethane, and NGLs propane, butane, and natural gasoline. Raw natural gas explored from a gas well (natural gas fields) is in an impure form that requires purification by using several methods. The major difficulty in the use of natural gas is transportation and storage because of its low density. It is usually more economical to transport either using a pipeline to the filling stations or directly bottling in the refinery.

33.5.2.4 USES OF NATURAL GAS

Natural gas is a vital component of the world's supply of energy and is one of the relatively cleanest, safest, and most useful of all energy sources. In particular, it is a major domestic energy source such as for kitchens, it cools and

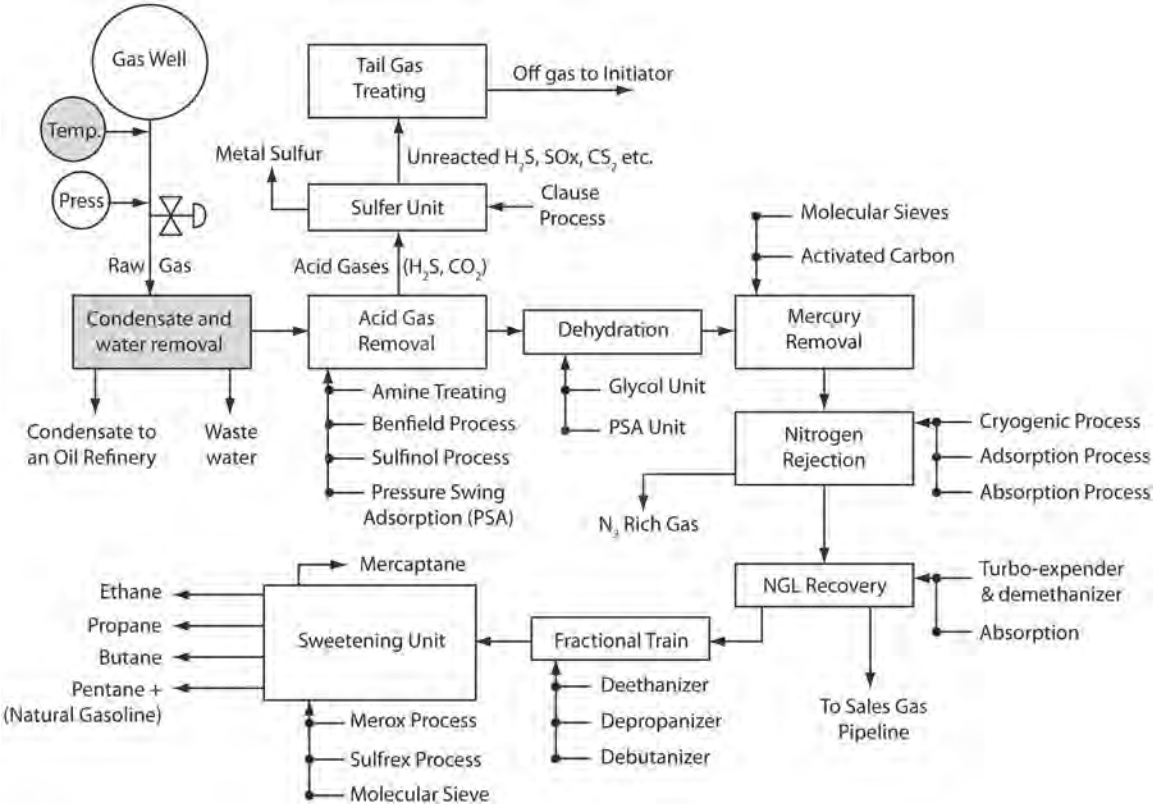


Figure 33.21—Technological aspects of clean natural gas and the refining of its petroleum products. Yellow = final products, blue = processes that are used for purification.

warms our homes and businesses, it is used to generate electricity, and it helps maintain our quality of life. The use of natural gas in different sectors is reported in Table 33.14 along with the expected increase in the different sectors.

33.5.2.5 NATURAL GAS PRICING

Quantities of natural gas are measured in normal cubic meters (corresponding to 0°C at 101.325 kPa) or in standard cubic feet (correspond to 16°C and 14.7 psia). It was calculated that 1 normal cubic meter of commercial-quality natural gas gross heat of combustion is approximately 11 kWh [4]. The price of natural gas varies greatly depending on location and the type of energy sector as shown in Figure 33.22. Natural gas is effectively used worldwide to produce electricity but to a lesser extent directly as motor fuel, which is most likely to be used relatively as cleaner fuel. Investigations in this direction have been performed to prepare more unconventional and better quality feed as shown in Figure 33.23.

TABLE 33.14—Projected Consumption Growth by Sector in Billion Cubic Feet (bcf)

Natural Gas Sector	2004	2010	Increase	Percentage Increase
Industrial[a]	8188	9046	858	10
Electrical generation	5226	6737	1513	29
Residential	4957	5524	567	11
Commercial	3103	3387	284	9
Others	664	737	73	11
Total	22168	25433	3265	15

[a] Projected growth of the consumption of natural gas in this sector is an average of 1.9 % annually between 2004 and 2030 [10].

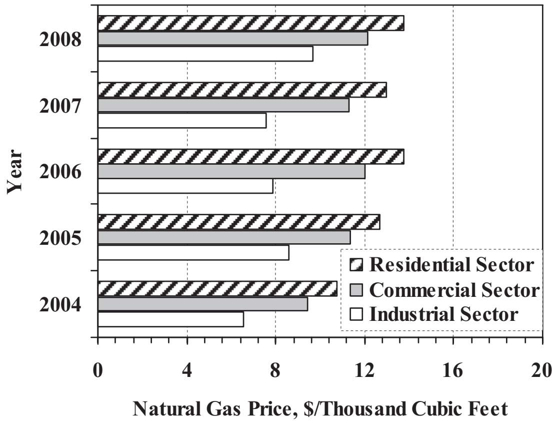


Figure 33.22—Natural gas prices for different sectors [10].

33.5.3 GTL Technologies

GTL technology was invented in 1923 when two German scientists, Franz Fischer and Hans Tropsch, discovered the catalytic conversion of CO and hydrogen (synthesis gas) into synthetic hydrocarbons [41,42]. GTL process routes are based on Fischer-Tropsch (F-T) technology, which involves the conversion of natural gas to synthesis gas, followed by the conversion of synthesis gas to heavy hydrocarbons and then the workup of the hydrocarbons into the final products [43,44]. The primary product of this process is a low-sulfur, nitrogen-, olefin-, and aromatic- high-cetane (≈70) diesel fuel (FT diesel). Natural gas (mainly methane) is considered to be a relatively clean source of energy and a feedstock for petrochemical industries. Its transportation from gas fields to energy consumption centers and chemical plants is a major impediment to the development of natural gas industries. However, by lowering the gas temperature down to –160°C, it is possible to liquefy the natural gas at high pressures and increase its energy density. Using the

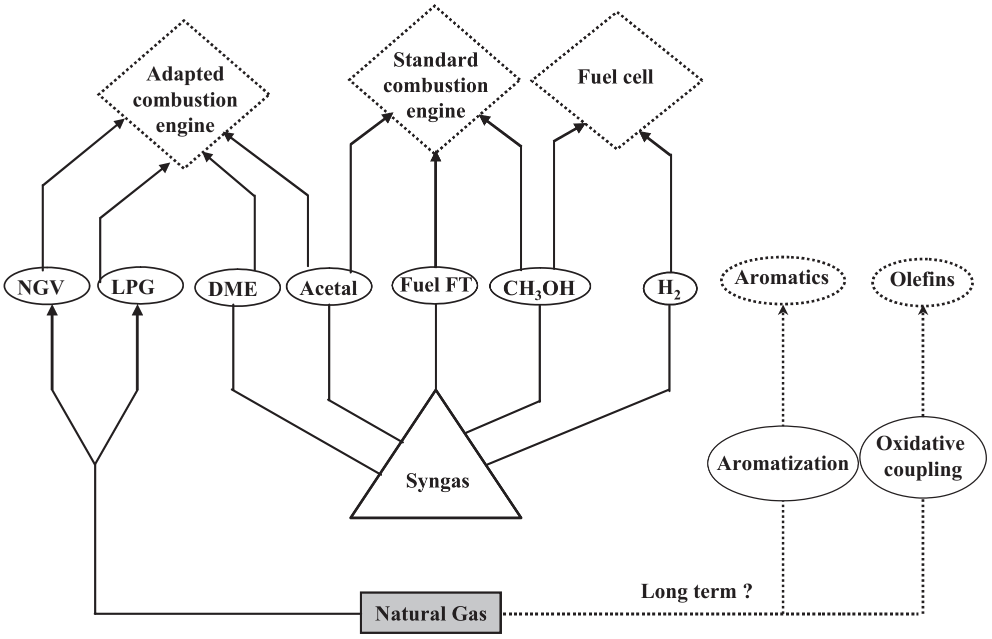


Figure 33.23—Different application of natural gas to produce alternative fuel. DME = dimethylether, LPG = liquefied petroleum gas, and NGV = natural gas vehicle [48].

gas in a liquefied form (known as LNG) or compressed state (known as CNG) are the other options, which require further attention to the commercial applicability of the process as well as the safe use of gas. Thus, an attractive alternative in natural gas utilization is to convert the gas into more valuable and easily transportable products such as liquid fuels. The gas conversion methods may classified as direct and indirect conversion. Direct conversion is the oxidative coupling of methane, of which work is going on in several laboratories and its technology is far from the commercialization process. However, the second category (GTL) process has been commercialized since the 1920s and the processes are used commercially by the different well-known companies (Table 33.2)—of course, using their own method of processing. Thus, the conversion of natural gas into liquid fuels is an attractive option to commercialize profuse gas reserves, which has virtually unlimited markets and offers a new way to release remote gas reserves by using traditional technologies.

33.5.3.1 GTL TECHNOLOGY AND ITS KEY PARAMETERS

GTL is a well-known refinery process [6–10] that converts natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons (liquid phase). Methane-rich gases are converted into liquid fuels either via direct conversion or syngas as an intermediate process such as the FT or Mobil process. Using such processes in a refinery alone or in combination, the gaseous waste products were converted into valuable transportation liquid fuel oils as shown in Figure 33.24. GTL conversion is an umbrella term for a group of technologies that can create liquid synthetic fuels from various feedstocks by using the FT process. This process can create identical liquids from various feedstocks, although the technical challenges are greater for biomass and coal. There are two main categories of natural gas-based FT process technology (1) at high temperature, usually an iron catalyst-based GTL process, which produces fuels such as gasoline and gas oil that are virtually free of sulfur, but contain aromatics; and (2) at low temperature, a cobalt catalyst-based GTL process, which produces an extremely clean synthetic fraction of gas oil that is practically free from sulfur and aromatics.

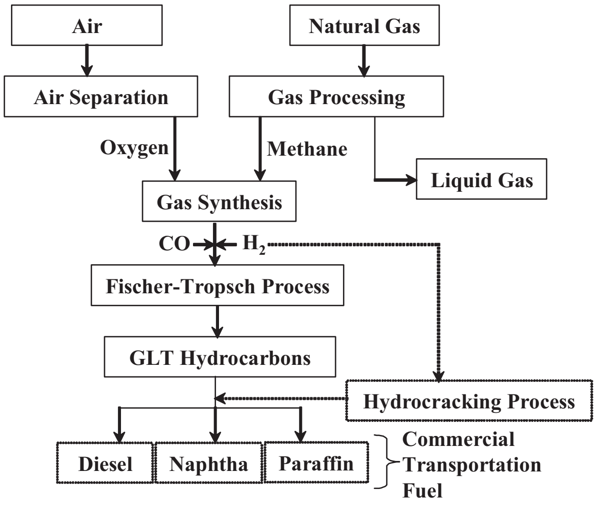


Figure 33.24—GTL process technology using the FT method.

33.5.3.2 IMPORTANCE OF LIQUID TECHNOLOGIES

In the refinery site either offshore or onshore several gases are expelled that are usually abandoned because there is no economical way to transport and use them effectively. Thus, these gases must be captured and converted into liquid barrels of synthetic, clean-burning fuels. There are only two practical ways of using natural gas: flowing it through a pipeline in gaseous form or condensing it at low temperature and transporting it as LNG. A third alternative, GTL technology, chemically converts natural gas into clean-burning liquid products that can be easily transported to market. In addition, diesel obtained from FT synthesis has nearly zero sulfur and nitrogen oxides, contains nearly no aromatics, burns with little or no particulate emissions, and has high cetane value.

33.5.4 FT Technology and Process Parameters

The FT process (or FT synthesis) is a heterogeneous catalytic chemical reaction in which synthesis gas (syngas, a mixture of CO and H_2) is converted into liquid hydrocarbons of various forms [43,44]. The most common catalysts are based on iron (Fe) and cobalt (Co) whereas nickel (Ni) and ruthenium (Ru) have also been used to a lesser extent. The principal purpose of this process is to produce a synthetic petroleum substitute, typically from coal, natural gas, and biomass or renewable transportation fuels. These synthetic fuels are able to run trucks, cars, and various aircraft engines; however, their use as diesel is increasing in recent years.

33.5.4.1 FT CATALYSTS

Various catalysts can be used for the FT process, but the most common are the transition metals Co, Fe, and Ru [45]. Ni can also be used, but tends to favor methane formation. Co seems to be the most active catalyst, although Fe also performs well and can be more suitable for low-hydrogen-content synthesis gases such as those derived from coal because of its promotion of the water-gas shift reaction. On the other hand, promoters such as potassium (K) and copper (Cu) are also tried along with the support effect such as silica, alumina, and zeolites. FT catalysts are sensitive to the presence of sulfur-containing compounds among other pollutants whereas Co-based catalysts are more sensitive than their Fe counterparts. In addition, Co-based catalysts have higher activity but require better feedstock quality whereas Fe catalysts are preferred for lower quality feedstocks such as coal or biomass. Thus, with high sulfur content feed a lower-cost Fe catalyst can be used effectively (economically) as a sacrificial catalyst at the top bed in a fixed-bed reactor.

33.5.4.2 FT PROCESS CONDITIONS

The FT process [46] is generally operated in the temperature range of 150–300°C. Higher temperatures lead to faster reactions and higher conversion rates, but they also tend to favor methane production. As a result, the temperature is usually maintained in the lower range whereas increasing the pressure leads to higher conversion rates and favors formation of long-chained alkanes, both of which are desirable. For Co-based catalysts the optimal H_2:CO ratio is approximately 1.8–2.1. Fe-based catalysts promote the water-gas shift reaction and thus can tolerate significantly lower ratios whereas synthesis gas derived from coal or biomass has relatively low H_2:CO ratios (<1).

33.5.4.3 PROCESS CHEMISTRY

The FT process involves various competing chemical reactions that lead to a series of desirable products (alkanes) and undesirable byproducts.

$$(2n+1)\,H_2 + nCO \rightarrow C_nH_{(2n+2)} + 2H_2O \qquad (33.1)$$

$$2H_2 + CO \rightarrow -CH_2- + H_2O \qquad (33.2)$$

where n = 1 results in the formation of methane. Process conditions and catalyst composition are usually chosen to favor higher reaction orders (n >1) and thus minimize methane formation. Most of the alkanes produced tend to be straight-chained, although some branched alkanes are also formed. Another important reaction is the water and gas known as the shift reaction:

$$H_2O + CO \rightarrow CO_2 + H_2 \qquad (33.3)$$

Although this reaction results in the formation of unwanted CO_2, it can be used to shift the H_2:CO ratio of the incoming synthesis gas.

33.5.4.4 SYNTHESIS GAS PRODUCTION

The initial reactants (synthesis gases) used in the FT process are hydrogen and CO, which are usually produced by one of two methods:

1. Partial combustion of a hydrocarbon:

$$2C_nH_{(2n+2)} + nO_2 \rightarrow 2(n+1)H_2 + 2nCO \qquad (33.4a)$$

when n = 1 (CH_4), the equation becomes

$$2CH_4 + O_2 \rightarrow 4H_2 + 2CO \qquad (33.4b)$$

2. Gasification of coal, biomass, or natural gas:

$$CH_x + H_2O \rightarrow (1+0.5x)H_2 + CO \qquad (33.5)$$

Here again x depends on the type of fuel; for example, natural gas has a greater hydrogen content (x = 5 to x = 3) than coal (x < 2). The mixture of CO and hydrogen is called synthesis gas or syngas, and the resulting hydrocarbon products are refined to produce the desired synthetic fuel.

33.5.5 Methanol-to-Gasoline Process (Mobil Process)

The Mobil process is an effective method to convert natural gas into gasoline (liquid hydrocarbons) fuel through methanol by heating with ZSM-5 zeolite catalyst, which was developed by Mobil in the early 1970s [47]. The process follows this three-step reaction using natural gas (CH_4) as the starting reaction.

$$\text{Steam reforming: } CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (33.6a)$$

$$\text{Water shift reaction: } CO + H_2O \rightarrow CO_2 + H_2 \qquad (33.6b)$$

$$\text{Synthesis: } 2H_2 + CO \rightarrow CH_3OH \qquad (33.6c)$$

The methanol thus formed may be converted into gasoline by the Mobil process. First, methanol is dehydrated to give dimethyl ether:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (33.7)$$

This is then further dehydrated over a zeolite catalyst (most likely ZSM-5) to give a gasoline or C_5+ hydrocarbon product.

The processing of natural gas appears to be a promising energy source for the transportation industry, especially when the product is synfuel, which can then be used directly in conventional engines. It must also be pointed out that GTL technology is an ideal solution for using the associated gas produced during petroleum production operations [48]. A few decades ago refining onsite gas was often simply burned in the refinery (at the top of a Christmas tree), which is almost forbidden because it releases large quantities of CO_2 to the environment. Thus, presently in refineries gas is sent back to the well or this stream is treated with one of the aforesaid processes for commercial use. On the other hand, with the GTL process industrialists are killing two birds with one stone: they are working an oil field and using the gas produced to make fuel.

33.6 REFINERY OF THE FUTURE

33.6.1 Crude Oil Upgrading Technology

33.6.1.1 EXISTING TECHNOLOGIES FOR CRUDE OIL AND RESIDUE PROCESSING

The objective of this chapter is to compare refining process schemes that are used for upgrading heavy feeds as well as natural gas. The focus is on the nature of feeds and their contamination, which indicate the limitation of the processes (catalytic as well as noncatalytic) as a function of the feedstock. Generally, for low-API gravity crude oil (extra-heavy crude oil) or residue, the target is to minimize the metal (V + Ni) content and to improve flow properties. These feeds are referred to as problematic and the metal content may range from 20 to 1000 ppm, which requires different operating conditions and catalysts as shown in Figure 33.25. It should be noted that the hydroprocessing application range has recently been reported to cover feeds with a larger amount of contaminants with lower API gravity. One of the objectives of this chapter is to make such information more readily available, and the details of the individual processes are given elsewhere [32,34].

The upgrading process is a combination of separation, thermal conversion, hydroconversion or hydrotreating, and fluid catalytic cracking (FCC). It is observed that thermal processes produce a large amount of coke and undesirable products and low liquid product yield whereas catalytic processes strongly favor the residue processing but require good quality feedstock. Therefore, selection of any of the previously mentioned processes for heavy feedstock depends on the feed quality and its composition [36]. Moreover, coking processes may be preferable for countries such as India where LPG is an effective use whereas in oil-producing countries coking processes may not be totally appropriate because they reduce liquid yield. Asphaltene is the target molecule, particularly in catalytic-based processes, and by considering thermal gravimetric analysis (TGA) results it gave us an impression that asphaltenes are impractical to convert by catalytic means as shown in Figure 33.26. The loss of asphaltene or high

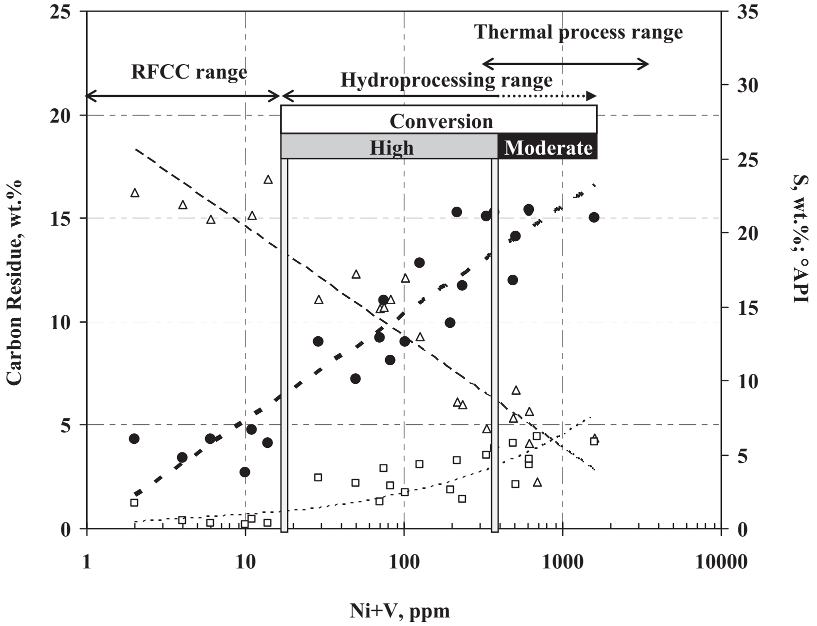


Figure 33.25—Selection of technologies for upgrading crude oils on the basis of feed properties of atmospheric residues. □ = sulfur, • = carbon residue, and Δ = API gravity [36].

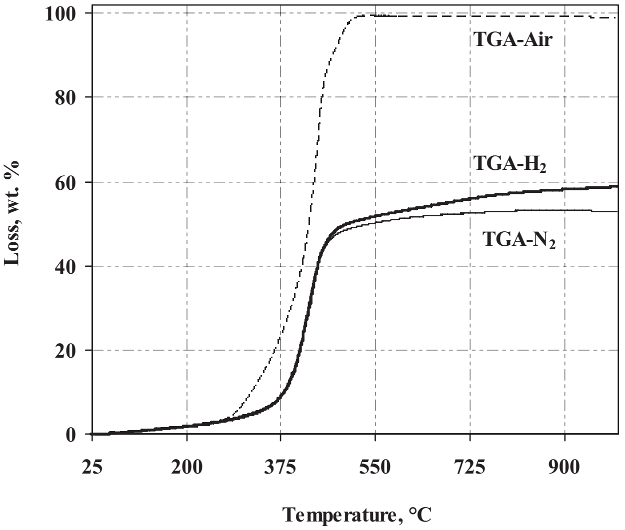


Figure 33.26—Effect of thermal liquefaction of asphaltene in different atmospheres. *Source*: [49].

conversion in the presence of air is due to oxidative combustion of asphaltene at high temperature (>250°C) whereas the difference between TGA-H_2 and TGA-N_2 can be understood by the reactive role of H_2 to the asphaltene molecule [49]. In this regard, for high asphaltene-containing (≥15 wt %) feedstock, an integrated approach can be effectively applied by using the SDA process. Hence, separation of asphaltene before hydroprocessing could be an option to modify the process and one step in the advance toward the deeper and stricter environmental legislation as well as catalyst stability. A proposed process that is based on these considerations is shown in Figure 33.27. The integrated process indicates that once the asphaltene is separated from the residue, the DAO is easier to process in hydroprocessing units. The heavy asphalt or pitch can be processed through thermal process using gasification to complete conversion, which will produce synthesis gas (CH_4, H_2, CO) as the major product. Further, depending on the need of fuel oil, the synthesis gas may be converted into kerosene or the gas oil pool by using FT synthesis and isomerization processes [48,50].

33.6.1.2 EMERGING OR FUTURE TECHNOLOGIES FOR HEAVY CRUDE OIL PROCESSING

An imperative need for the upgrading of heavy and extra-heavy oils is due to the depletion of light crude oil, which forces researchers and refiners to develop new-fangled technologies to convert heavy petroleum into more valuable products. The main objective in such developments is to increase the API gravity and reduction in impurities (S, N, O, etc.) along with selective liquid yield of gasoline and middle distillates. A compilation of such technologies is difficult because most of the work is at the laboratory scale or in the scale-up level; nevertheless, some of them are reported in Table 33.15. However, these technologies are in the embryonic era and are either in the development stage or tested at different scales (laboratory, bench, pilot plant, and semicommercial). Because the details of such processes are limited, it is difficult to infer any conclusion about their commercial applicability; thus, only basic information can be obtained from the Internet and in the open literature [34,51–59]. These technologies have definitively attracted the attention of the refiners. Most of them may be good for one feedstock but not for others because the nature of the individual is focused on their own. Thus, there is unfortunately not a general rule that can give a solution to all refineries in one option because there are many factors such as oil and product prices, market trends, local needs, physical and chemical properties of the available heavy oil and residua, and refinery configuration that are all involved and must be taken into account to define a specific upgrading process scheme. Therefore, each refinery will define its own scheme for heavy oil upgrading. In other words, there is no one single upgrading solution that is suitable for all refineries.

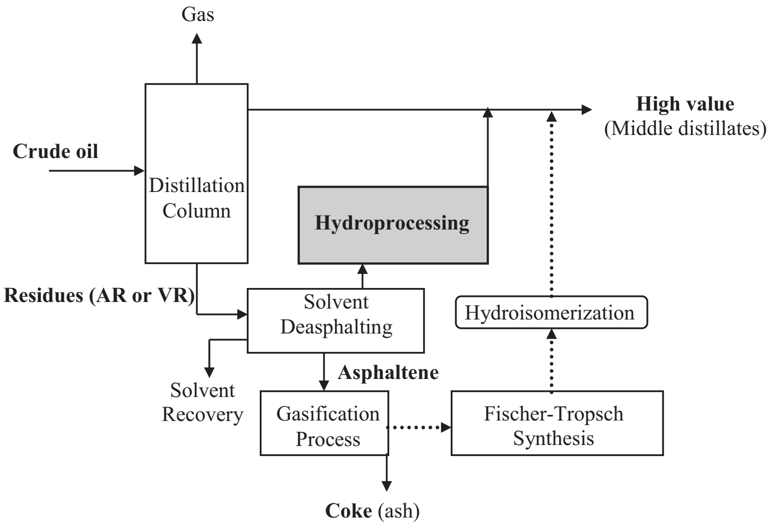


Figure 33.27—Proposed hybrid process scheme for upgrading heavy petroleum [36].

TABLE 33.15—Emerging Technologies for Heavy and Extra-Heavy Crude Oil and Residue Processing Technologies

Emerging Technology	Remarks	Reference
GHU process technology (Genoil Inc., formerly CE^3)	• Multiple fixed-bed reactor system. • Feedstocks ranging from 6.5° to 17.5° API gravity. • Only tested with feed that has a relatively low metal content.	50
HCAT™ process technology (Headwaters Heavy Oil)	• Reported as a breakthrough process to convert low-quality feedstock (high asphalt and metals). • Conversion up to 95% and higher reactor throughput. • Uses a molecule-sized catalyst (slurry-phase reactor). • Technology offers several significant advantages over processes that have been based on supported catalysts.	51
HTL (Heavy-to-Light) process technology (Ivanhoe Energy)	• Technology is fundamentally a short contact time thermal conversion process (rapid thermal processing). • Operates at moderate temperatures and at atmospheric pressure. • Unique thermal cracking technology that solves some of the disadvantages that exist for the delayed coking, fluid coking, and visbreaking processes.	52
IMP (Mexican Institute of Petroleum) process technology	• A low- or moderate-pressure technology for upgrading heavy oils and residua. • Catalysts with improved stability as well as operating conditions and proper selection of reactors and feedstock to work under a moderate conversion regime. • Process offers low sediment formation at high asphaltene content.	53
ISO-CRACK process technology (Chevron Lummus Global)	• An ebullated-bed residue hydrocracking process representing the next generation of LC-FINING technology for heavy-oil upgrading.	54
HySCOP™ process technology	• Idemitsu Kosan licensed its hydrocracking catalyst technology to Axens Hyvahl™ hydroprocessing technology. • Technology is suitable for upgrading heavy crude oil produced by oil-producing countries.	55
Sonocracking™ (SulphCo, Inc.)	• Ultrasound technology to desulfurize and hydrogenate heavy crude oil. • The transfer of hydrogen from water to the numerous petroleum streams leads to the conversion of crude oil, and it has 30,000 bbl/day of processing capacity.	56
Dispersed technology (slurry technology or nanoprocess)	• Several processes are proposed or even patented by using dispersed-phase catalyst (aqueous ammonium molybdates or tungstates, ammonium tetrathiomolybdate, MoS_2, ferric sulfate, and ferric alum, etc.) in the slurry process, but none of their performances thrive at the commercial scale.	57,58
VEBA-combi-German, CANMET-Process-Canada, Microcat-ExxonMobil, HDH-INTEVEP Venezuela, Aurabon Technology (UOP)	• Only being tested on an experimental scale since 1942. Limitations associated with these processes include a large dose of catalyst, expensive catalysts, and separation of catalyst and product, etc.	

33.6.2 Clean Fuel Technology

Combustion of fossil fuels produces environmental contamination such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), and particulate matter (PM) during automotive emissions; thus, it is necessary to reduce the sulfur and nitrogen content in fuel to their minimum levels to protect the environment and catalyst (noble metal) for exhaust emission reduction. In this regard, it is necessary to develop a hydrotreating catalyst that is able to produce ultralow levels of sulfur (<10 ppmw S) and nitrogen in gasoline and diesel fuel.

33.6.2.1 ULTRALOW-SULFUR DIESEL FUEL

Gas oil contains hard-to-desulfurize sulfur compounds (e.g., alkyl dibenzothiophene) that are difficult to remove with conventional desulfurization catalysts because of the molecular steric hindrance of organosulfur molecules (Figure 33.17). It is essential to remove these hard-to-desulfurize sulfur compounds to obtain ultralow sulfur diesel (ULSD), which can now be produced by using a new generation catalyst in an existing commercial desulfurization unit without installation of new facilities. Despite the last 50 years, hydrotreating (HDT) catalysis has been recognized as a multidisciplinary work about the support effect, catalyst characterization, and catalytic activity for deep hydrodesulfurization [60]. There are now a few advanced commercial catalyst formulations that are used by refiners, such as NEBULA (NEw BULk Activity, ExxonMobil), STARS (Super Type II Active Reaction Sites, Akzo Noble Catalyst), and Topsøe catalysts for middle-distillate hydrodesulfurization [61].

33.6.2.2 CLEAN FUEL UTILIZATION TECHNOLOGY

There are several ways to utilize clean fuel technologies (e.g., hydrogen, fuel cell, etc.) that address the utilization of hydrogen in transportation and stationary energy applications. Fuel cells are another important clean energy source that is expected to be the most favorable choice for utilization of hydrogen in both of these applications. However, market demand and the economical aspects of fuel cell technology are still a matter of further research, but this is one option that is much safer than any other technology. Hydrogen and hydrogen-containing natural gas blends can be effectively used directly as fuels for stationary and transportation reciprocating engines. This approach provides a bridge to future fuel cell usage in transportation applications and is in agreement with the objective of the environmental norms. On the other hand, by using ULSD fuel, we are striving to use technologies for more efficient utilization of energies and fuels that are applicable to air quality improvement to contribute to the diversification of fuels and the efficient reduction of greenhouse gases, such as SO_2, NO_x, CO_2, and petroleum hydrocarbon (PH), which will be much less but it will never provide clean fuel such as hydrogen or fuel cells. Nevertheless, fossil-fuel-based clean fuel (ultralow-level contamination fuel) is relatively economical and easy to use by end users. In this respect, there are several catalyst-based technologies [57] where some of them are well reported by their emblematic name such as Albemarle, Akzo Nobel, Topsøe using their recently developed NEBULA [61], STARS [62,63], and BRIM [64] catalysts in the refineries, respectively. Embryonic alternative fuel and emerging energy technologies are compiled in a subsequent section.

33.6.3 Emergence of New Fuel and Technologies

This section reports technologies for the production and utilization of alternative fuels having less environmental consignment to prevent air pollution and global warming [65–69]. These technologies may be relatively new to the market but are far from required demand, which is evident from the energy growth in the last few years. However, refiners (or energy source dealer) will have to show greater prudence while devising their marketing and distribution strategies and identifying potential growth areas. The principal objective is to produce an energy source with greater promise for environmental legislation. The energy source should be inherently safe to produce, store, and use commercially anywhere. Although this topic has the content of a review, this chapter will only discuss the basic ideas about these processes, which are relatively new in the energy sector.

33.6.3.1 BIOMASS FUELS

Regarding biomass fuels (biodiesel fuel [BDF]), it becomes particularly important to conduct the verification related to the utilization of biomass fuels mixed with transportation fuels such as gasoline. The resulting biodiesel (ethyl tertiary-butyl ether [ETBE] is mixed with gasoline) could ultimately be made 100 % green by using ethanol, which is derived from biomass instead of methanol, which is obtained from natural gas. The *Esterfip-H*™ process is a biodiesel process that is already tested by Institut François du Petrol (IFP), and 100 % green biodiesel is produced from low-cost ethanol; therefore, IFP is examining the feasibility of new, cheaper production processes that will involve the biological conversion of biomass such as cereal straw, corn stalks, wood waste, etc. [70]. One approach to biofuels is categorized into various types—ethanol (produced by enzyme hydrolysis of lignocellulosic biomass) and biodiesel (produced by transesterification of vegetable oils)—whereas another approach is biomass-to-liquid (BTL), which uses FT synthesis to produce good quality fuel, unlike the GTL or coal-to-liquid (CTL) approaches. However, BDF has to leave behind its storage stability test because it may have some carcinogenic effect and it requires much agricultural land. Some countries are eliminating their forests to obtain the land, including Brazil, which is ravaging its forests every year. Thus, ethanol production could be an ecodisaster. Of Brazil's 2 million acres of land, approximately 1400 acres contain native forests, two thirds of which are in the Amazon [71,72], where deforestation is high.

It is expected that the cost of these biomass- or vegetable-oil-based fuels should be relatively stable compared with that of petroleum fuels, and it even tends to decrease steadily with time [73,74]. Apart from these benefits, the commercial applicability of biomass is still in the primary steps and requires approximately a decade before full commercial application. Biomass often involves a burning process that produces emissions such as NO_x and CO_2, but fortunately far less than those emitted by fossil fuels. Using biofuel seems to offer some possibilities in terms of CO_2 mitigation, but at same time it is also expected that forests can absorb more CO_2 than the production of biofuels [75].

Apart from the environmental concerns, there is much trepidation about the balance between biofuel and food [76,77]. The "food versus fuel" debate depends on the location; for example, in the United States only approximately

9 % of corn is used for human consumption in products such as cereals, sweeteners, etc., but in a few other countries corn may not be a good option for ethanol. Thus, many new ethanol plants are looking for better or more efficient methods of ethanol production (e.g., algae), and other waste products such as cellulosic-based ethanol can be a good source of energy. Cellulosic refining has the ability to significantly reduce greenhouse gases and can be refined using low-value (nonedible) products such as wheat and barley straw, sugarcane or rice bagasse, sawdust, paper pulp, switchgrass and other perennial grasses, and even municipal waste or household garbage. However, cellulose is in nearly every natural free-growing plant, tree, and forests field throughout the world and does not require agricultural effort or cost to make it grow. Its processing is also easy because a few bacteria can convert cellulose into ethanol, which can then be used as a biofuel.

33.6.3.1.1 Energy Balance

Net energy balance is a term that is used to describe how much energy is needed to produce a product versus how much energy that product provides. For example, corn-ethanol production and its energy efficiency yields 34 % more energy than it takes to produce it, including growing, harvesting, transporting, and distilling the corn into ethanol [78]. A few critics of ethanol claim that it has a negative energy balance, but this is simply not true and has been debunked again and again by researchers. Thus, prices are sometimes exaggerated or limited by critics who are sometimes too speculative; however, such predictions are very useful to stir up discussions and interest by others. For example, some studies suggest that corn-based ethanol has a negative energy balance, meaning it takes more energy to produce the fuel than the amount of energy the fuel provides [66,79,80]. Thus, they claim that corn-ethanol is not a fossil fuel energy substitute and that increasing its production does little to displace oil imports and increase energy security. Keeney and DeLuca [81] also reported a negative net energy value (NEV), but their energy deficit was only approximately 8440 Btu/gal and they did not consider corn-processing byproducts; however, they showed that a positive energy balance could be attained with low-input corn production.

33.6.3.2 HYDROGEN AS A FUEL

Hydrogen is mainly used in industries, particularly to refine petroleum products and produce ammonia and methanol in small amounts for the aerospace industry. It is assumed that hydrogen demand will increase with the more widespread use of fuel cells in the future, which is one of the solutions that should be considered to reduce fossil fuel use and to reduce greenhouse gas emissions—of course, if the hydrogen is not produced from fossil fuel. Hydrogen is one of the most abundant elements on the planet; it does not exist in the form of a deposit that can be tapped directly. Moreover, it is not a primary source of energy like fossil fuels or even the wind and sun, which can be alienated either from oxygen or carbon. Thus, hydrogen can be produced from sources of water (as in water), biomass, or fossil fuel (as with natural gas, oil, coal, or biomass). Hence, it is considered that hydrogen is not a renewable fuel source of energy [82]. The major problem with hydrogen fuel is its storage, transportation, distribution, and safe use. Because of its volatility, hydrogen must be stored onboard a vehicle in compressed (35 or even 70 MPa) or liquid form at a temperature of –253°C. However, the storage type (in vehicles) and its capacity may vary on-site or with vehicle mileage.

33.6.3.3 FUEL CELLS

Solid oxide-type fuels have a high power generation efficiency and can be effectively used without producing pollutant emissions [83–86]. Fuel cells are highly expected as cogeneration (combined heat and power) with excellent energy saving capability. To increase fuel cell applicability in vehicles, it is necessary to expand the infrastructure that limits the supply of hydrogen as fuel.

A fuel cell is an electrochemical conversion device that produces electricity on two electrodes where fuel (at anode) and oxidant (at cathode) are catalytic and relatively stable and react in the presence of an electrolyte. A hydrogen cell uses hydrogen as fuel and oxygen as oxidant. The reactants flow into the cell, and the reaction products flow out of it in the form of electricity while the electrolyte remains within the cell. Therefore, fuel cells can operate practically continuously as long as the necessary flows are preserved. Hence, fuel cells vary from electrochemical batteries where they consume reactant.

33.6.3.4 PHOTOVOLTAIC ENERGY

Photovoltaic energy is the current field of energy research associated with the application of solar cells by the direct conversion of sun energy into electricity at the atomic level. Therefore, "photovoltaic" literally means "electricity through light." The manufacture of solar cells and photovoltaic arrays is becoming the world's fastest growing energy sector. Although most people are under the impression that the field of photovoltaic energy is new, this is not actually the case [87,88]. The capture of solar energy in the form of light and its conversion into electricity requires a material called a semiconductor, which are based on the photovoltaic (PV) effect in which light falls on a two layer semi-conductor (mainly p-type and n-type) device that produces a photovoltage or potential difference between the layers. Solar cells are mostly based on crystalline silicon, which is relatively higher priced than grid electricity. Recent nanosolar technology involves a thin film of copper, indium, gallium, and selenium (CIGS) that absorbs sunlight and converts it into electricity [69]. Moreover, unlike fossil-fuel-based technologies, solar power does not lead to any harmful emissions during operation, but the production of the panels leads to some amount of pollution.

33.6.3.5 AQUAFUEL TECHNOLOGY

Aquafuel is a reliable, inexpensive, and nonpolluting process that is simple and promising for energy and chemical production. Aquafuel burns in conventional engines so cleanly that internal combustion engine exhaust is actually cleaner than with any fossil fuel and there are no vicious smells; in fact, there is no smell at all. Aquafuel is inherently safe to produce and store because all oxygen resulting from the separation of the water is combined with the carbon, which is then released only during combustion. Moreover, NO_x and CO emissions are negligible even without any pollution control equipment. However, this process is fairly innovative and it uses carbon arc technology, which is a relatively indefinite process that is being used underwater to produce ultraclean, low-cost, alternative synthesis gas. This process is being investigated and demonstrated at the bench-scale level, and technological aspects are being experienced in demonstration units and are now undergoing tests in engines and research laboratories [89].

33.7 PERSPECTIVES, CHALLENGES, ALTERNATIVE APPROACHES, AND FUTURE TRENDS

Hydrocarbon resources are limited, and with the increase in demand for global energy, the existing resources are decreasing rapidly. At the same time, crude oils that remain and will be produced in the future are heavier, contain more sulfur, and have lower quality than those crude oils already produced. As we have seen in this book, the main role of a refining industry is to convert crude oil into various forms of fuels to drive vehicles and aircrafts or to generate heat in power plants. However, the lighter and gaseous products of refineries are the feed into petrochemical plants. Light olefins include ethylene, propylene, butylenes, and butadiene, which are some of the key hydrocarbons used in petrochemical industries. These hydrocarbons are the primary building blocks in the production of such products as polyethylene, polypropylene, poly(vinyl chloride) (PVC), ethylene glycol, and SBR/PBR rubber [90].

For example, C_2 (ethylene) and C_3 (propylene) are produced from a steam cracker unit, and the ratio of C_3 to C_2 from such a unit is decreasing from 0.4 in 2004 to a projected 0.36 in 2014 whereas the demand is on the rise from 0.59 in 2004 to a projected 0.62 in 2014 as forecasted by chemical companies [91]. The rate of increase in demand for polypropylene in the coming years is expected to be approximately 2.5 Mt/year. This indicates that processes should be modified in a way that more C_3 should be produced in future refineries according to the market demand. Refineries of the future should be more concerned with an increase in downstream products to produce lighter components and fewer residues. This requires more cracking and FCC units. In fact, with a high-severity FCC unit it is possible to increase the propylene yield from 3–5 wt % to 14–20 wt % with more production of aromatics (benzene, toluene, and *p*-xylene [BTX]) rather than gasoline. The future FCC units should be more flexible to operate between propylene and gasoline units.

Future refineries should reduce capital and operating costs as well as lower the feedstock costs for petrochemical plants. Light gases of C_2 and C_3 may also be produced from catalytic cracking of the C_4 to C_7 olefins that are produced from FCC units. Light olefins with methanol can be used to produce ethylene and propylene. In revamping refinery processes, it is important to integrate newly developed processes into existing processes to lower the capital cost. As an example, world demand for propylene is expected to increase from 63 million MTA (metric tons/year) in 2004 to approximately 97 million MTA projected in 2015 with an annual increase in demand of approximately 5 %. Refinery needs are challenging, and according to UOP they could be summarized as lowering hydrogen consumption and increasing the activity, selectivity, product quality, and processing flexibility during a processing cycle. Evolving refineries also require new catalyst development with more options to maximize returns and eliminate residues and heavy products. New catalysts should also have higher activity, selectivity, and stability [92]. The FT diesel (FTD) fuel technique is able to produce acceptable cold-flow specifications that are imperative to pour point, cloud point, and freezing point with a slightly lower cetane index value that must be sacrificed to adjust cold-flow properties. In addition, such FTD fuel is effectively used in trucks and buses and does not require any changes to vehicles or their engines.

Another group of products with higher demand in refineries are the aromatics, in particular BTX. The need for BTX is expected to increase approximately 10 %, and for the decade from 1999 to 2009, the demand increased approximately 25 MMT (25 million metric tons). Just for benzene this increase in demand is approximately 1.3 MMT/year for this decade (~13 MMT for the entire decade of 1999–2009). Benzene is mainly used for the production of styrenics, phenolics, and cyclohexane products. On the basis of price and demand forecasting, refiners may adjust their products to meet the demand. In general, new processes must be flexible so that the design is appropriate for local, regional, and global market demand and values. For example, the global ratio of benzene to *p*-xylene is approximately 0.5 whereas in the Middle East this ratio of demand could vary from 1 to 2 [93].

Chemical Market Associates, Inc. (CMAI), which is based in Houston, TX, presents yearly market analysis, supply, and demand as well as forecasting, trade patterns, pricing relationships, production economics, and technology for major chemicals—in particular petrochemicals. The recent volatility in global economics and the dynamic fluctuations in energy prices have had a significant effect on the petrochemical value chain. According to their analysis, the Middle East and China continue with major capacity expansions, impacting prices, producer margins, and global operating rates. Between 2008 and 2009 there was a transition in supply/demand for polyethylene as recent investments in the Middle East and China began to affect the market. The prices of such products have recently been at historical highs and had positive effects on producer margins. Regional economics also influence operating costs, trade flow, and producer margins. Iran is also enhancing its polyethylene market, which is likely to increase the production and export of polyolefins from the Middle East to Asia, West Europe, and eventually the Americas. Plastic finished products will continue to flow out of China to the United States, Europe, and Japan. Other developing economies such as India, the Middle East, Central Europe, and Russia will participate in the trade of finished products. The Middle East in particular is seeking international investors to build manufacturing facilities for such finished products for export [94]. Domestic unemployment in Middle Eastern countries is on the rise, and new industry intends to overcome this problem in the future.

With limited natural hydrocarbon resources, the industry should perhaps focus on the development of efficient methods to convert biofeedstocks such as oils from plants and algae, grease, and waste products into high-quality fuels and products without serious environmental and economical impact on the existing infrastructure. Some chemical companies have developed a new process that deoxygenates various kinds of biofeedstocks by adding hydrogen to produce a highly stable green diesel fuel with a higher cetane value, lower cloud point, and lower emissions than biodiesel and traditional petrodiesel fuels. For example, the cetane number of green diesel is in the range of 75–90 whereas the cetane number of petrodiesel is in the range of 40–55 and that of biodiesel is in the range of 50–65. Green diesel also has excellent stability to oxidation in comparison with other types of diesels. Green diesel is indistinguishable from traditional diesel, can work in existing petrodiesel engines, and can be blended in any proportion with biodiesel or traditional petrodiesel. They claim that green diesel offers superior cold-flow properties that make it suitable for very cold climate conditions. In addition, green diesel has a higher energy per volume and reduces the emission of greenhouse gases and NO_x into the environment. Likewise, other types of green fuels show major advantages over traditional petrofuels. Green jet fuels produced from renewable biofeedstocks should meet the major specifications set for jet fuels, which are a freezing point of –47°C and a flash point of 38°C [90].

During approximately the past decade, some major refineries in Europe began renovations by retiring some units and adding new ones. For example, for a Shell operating refinery in the Netherlands, major units added included FCCs, thermal crackers, a hydrofloric acid (HF) alkylation unit, and hydrodesulfurization (HDS) units. The major objectives from such renovations were tightening environmental regulations governing SO_2, NO_x, catalyst fines and oil in water, stricter product quality requirements by the market, and shifting the product yield pattern away from motor gasoline, cycle oils, and fuel oil toward light olefins, naphtha, and middle distillates. Moreover, Shell saw the potential to improve profits by increasing manpower efficiency, modernizing operations by installing state-of-the-art advanced process control strategies, and increasing conversion from a cheaper (heavier) crude package by adding hydrocracking and gasification units. They found some advantages in hydrocracking units over an FCC unit. A hydrocracker unit is capable of producing gasoline with less sulfur and olefin whereas gasoline produced from FCC has more sulfur and olefins. In addition, a hydrocracker unit has the flexibility of maximizing production of either gasoline or diesel fuel, depending on the market conditions. Shell has designed a gasification unit over a steam methane reforming (SMR) process to produce hydrogen because gasification does reduce fuel oil production. The new units also significantly reduced SO_2 emissions into the atmosphere [95]. There is apparently a surplus of petroleum coke in a few parts of the world. Thus, the integrated gasification combined cycle (IGCC) would be an obvious route to follow because of its flexibility, higher thermal efficiency, and much better environmental performance compared with other combustion technologies [96–98]. IGCC is a combination of two leading technologies: clean-burning syngas (i.e., coal gasification) and an efficient method of producing electricity (combined cycle). IGCC is an advanced technology that represents the cleanest process for conventional coal-based power generation systems that includes high efficiencies (30–40 %), lower emissions (~10 %), and better product or byproducts for transport fuels, even for fuel cells.

In summary, the most advanced and profitable refineries are those that can take the cheapest and heaviest crude oil and convert it into the lightest products with almost no residue or heavy product. Refineries must be safe, economical, and environmentally friendly. Research and development in the petroleum industry can play a significant role in achieving the ultimate goals. For example, by developing a new catalyst for the desulfurization process one can perform several processes in one step, reducing significant operational and capital costs [99]. In another example, replacement of catalyst in the FCC unit of a refinery in Thailand caused production of more propylene through the deep catalytic cracking (DCC) process. Using DCC also increases refinery margin in comparison with a traditional FCC plant [100]. The efficiency of FCC units can be further improved by adding specially developed additives to further the cracking of bottom products, yielding more middle distillates from FCC. Although catalysts are very expensive and costly for refiners, by selecting the right catalysts for refinery processes many further expenses caused by unscheduled shutdown can be prevented, resulting in an overall improvement of refinery margins. The catalysts must be tested, selected, and monitored continuously during the operations.

Another study shows that by advancing the online control system in a refinery in Texas City, TX (operated by Marathon), payout can be achieved within only 6 weeks. The results of such control systems are reducing product quality variability or process variability and operating closer to product quality limits or process constraints. The inferred-property controls reduced quality variability by 46 % [101].

Managing major oil companies is also a challenge for future industry. As the globalization process takes shape, oil companies are merging together to survive tight competition. However, restructuring and cost-cutting—even re-engineering—may not be enough to ensure survival of a major oil company in the 21st century. Oil companies must think of themselves not as an oil company but as an energy company, providing products to satisfy their customers. Companies that fail to adapt to changing times and conditions and that fail to restructure their efforts in terms of their future customers and markets will fall by the wayside. Future oil companies must provide returns to their shareholders that are commensurate with risks. They must be an efficient and highly decentralized company in which all segments operate as autonomous entities. A future oil company will have fewer employees, perhaps as little as one third of its professional personnel today [102].

In the last few decades we have seen dramatic advances in computer and communication technology. In the United States today, there are more people employed by the computer industry than all transportation sectors (airlines, railroads, etc.). Refineries of the future must adapt to new technologies, especially by computerization of the whole industry. Factors that affect new and future refineries over time are finances, technology, people/organization, business, and environment. The refinery business has been always a global business (with total of ~$125 billion), and refineries are in competition worldwide. Regardless of government regulations, future refineries should have safe operations with fewer explosions, fires, spills, etc. as well as fewer environmentally undesirable emissions. A refinery should also meet the future environmental plan, and it should be economical. As the business, process, and equipment models advance in coming years we can manage the market, plant, and organization. For a refinery to be competitive in the 21st century it must develop programs for new technologies in the most cost-effective way. The key should be training, planning, and implementation [103].

Major companies are faced with swift changes in the business environment and toward the international and global market. Information technology plays a key role because it represents a real answer to companies' and organizations' needs for operational efficiency and high-quality products. Information technology can provide solutions to companies' technological and product needs. Environmental, health, and safety regulations have increased refinery capital costs in the United States by nearly 50 %, giving advantage to those refineries located in countries without strict regulations [104].

Although the current prices of gasoline and other middle distillates are 50–60 % higher than crude oil prices, the price of some petrochemicals such as *p*-xylene or petroleum resins are approximately 3 times that of crude prices. This suggests that future refineries may be used to produce more petrochemicals and feedstocks rather than fuels for vehicles. Integration of refineries and petrochemicals is also an attractive objective being considered by some companies to add more value to crude and return on investments. Despite the current world economy slowdown and drop in oil prices, the price of hydrocarbons (oil and gas) will increase in the future. Some of the major gas-producing countries (Russia, Iran, Qatar, and Algeria) are in negotiations to form a cartel similar to OPEC (Organization of Petroleum Exporting Countries) to have better control of the world hydrocarbon market. Oil demand is expected to increase at an annual rate of approximately 1.5 % in the coming years, and this requires an increase in refining capacity of approximately 10–12 million bbl/year by 2015. With limited oil reserves, it is expected that the processing of other types of hydrocarbon fuels such as natural gas, heavy oil, extra-heavy nonconventional oils such as oil shale and oil sand (tar sand or bituminous sand), and coal will increase in the future to complement the conventional crude oil supply. At the same time, many governments in industrialized countries encouraged by recent high oil prices are taking some bold actions to make more use of other forms of energy produced from nuclear, wind, solar, and hydro sources in addition to biomaterial resources. However, within the next few decades contribution of wind and solar renewable energies will remain less than 3 % of world energy consumption. Another scenario in less dependency on fossil fuels will be the development of new technologies in the automobile industry. Some automaker companies in the United States and China encouraged by high oil prices are working toward the manufacture of electric cars. It is expected that China's BYD company, located in Shenzhen (South China), will launch its first electric cars into the U.S. market by 2013. These cars (EVs) are priced at approximately $22,000 and will work using batteries that are charged by an AC adapter in seven hours. These batteries can run the cars up to 60 miles (~100 km) and have a small gasoline engine backup. China has given strong support for the use of electric vehicles but the safety of the batteries used in such vehicles remain of major concern to users.

In this century, the main growth in petroleum refining and petrochemicals will be concentrated in Asia and the Pacific, particularly China and India, with their rapid economic development and rising demand; the Middle East with its huge oil and gas reserves; and the countries of the former Soviet Union, especially Azerbaijan, Turkmenistan, and Kazakhstan. The major challenges of the global refining industry can be summarized as more deep conversion technologies, regulations (product quality and environmental standards), and changes in the market with the Asia/Pacific region. Therefore, the potential areas for refining growth are processing effectively heavier and sourer crude and concurrent integration of different refinery streams. In the market, sweeter crude oil from the North Sea will be replaced with more sour crude from the Middle East. The refining industries in the Middle East, South and Central Americas, Eastern Europe, and the former Soviet Union need major investments to meet the challenges of environmental requirements. Worldwide petroleum refining industry margins are minimal, and the low margins are attributed to the steadily increasing cost of feedstocks and weaker product costs. The sectors of international oil companies that are able to balance losses are on the downstream side with petrochemical profits. Applications of information technology and company movement toward an information-based organization are seen as keys to profitability and survival. Technical and engineering documentation is one of the key assets in the refining industry. Refineries are entities within major oil companies, and the strategies come from the oil company headquarters and not from refinery management. The optimized planning results determine the refinery's objectives and production plans. Computer simulation may be used to monitor the environment surrounding the refinery and to detect, control, and prevent any potential critical situation [104].

Another scenario sparked by surging oil, a dramatic rise in the value of old plastic, is encouraging waste companies across the world to dig for buried riches in rotting rubbish dumps. Long a symbol of humanity's throwaway culture, existing landfill sites are now being viewed as mines of potential, which as the world population grows could also help reinforce the planet's dwindling natural resources. Over many decades there has been a policy of burying whatever we can in a landfill site; therefore, there are valuable resources in those sites. And wherever there are valuable resources, there is always the temptation to investigate if it is worth recovering them. The logic is sound, but the practicalities are complex, and one has to balance those out with the commercial viability according to experts in the field [105].

33.8 CONCLUDING REMARKS

Most of what has been discussed in this chapter is well known—the vast majority of the fuels presented were available dating back at least 50 years. The deciding factors that led to the environmental issues were mostly man-made. However, awareness of what the appropriate actions were was limited. In the 21st century we already have plenty of pollution or global warming (because of the greenhouse gas emissions) and still we are looking for better-quality energy fuel. Oil will still remain the principal source of liquid motor fuel for a long time. Fossil-fuel refining technologies are currently on the boom toward heavy or extra-heavy (bitumen) petroleum. The superior process technologies, catalyst formulations, and their combined effect on product selectivity and on clean fuel are the prime goals for refiners to achieve, which may compensate to some extent for the effect of crude oil prices compared with alternative fuels. The development of process technologies for upgrading heavy feeds will be necessary in view of the growing demand of lighter fractions and the increasing need for new-generation processes. Catalytic conversion of heavy feeds is in strong competition with thermal and other alternative fuel processes.

Moreover, approximately 20 years ago the scenario of fossil fuel reserves running out encouraged governments to promote alternative energy resources (e.g., biomass, fuel cells, and hydrogen fuels) that decrease exhaust emission gas. The share of gas will gradually increase, and hydrogen is proposed to play an important part as an energy carrier whereas the use of biomass will develop, but at a modest level. New techniques for testing are being developed for fossil gases, along with their consequences such as GTL, BTL, and even CTL, with a view to cutting costs and providing better environmental concerns. Biofuel corresponds to a small but substantial way of breaking total reliance on fossil fuels. It is environmentally friendly because its combustion emission gases are nontoxic and extremely biodegradable.

The petroleum (both oil and gas) industry is a complex industry and is becoming even more complex than before with respect to environmental and economical constraints. In addition, the amount of oil and gas remaining in reserves is decreasing faster than before as demand is increasing and resources are diminishing. In summary, refineries of the future will be more technology-based industries with more valuable products. The objective of this book was to provide a new resource covering all subjects of importance for those who are involved in this industry. However, the data presented on the amount of oil and gas reserves vary from one source to another, but they provide us a general picture of how many hydrocarbon resources remain or how long they will last. This book presented the most recent advances and data regarding processing techniques, economic issues, environmental considerations, product quality and specifications, market demand and forecasting, management of the industry, and international import/export and regulations by experts in the field. In addition, alternative and possible future forms of fuel (i.e., hydrogen and biofuels) and their manufacturing and economy were also discussed. We hope this reference will contribute to the main goal of the industry to use the remaining hydrocarbon resources in the most economical and environmentally sound ways.

REFERENCES

[1] Ancheyta, J., and Speight, J.G., Eds., *Hydroprocessing of Heavy Oils and Residua*, Taylor & Francis, New York, 2007.

[2] Furimsky, E., "Catalyst for Upgrading Heavy Petroleum Feeds," in *Studies Surface Science and Catalysis*, Vol. 169, Elsevier, New York, 2007.

[3] "Price Records, Violence and Dollar Weakness," *Oil & Energy Trend*, Vol. 33 (4), 2008, http://onlinelibrary.wiley.com/journal/10.1111/(ISSN)1744-7992/issues.

[4] "World Energy Outlook, 2008," http://www.iea.org/textbase/nppdf/free/2008/weo2008.pdf.

[5] Zhang, F., Fan, X., and Ding, J., "Field Experiment of Enhancing Heavy Oil Recovery by Cyclic Fuel Gas Injection," in *Proceedings of the International Oil and Gas Conference and Exhibition in China, IOGCEC*, 2000, pp. 527–535.

[6] Davies, R., "Gas to Liquids (Fischer Tropsch Diesel) Supply and Economics," paper presented at the *Shell Gas and Power Alternative Diesel Fuels Symposium*, August 19–20, 2003.

[7] Rahimpour, M.R., and Elekaei, H., "A Comparative Study of Combination of Fischer-Tropsch Synthesis Reactors with Hydrogen-Perm Selective Membrane in GTL Technology," *Fuel Process. Technol.*, Vol. 90, 2009, pp. 747–761.

[8] van Vliet, O.P.R., Faaij, A.P.C., and Turkenburg, W.C., "Fischer-Tropsch Diesel Production in a Well-to-Wheel Perspective: A Carbon, Energy Flow and Cost Analysis," *Energy Convers. Manage.*, Vol. 50, 2009, pp. 855–876.

[9] Henrich, E., Dahmen, N., and Dinjus, E., "Cost Estimate for Biosynfuel Production via Biosyncrude Gasification," *Biofuels, Bioproducts, Biorefining*, Vol. 3, 2009, pp. 28–41.

[10] U.S. Energy Information Administration, "Petroleum and Other Liquids," 2008, http://www.eia.doe.gov/oil_gas/petroleum/info_glance/petroleum.html.

[11] U.S. Department of Energy (DOE), *Clean Cities Alternative Fuel Price Report: Energy Efficiency and Renewable Energy*, DOE, Washington, DC, 2007, http://www.afdc.energy.gov/afdc.

[12] Bauer, G., *De Natura Fossilium*, translated 1955, M.C. Bandy and J.A. Bandy, Trans., Mineralogical Society of America, New York, 1546.

[13] Zayn, B., "The Oil Weapons," *Saudi Aramco World*, January-February, 1995, pp. 20–27.

[14] Riva, J.P. Jr., and Gordon, I.A., "Petroleum," *Encyclopedia Britannica* (accessed June 30, 2008).

[15] de la Rue du Can, S., and Price, L., "Sectoral Trends in Global Energy Use and Greenhouse Gas Emissions," *Energy Policy*, Vol. 36, 2008, pp. 1386–1403.

[16] Starr, C., Searl, M.F., and Alpert, S., "Energy Sources: A Realistic Outlook," *Science*, Vol. 256, 1992, pp. 981–987.

[17] Lovejoy, D., "Some Current Trends in Renewable Energy for Developing Countries," *Renewable Energy*, Vol. 5, 1994, pp. 215–224.

[18] Bowman, M., Hilligoss, D., Rasmussen, S., and Thomas, R., "Bio-diesel: A Renewable and Biodegradable Fuel," *Hydrocarbon Processing*, February, 2006, pp. 103–106.

[19] Yang, C.W., Hwang, M.J., and Huang, B.N., "An Analysis of Factors Affecting Price Volatility of the US Oil Market," *Energy Econ.*, Vol. 24, 2002, pp. 107–119.

[20] Awerbuch, S., and Sauter, R., "Exploiting the Oil-GDP Effect to Support Renewables Deployment," *Energy Policy*, Vol. 34, 2006, pp. 2805–2819.

[21] Menegaki, A., "Valuation for Renewable Energy: A Comparative Review," *Renew. Sustain. Energy Rev.*, Vol. 12, 2008, pp. 2422–2437.

[22] Aguilera, R.F., and Aguilera, R., "Assessing the Past, Present, and Near Future of the Global Energy Market," *J. Petrol. Technol.*, Vol. 60, 2008, pp. 36–39.

[23] Odell, P. R., "Global Energy Market in the Long Term: The Continuing Dominance of Affordable Non-Renewable Resources," *Energy Explor. Exploit.*, Vol. 18, 2000, pp. 131–145.

[24] Asche, F., Gjlberg, O., and Völker, T., "Price Relationships in the Petroleum Market: An Analysis of Crude Oil and Refined Product Prices," *Energy Econ.*, Vol. 25, 2003, pp. 289–301.

[25] Riazi, M.R., *Characterization and Properties of Petroleum Fractions*, 1st ed., ASTM International, West Conshohocken, PA, 2005.

[26] Speight, J.G., *The Chemistry and Technology of Petroleum*, 4th ed., CRC Taylor & Francis Group, Boca Raton, FL, 2006.

[27] Ancheyta J., Trejo, F., and Rana M.S., *Asphaltenes: Chemical Transformation during Hydroprocessing of Heavy Oils*, Taylor & Francis, New York, 2009.

[28] Dickie, J.P., and Yen, T.F., "Macrostructures of the Asphaltic Fractions by Various Instrumental Methods," *Anal. Chem.*, Vol. 39, 1967, pp. 1847–1852.

[29] Tynan, E.C., and Yen, T.F., "General Purpose Computer Program for Exact ESR Spectrum Calculations with Applications to Vanadium Chelates," *J. Magn. Reson.*, Vol. 3, 1970, pp. 327–335.

[30] Merdrignac, I., and Espinat, D., "Physicochemical Characterization of Petroleum Fractions: The State of the Art," *Oil Gas Sci. Technol.*, Vol. 62, 2007, pp. 7–32.

[31] Ancheyta, J., Rana, M.S., and Furimsky, E., "Hydroprocessing of Heavy Petroleum Feeds: Tutorial," *Catal. Today,* Vol. 109, 2005, pp. 3–15.

[32] Rana, M.S., Maity, S.K., and Ancheyta, J., "Maya Heavy Crude Oil Hydroprocessing Catalysts," in *Hydroprocessing of Heavy Oil and Residua*, J. Ancheyta and J.G. Speight, Eds., Taylor & Francis, New York, 2007, pp. 191–238.

[33] Ramírez, J., Rana, M.S., and Ancheyta, J., "Characteristics of Heavy Oil Hydroprocessing Catalysts," in *Hydroprocessing of Heavy Oils and Residua*, J. Ancheyta and J.G. Speight, Eds., Taylor & Francis, New York, 2007, pp. 121–190.

[34] Ancheyta, J., and Rana, M.S., "Future Technology in Heavy Oil Processing," in *Encyclopedia of Life Support Systems (EOLSS)*, Eolss Publishers, Oxford, UK, 2008.

[35] Ancheyta, J., "Reactors for Hydroprocessing," in *Hydroprocessing of Heavy Oils and Residua*, J. Ancheyta and J.G. Speight, Eds., Taylor & Francis, New York, 2007, pp. 71–120.

[36] Rana, M.S., Samano, V., Ancheyta, J., and Diaz, J.A.I., "A Review of Recent Advances on Process Technologies for Upgrading of Heavy Oils and Residua," *Fuel*, Vol. 86, 2007, pp. 1216–1231.

[37] Russell, G., "A Famed Dry Hole Gets a Second Shot," *Wall Street Journal*, July 21, 2008, pp. B1–B2.

[38] Kurimura, H., Rochelle, G.T., and Sepehrnoori, K., "Expert System to Select Acid Gas Treating Processes for Natural Gas Processing Plants," *Gas Separ. Purif.*, Vol. 7, 1993, pp. 151–158.

[39] Ohlrogge, K., Wind, J., and Brinkmann, T., "Membrane Technology for Natural Gas Processing," in *SPE Proceedings—Gas Technology Symposium*, April 30–May 2, 2002, Calgary, Canada, pp. 63–68.

[40] Baker, R.W., and Lokhandwala, K., "Natural Gas Processing with Membranes: An Overview," *Ind. Eng. Chem. Res.*, Vol. 47, pp. 2109–2121.

[41] Fischer, F., and Tropsch, H., "Über die Reduktion des Kohlenoxyds zu Methan am Eisenkontakt under Druck," *Brennstoff-Chemie*, Vol. 4, 1923, pp. 193–197.

[42] Fischer, F., and Tropsch, H., German patent 484,337, July 22, 1925.

[43] de Klerk, A., "Fischer-Tropsch Refining: Technology Selection to Match Molecules," *Green Chem.*, Vol. 10, 2008, pp. 1249–1279.

[44] de Klerk, A., "Can Coal-to-Liquids Be Clean? Improvements in Carbon Efficiency That Are Paving the Way," presented at the *Golden Research Conferences on Green Chemistry*, August 3–8, 2008, Bates College, Lewiston, ME.

[45] Bromfield, T.C., and Vosloo, A.C., "Recent Advances in the Development of Fischer-Tropsch Catalysts at Sasol," presented at the *Macromolecular Symposia*, No. 193, 2003, pp. 29–34.

[46] Dry, M.E., "The Fischer-Tropsch Process: 1950-2000," *Catal. Today*, Vol. 71, 2002, pp. 227–241.

[47] Lee, W., Maziuk, J., Weekman V.W. Jr., and Yurchak, S., "Mobil Methanol-to-Gasoline Process," *Chem. Eng. Mono.*, Vol. 10, 1979, pp. 171–190.

[48] Marcilly, C., "Present Status and Future Trends in Catalysis for Refining and Petrochemicals," *J. Catal.*, Vol. 216, 2003, pp. 47–62.

[49] Trejo, F., Rana, M.S., and Ancheyta, J., "Thermogravimetric Determination of Coke from Asphaltenes, Resins and Sediments and Coking Kinetics of Heavy Crude Asphaltenes," *Catalysis Today*, Vol. 150, 2010, pp. 272–278.

[50] Courty, Ph., Chaumette, P., and Raimbault, C., "Synthetic or Reformulated Fuels: A Challenge for Catalysis," *Oil Gas Sci. Technol.*, Vol. 54, 1999, pp. 357–363.

[51] Lifschultz, D.K., "Heavy Oil Upgrading Enhances Profit Streams," *American Oil and Gas Reporter,* January, 2006, pp. 135–141, http://www.genoil.net/GHU_story.htm.

[52] Headwaters Heavy Oil, "HCAT™ Technology: Innovative Process & Catalyst for Heavy Oil Upgrading," http://www.htigrp.com/data/upfiles/pdf/HCAT%206.07.pdf.

[53] Veith, E.J., "Performance of a Heavy-to-Light Crude Oil Upgrading Process," *J. Petrol. Technol.*, December, 2007, pp. 48–53, http://www.ivanhoeenergy.com/index.php?page=htl_process_overview.

[54] Ancheyta, J., Betancourt, G., Marroquin, G., Centeno, G., Muñoz, J.A.D., and Alonso F., Process for the Catalytic Hydrotreatment of Heavy Hydrocarbons of Petroleum, U.S. 2007187294 (Appl. number US20030563577 20030709), 2007.

[55] Chevron, "Isocracking," http://www.chevron.com/products/sitelets/refiningtechnology/isocracking_2a.aspx.

[56] Toulhoat, H., Hudebine, D., Raybaud, P., Guillaume, D., and Kressmann S., "Thermidor: A New Model for Combined Simulation of Operations and Optimization of Catalysts in Residues Hydroprocessing Units," *Catalysis Today*, Vol. 109 (1–4), 2005, pp. 135–153.

[57] Stanislaus, A., Marafi, A., and Rana, M.S., "Recent Advances in the Science and Technology of Ultra Low Sulfur Diesel (ULSD) Production," *Catalysis Today*, Vol 153, 2010, pp. 1–68.

[58] Schobert, H.H., and Song, C., "Chemicals and Materials from Coal in the 21st Century," *Fuel*, Vol. 81, 2002, pp. 15–32.

[59] ENI Innovation and Technology: Total Conversion of the Barrel, http://www.eni.com/en_IT/innovation-technology/technological-answers/total-conversion-barrel/total-conversion-barrel.shtml.

[60] Topsøe, H., Clausen, B.S., and Massoth, F.E., *Hydrotreating Catalysis Science and Technology*, Vol. 11, J.R. Anderson and M. Boudart, Eds., Springer-Verlag, Berlin, 1996.

[61] Pappal, D.A., Plantenga, F.L., Tracy, W.J., Bradway, R.A., Chitnis, G., and Lewis, W.E., "Stellar Improvement in Hydroprocessing Catalyst Activity," presented at the NPRA, Annual Meeting, March 23–25, 2003, San Antonio, TX.

[62] Mayo, S., Brevoord, E., Gerritsen, L., and Plantenga, F., "Process Ultra-Low Sulfur Diesel," *Hydrocarbon Process.*, Vol. 80, 2001, p. 84-A.

[63] Mayo, S., Plantenga, F., Leliveld, B., and Miyauchi, Y.A., "Elegant Solutions for Ultra Low Sulfur Diesel," in *Proceedings of the NPRA 2001 Annual Meeting*, March 18–20, 2001, New Orleans, LA, Paper AM-01-09.

[64] Topsoe, H., Knudsen, K.G., Skyum, L., and Copper, B.H., "ULSD with BRIM Catalyst Technology," in *Proceedings of the NPRA 2005 Annual Meeting*, March 13–15, 2005, San Francisco, CA, pp. 16–21.

[65] Oliveira, A.C., "The Energy Shift: Towards a Renewable Future," *Int. J. Low Carbon Technol.*, Vol. 2, 2002, pp. 289–299.

[66] Pimentel, D., "Limits of Biomass Utilization," in *Encyclopedia of Physical Science and Technology*, New York: Academic Press, 2002, pp. 159–171.

[67] Keeney, D.R., and DeLuca, T.H., "Biomass as an Energy Source for the Midwestern U.S." *Am. J. Alt. Ag.*, Vol. 7, 1992, pp. 137–143.

[68] Crutzen, P.J., Mosier, A.R., Smith, K.A., and Winiwarter W., "N_2O Release from Agro-Biofuel Production Negates Global Warming Reduction by Replacing Fossil Fuels," *Atmos. Chem. Phys.*, Vol. 8, 2008, pp. 389–395.

[69] Bullis, K., "Large-Scale, Cheap Solar Electricity," *Technology Review (Published by MIT)*, June 23, 2006.

[70] "Hydrocarbon Processing," May 1, 2006, 85(5), pp. 38. (Perstorp Oxo Uses Axens Biodiesel Technology, *Focus on Catalysts*, 7, July 2006, pp. 5.)

[71] Hearn K., "Ethanol Production Could Be Eco-Disaster, Brazil's Critics Say," *National Geographic News*, February 8, 2007.

[72] Roach J., "Global Warming 'Very Likely' Caused by Humans, World Climate Experts Say," *National Geographic News*, February 2, 2007.

[73] Gallezot, P., "Process Options for the Catalytic Conversion of Renewables into Bio-products," in *Catalysis for Renewables From Feedstock to Energy Production*, G. Centi and R.A. van Santen, Eds., Wiley-VCH, Weinheim, Germany, 2007.

[74] Huber, G.W., Iborra, S., and Corma, A., "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," *Chem. Rev*. 2006, Vol. 106, pp. 4044–4098.

[75] Bradshaw, C.J.A., Sodhi, N.S., Peh, K.S.-H., and Brook, B.W., "Global Evidence That Deforestation Amplifies Flood Risk and Severity in the Developing World," *Global Change Biol.*, 2007, Vol. 13, pp. 2379–2395.

[76] Haber, W., "Energy, Food, and Land—The Ecological Traps of Humankind," *Environ. Sci. Pollut. Res.*, Vol. 14, 2007, pp. 359–365.
[77] Borlaug, N., "Feeding a Hungry World," *Science*, Vol. 318, 2007, p. 359.
[78] Shapouri, H., Duffield, J.A., and Wang, M., "The Energy Balance of Corn Ethanol: An Update, United States Department of Agriculture," *Agricultural Economic Report Number 813*, U.S. Department of Agriculture, Washington, DC, 2002.
[79] Ho, S.P., "Global Warming Impact of Ethanol Versus Gasoline," presented at the 1989 National Conference, "Clean Air Issues and America's Motor Fuel Business," Washington DC, October, 1989.
[80] Pimentel, D., "Ethanol Fuels: Energy Security, Economics, and the Environment," *J. Ag. Environ. Ethics*, Vol 4, 1991, pp. 1–13.
[81] Keeney, D.R., and DeLuca, T.H., "Biomass as an Energy Source for the Midwestern U.S," *Am. J. Alt. Ag.*, Vol. 7, 1992, pp. 137–143.
[82] Cascone, R., "Bio-Fuels: What Is Beyond Ethanol and Biodiesel?" *Hydrocarbon Processing*, September, 2007, pp. 95–109.
[83] Mohamed, M.S., "Modified Hybrid Power Cycle for Better Efficiency and Less Pollution Levels," *J. Eng. Appl. Sci.*, Vol. 48, 2001, pp. 309–328.
[84] Zhao, H., and Burke, A.F., "Optimization of Fuel Cell System Operating Conditions for Fuel Cell Vehicles," *J. Power Sources*, Vol. 186, 2009, pp. 408–416.
[85] Mueller, F., Jabbari, F., and Brouwer, J., "On the Intrinsic Transient Capability and Limitations of Solid Oxide Fuel Cell Systems," *J. Power Sources*, Vol. 187, 2009, pp. 452–460.
[86] Birkle, S., Kircher, R., Nolscher, C., and Voigt, H., "Electric Drives. Toward a Cost-Effective Alternative to the Internal Combustion Engine," *Siemens Rev.*, Vol. 61, 1994, pp. 27–32.
[87] Awerbuch, S., "Investing in Photovoltaics: Risk, Accounting and the Value of New Technology," *Energy Policy*, Vol. 28, 2000, pp. 1023–1035.
[88] Awerbuch, S., Carayannis, E., and Preston, A., "The Virtual Utility: Some Introductory Thoughts on Accounting, Learning and the Valuation of Radical Innovation," in *The Virtual Utility: Accounting Technology and the Emerging Industry*, S. Awerbuch and A. Preston, Eds., Kluwer Academic Publishers, Boston, 1997.
[89] Borg, X., "Aquafuel™ Generator," Blaze Labs Research, http://www.blazelabs.com/n-aquagen.asp.
[90] Universal Oil Products, Inc. (UOP), Des Plaines, IL, 2008, http://www.uop.com/processing-solutions/refining/.
[91] Universal Oil Products, Inc. (UOP), Seminar Presentations, Kuwait, November 19, 2005, http://www.uop.com/middle-east-lpg-growth-driving-petrochemical-developments-region/.
[92] Poparad, A., Ellis, B., Glover, B., and Metro, S., "Reforming Solutions for Improved Profits in an Up-Down World," in *Proceedings of the NPRA 2011 Annual Meeting*, March 24, 2011, San Antonio, Paper AM-11-59.
[93] Al-Khattaf, S., Akhtar, M.N., Odedairo, T., Aitani, A., Tukur, N.M., Kubu, M., Musilova-Pavlackova, Z., and Cejka, J., "Catalytic Transformation of Methyl Benzenes over Zeolite Catalysts," *Applied Catalysis* A: Gen.l 394, 2011, pp. 176–190.
[94] Chemical Market Associates, Inc. (CMAI), Houston, TX, 2008, http://www.cmaiglobal.com.
[95] Rhodes, A.K., "Dutch Refinery Nears Completion of Major Renovation," *Oil & Gas Journal*, March 17, 1997, pp. 60–67.
[96] Gnanapragasam, N., Reddy, B., and Rosen, M., "Reducing CO_2 Emissions for an IGCC Power Generation System: Effect of Variations in Gasifier and System Operating Conditions," *Energy Convers. Manage.*, Vol. 50, 2009, pp. 1915–1923.
[97] Schmoe, L. A., Tam, S. S., Walters, A. B., and Weber, W., "Enhancement of IGCC through Clean By-Product Fuel Coproduction," in *Proceedings of the American Power Conference*, Vol. 53, 1991, pp. 726–731.
[98] Akimoto, K., Tomoda, T., and Fujii, Y., "Development of a Mixed Integer Programming Model for Technology Development Strategy and Its Application to IGCC Technologies," *Energy*, Vol. 30, 2005, pp. 1176–1191.
[99] Dercy J., "New Technology Appears to Perform Several Processes in One Step," *Oil & Gas Journal*, Vol. 95, March 17, 1997, pp. 80–84.
[100] Fu, A., Hunt, D., Boonilla, J.A., and Batachari, A., "Deep Catalytic Cracking Plant Produces Propylene in Thailand," *Oil & Gas Journal*, June 12, 1998, pp. 49–52.
[101] Bullerdiek, E.A., and Hobbs, J.W., "Advanced Controls Pay Out in 6 Weeks at Texas Refinery," *Oil & Gas Journal*, September 19, 1995, pp. 46–52.
[102] Carroll, P.G., "How Oil Companies Must Adapt to Survive in 2000 and Beyond," *Oil & Gas Journal*, November 20, 1995, pp. 34–36.
[103] Riazi, M.R., and Roomi, Y.A., "General Refinery Knowledge," Booknote Materials Prepared for an Industrial Course, Kuwait National Petroleum Company (KNPC), Kuwait, 2001.
[104] An introductory note by Infopetroleum, Chapter 15 of "General Refinery Knowledge" of reference [9].
[105] Al-Salem, S.M., Lettieri, P., and Baeyens, J., 2009, "Recycling and Recovery Routes of Plastic Solid Waste (PSW): A Review," *Waste Management*, Vol. 29, 2009, pp. 2625–2643.

Index

M. R. Riazi

Dr. M. R. Riazi is currently a Professor of Chemical Engineering at Kuwait University. He was previously an Assistant Professor at Pennsylvania State University (USA), where he also received his MS and PhD. He was also a visiting professor at various universities in the U.S., Canada, Europe and the Middle East. He has been consultant and invited speaker to more than 50 oil companies and research institutions in Canada, the U.S., Europe, India, China, Malaysia, Australia, the Middle East and North Africa, including invited speaker to the World Economic Forum. He is the author/co-author of more than 100 publications, including three books mainly in the areas of petroleum and chemical technology. He is the founding and Editor-in-Chief of IJOGC and an associate editor of some other international journals. He was awarded a Diploma of Honor from the National (American) Petroleum Engineering Society, as well as teaching and research awards from various universities. He is a member of AIChE and the Research Society of North America. (www.RiaziM.com)

Semih Eser

Semih Eser is a Professor of Energy and Geo-Environmental Engineering at Penn State University. He received his B.S. and M.S. degrees in Chemical Engineering from Middle East Technical University in Ankara, Turkey and his Ph.D. in Fuel Science from Penn State University. Professor Eser teaches courses on petroleum refining and energy engineering at John and Willie Department of Energy and Mineral Engineering and directs the Carbon Materials Program at the EMS Energy Institute at Penn State. He has served as Program Chair, Chair, and Councilor in the Fuel Chemistry Division of the American Chemical Society and as member of the Advisory Committee of the American Carbon Society.

Suresh S. Agrawal

Dr. Suresh S. Agrawal is founder and president of Offsite Management Systems LLC (www.globaloms.com) and has developed and installed innovative and technologically advanced automation software products, and integrated solutions for the automation of offsite operations of Chemical, Oil and Gas (COG) Industries. Dr. Agrawal has 25+ years of experience at senior positions with companies, including being Director of Refinery Offsite Operations at ABB Industrial Systems, Inc., Houston, Texas. He worked earlier with reputable companies such as 3X Corporation and Exxon Corporation in New Jersey. Dr. Agrawal has successfully managed many advanced offsite refinery control projects in numerous countries. He has a doctorate degree (Ph.D.) in Chemical Engineering from the Illinois Institute of Technology, Chicago, and a Bachelors Degree in Chemical Engineering from Indian Institute of Technology (I.I.T.), Mumbai, India. He has published more than 20 technical papers in the area of refinery offsite automation.

José Luis Peña Díez

José Luis Peña Díez is a consultant at the Technology Center at Repsol in Madrid, Spain. His professional activity includes more than twenty years of experience leading and participating in research projects in upstream and downstream petroleum technologies.

Following his studies in chemical sciences at the Complutense University of Madrid, he collaborated with universities and academic institutions to coordinate activities in the areas of chemical engineering and special process simulation. He is currently a part-time associate professor in chemical engineering at the Rey Juan Carlos University of Madrid.

Peña Díez is the author of forty technical articles and presentations at international conferences in the fields of petroleum fluids characterization, process engineering and control, and process simulation, areas in which his expertise contributed to this book.

www.astm.org

ISBN: 978-0-8031-7022-3
Stock #: MNL58