Alcohols and Ethers

A Technical Assessment of Their Application as Fuels and Fuel Components

API PUBLICATION 4261
THIRD EDITION, JUNE 2001

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Downstream Segment

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FOREWORD

This publication was prepared by a task force of the Fuels Committee, a committee of the API Downstream Segment. Dr. Robert Barter and Dr. Bruce Bauman of API's Regulatory and Scientific Affairs Department assisted the work. It is based on published information and on private reports made available through November 1999 from API member companies. The assistance of these companies is gratefully acknowledged. Richard L. Courtney, Herman L. Muller, and Robert E. Reynolds served as consultants to the task force.

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Suggested revisions are invited and should be submitted to Jim Williams, Downstream Segment, American Petroleum Institute, 1220 L Street, N.W., Washington, D.C. 20005.

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Alcohols and Ethers—A Technical Assessment of Their Application as Fuels and Fuel Components

1 Introduction and Scope

1.1 GENERAL

1.1.1 In 1971 the American Petroleum Institute (API) studied the feasibility of blending ethanol with gasoline to augment domestic fuel supplies for transportation.[1] After the first Arab oil embargo in 1974, interest in using alcohols as fuels expanded to include methanol, not only as a transportation fuel, but also as a fuel for stationary power sources. In response to that expanded interest, the API published an updated technical assessment in 1976.[2]

1.1.2 Since 1976, many changes have occurred in the use of petroleum and non-petroleum fuels, both neat and in blends with hydrocarbon components. The earlier objective of augmenting domestic energy sources was joined by two additiional objectives: a) to produce high octane gasoline without the use of lead alkyls, and b) to reduce the contribution of motor vehicles and stationary sources to air pollution. In response to the expanded use of oxygenates, API published a second updated technical assessment in 1988.[3] Today, federal law requires that oxygenates be blended with gasoline in the wintertime in certain areas and be a part of reformulated gasoline in specified areas of the United States.

1.1.3 The Clean Air Act Amendments of 1977 expanded the interest in alcohols and ethers. The Clean Air Act Amendments of 1990 mandated the use of oxygenates to reduce wintertime carbon monoxide emissions in carbon monoxide nonattainment areas. It also required oxygenates in reformulated gasoline (RFG) which is mandated for use in extreme and severe ozone nonattainment areas and other ozone nonattainment areas which opt to require reformulated gasoline. Nonattainment areas are those areas not meeting the statutory federal standards for ambient carbon monoxide (carbon monoxide nonattainment areas) and ozone (ozone nonattainment areas).

1.1.4 New policy issues regarding oxygenates are expected in the future. An important objective of this publication is to provide an updated and expanded technical assessment suitable as a foundation for policy discussion.

1.1.5 The transportation fuels industry has been shaped by six important events since the issuing of the Clean Air Act Amendments of 1977: a) the increased use of alcohols as blending components, b) the appearance of marketplace concerns resulting from the misuse of alcohols as blending components, c) the implementation of federal environmental regulations covering the composition of motor fuels, d) the onset of federal regulations requiring the use of oxygenates, e) the use of several different ethers as fuel components, and f) the ban on MTBE in California by 2002. In the future, the registration of fuels and fuel additives and the required toxicology testing may affect motor fuel composition and the use of oxygenates.

1.1.6 This technical assessment, therefore, has been expanded to include a review of the oxygenate regulations and the technical literature that has been published between 1988 and 1999. This publication summarizes information on producing and applying alcohols and ethers as fuels and fuel components. The alcohols and ethers that are considered include a) methanol, ethanol, isopropyl alcohol (IPA), tertiary-butyl alcohol (TBA), methyl tertiary-butyl ether (MTBE), tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE), and diisopropyl ether (DIPE) as fuel components; b) methanol and ethanol (both neat and mixed with low levels of hydrocarbons) as transportation fuels; and c) methanol in stationary power sources. This publication assesses the technical advantages and disadvantages of alcohols and ethers with respect to hydrocarbon fuels. The analysis also addresses the following factors: a) the costs associated with producing alcohols and ethers, b) distribution, storage, and fire protection and safety concerns, and c) health and environmental concerns.

1.2 REFERENCES

1. American Petroleum Institute Committee for Air and Water Conservation, "Use of Alcohol in Motor Gasoline—A Review," API Report No. 4082, August 1971.

2. American Petroleum Institute Alcohol Fuels Task Force, "Alcohols—A Technical Assessment of Their Application as Fuels," API Report No. 4261, July 1976.

3. American Petroleum Institute Alcohol Fuels Task Force, "Alcohols and Ethers—A Technical Assessment of Their Application as Fuels and Fuel Components," API Report No. 4261, July 1988.

2 Chemical and Physical Properties of Alcohols and Ethers

2.1 GENERAL

2.1.1 The molecular formulae of several alcohols and ethers usable as gasoline blending components or as neat fuels are summarized in Table 1. Commonly accepted abbreviations will be used in the following discussions.

Table 1—Nomenclature of Oxygenates Commercially Used as, or in, Fuels

Name	Abbreviated Name	Formula
Methyl Alcohol (Methanol)	MeOH	CH_3OH
Ethyl Alcohol (Ethanol)	EtOH	C_2H_5OH
Isopropyl Alcohol (Isopropanol)	IPA	$(CH_3)_2CHOH$
Tertiary-Butyl Alcohol (t-Butanol)	TBA or GTBA[a]	$(CH_3)_3COH$
Methyl Tertiary-Butyl Ether	MTBE	$(CH_3)_3COCH_3$
Tertiary-Amyl Methyl Ether	TAME	$(CH_3)_2(C_2H_5)COCH_3$
Ethyl Tertiary-Butyl Ether	ETBE	$(CH_3)_3COC_2H_5$
Diisopropyl Ether	DIPE	$(CH_3)_2CHOCH(CH_3)_2$

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[a] GTBA ("Gasoline grade" TBA) is a mixture of TBA and solvents which lower the freeze point of TBA. Neat TBA freezes at 78.5°F.

2.1.2 Oxygenates are comprised of hydrogen, carbon, and oxygen. The properties of an oxygenate are affected by the position of the oxygen atom in the molecule and the hydrocarbon content. Molecular construction also influences interactions in blends with hydrocarbons. Characteristics of gasoline-oxygenate blends are covered in Chapter 5. Some key properties of alcohols and ethers are listed in Tables 2 and 3.

2.2 HEATING VALUE

Because molecules of alcohols and ethers carry oxygen, they require less oxygen for complete combustion than do hydrocarbons with corresponding numbers of hydrogen and carbon atoms. Table 4 shows the oxygen requirements for complete combustion of oxygenates. The oxygen content of an alcohol or ether produces no heat of combustion and, thus, a volume or weight of oxygenate produces less heat from combustion than that of a hydrocarbon. The lowest molecular weight oxygenate of interest, methanol or MeOH, produces about one-half the heat energy of gasoline, either on a weight or volume basis. Higher molecular weight oxygenates produce as much as 85 to 90% of the heat energy of gasoline.

2.3 MOLECULAR POLARITY

2.3.1 Although both alcohols and ethers contain oxygen, the location of the oxygen atom in an alcohol molecule imparts properties that are much different from those of gasoline and ethers. The molecular structures of MeOH and EtOH are compared with water, gasoline and MTBE in Figure 1. An alcohol molecule contains an OH group, or hydroxyl group, the same functional group as a molecule of water. The OH group is attached at the end of the hydrocarbon structure and is highly polar. In contrast, the oxygen atom in an ether molecule is bound within the hydrocarbon structure and creates little, if any, polarity. In the MTBE molecule, shown in Figure 1, the oxygen atom is bound into, and surrounded by, hydrocarbon.

2.3.2 As a consequence of the OH group, an alcohol has polar characteristics similar to water. The molecular polarity is stronger for alcohols with lighter hydrocarbon structure. MeOH has the greatest polarity of all oxygenates considered as fuel.

2.3.3 The phenomenon of molecular polarity has important consequences for blends of alcohols in hydrocarbons. Occasionally, problems with vehicle driveability and fuel system water occurred with the use of gasoline-alcohol blends. The molecular polarity of alcohol was the cause of the difficulties. See Chapter 5 for further discussion.

2.4 POLAR PROPERTIES OF ALCOHOLS

2.4.1 Polar molecules have affinity for other molecules in proportion to the degree of mutual polarity. Because of the polar nature of alcohols, vapor pressure anomalies with hydrocarbon blends and water interactions can occur. The vapor pressure of alcohols, 1.8 to 4.6 psi, listed in Table 2, is much less than that of typical blended gasoline. However, as described in Chapter 5, these values are deceptive in predicting vapor pressure of gasoline-alcohol blends due to the unusual polar behavior of alcohols. At room temperature, low molecular weight substances like water or MeOH would be gases were they not collapsed into liquids by the highly cohesive molecular forces of hydrogen bonding. When molecules of MeOH are dissolved in a nonpolar hydrocarbon solvent, like gasoline, they become physically separated. This physical separation weakens molecular cohesion and MeOH behaves like a gas. This results in an otherwise anomalous increase in vapor pressure that peaks at quite low MeOH concentrations.

Table 2—Some Properties of Alcohols, Gasoline, and No. 2 Diesel Fuel[c]

Property	MeOH	EtOH	IPA	GTBA[2]	Gasoline[a]	No. 2 Diesel Fuel
Molecular weight	32.04	46.07	60.09	73.5	100–105	~200
Composition, weight %						
Carbon	37.5	52.2	60.0	65.0	85–88	84–87
Hydrogen	12.6	13.1	13.4	13.7	12–15	13–16
Oxygen	49.9	34.7	26.6	21.3	0	0
Relative Density, 60/60°F	0.796	0.794	0.789	0.781	0.69–0.793[2]	0.81–0.89
Density, lb/gal @60°F	6.63	6.61	6.57	6.50	5.8–6.63[2]	6.7–7.4
Lower Heating value (liquid fuel—water vapor)						
Btu/lb	8,570	11,500	13,300	14,500	18K–19K	18K–19K
Btu/gal @60°F	56,800	76,000	87,400	94,100	109K–119K	126K–131K
Boiling temperature, °F	148	173	180	176–181	80–437	370–650
Freezing point, °F	–143.8	–173.4	–126.2	78.5 (TBA)	–40	–40 to 30
Vapor pressure, psi	4.6	2.3	1.8	1.8	7–15	<0.2
Research octane number[b]	—	—	—	—	88–100	—
Motor octane number[b]	—	—	—	—	80–90	—
Cetane number[b]		0-54[2]	—	—	—	40–59
Water solubility, @70°F						
Fuel in water, volume %	100	100	100	100	Negligible	Negligible
Water in fuel, volume %	100	100	100	100	Negligible	Negligible
Viscosity, mm/s						
@68°F	0.74	1.50	3.01	5.31	0.5–0.6	2.8–5.0
@–4°F	1.345[2]	3.435[2]	11.465[2]	Solid	0.8–1.0	9.0–24.0
Flash point, closed cup, °F	52	55	53	52	–45	165
Autoignition temperature, °F	~867	~793	~750	~892	~ 495	600
Flammability limits, volume %						
Lower	7.3	4.3	2.0	2.4	1.4	1.0
Higher	36.0	19.0	12.0	8.0	7.6	6.0
Latent heat of vaporization						
Btu/lb @60°F	506	396	320	258	~150	~100
Btu/gal @60°F	3,340	2,378	2,100	1,700	~900	~ 710
Stoichiometric air/fuel, weight	6.45	9.00	10.3	11.1	14.7	14.7
Moles product/moles charge	1.06	1.07	1.07	1.07	1.06	1.06
Moles product/moles $O_2 + N_2$,	1.21	1.14	1.12	1.10	1.08	1.07

Notes:

[a] Gasoline properties listed are representative of non-oxygenated gasoline with 100% hydrocarbon content.

[b] Conventional laboratory engine test methods for Research octane number, Motor octane number and cetane number are not suitable for neat alcohols. See Table 15 for Octane Blending Values of alcohols in gasoline.

[c] Superscripted numbers refer to references at the end of each section.

Table 3—Some Properties of Ethers and Gasoline[c]

Property	MTBE	TAME	ETBE	DIPE	Gasoline[a]
Molecular weight	88.15	102.18	102.18	102.18	100–105
Composition, weight %					
Carbon	68.1	70.5	70.5	70.5	85–88
Hydrogen	13.7	13.8	13.8	13.8	12–15
Oxygen	18.2	15.7	15.7	15.7	0
Relative Density, 60/60°F	0.746	0.776	0.745	0.729	0.69–0.79
Density, lb/gal @6°F	6.21	6.46	6.20	6.07	5.75–6.58
Lower Heating value (liquid fuel—water vapor)					
Btu/lb	15,100	15,600	15,600	16,500	18,000–19,000
Btu/gal @60°F	93,500	100,600	97,000	100,000	109,000–119,000
Boiling temperature, °F	131	187	161	155	80–437
Freezing point, °F	–163		–137	–122	–40
Vapor pressure, psi	7.8	1.5	4.0	4.9	7–15
Research octane number[b]	116[6]	—	—	—	88–100
Motor octane number[b]	101[5]	—	—	—	80–90
Water solubility, @70°F					
Fuel in water, volume %	4.8	1.15	1.2	1.1	Negligible
Water in fuel, volume %	1.5	0.6	0.5	0.6	Negligible
Viscosity, mm/s					
@ 68°F	0.47[7]	0.44[5]	0.53[5]	0.47[5]	0.5–0.6
@ –4°F	0.77[7]	0.71[5]	0.89[5]	0.76[5]	0.8–1.0
Flash point, closed cup, °F	–14	11	–3	9	–45
Autoignition temperature, °F	~815	860[5]	580	~830	~ 495
Flammability limits, volume %					
Lower	1.6	1.0	1.0	1.4	1.4
Higher	8.4	7.1	6.8	7.9	7.6
Latent heat of vaporization					
Btu/lb @60°F	138	135	134	148	~150
Btu/gal @60°F	863	870	830	900	~900
Stoichiometric air/fuel, weight	11.7	12.1	12.1	12.1	14.7
Moles product/moles charge	1.07	1.07	1.07	1.07	1.06
Moles product/moles $O_2 + N_2$	1.10	1.09	1.09	1.09	1.08

Notes:

[a] Gasoline properties listed are representative of non-oxygenated gasoline with 100% hydrocarbon content.

[b] Conventional laboratory engine test methods for Research octane number and Motor octane number are not suitable for neat oxygenates. See Table 15 for Octane Blending Values of ethers as gasoline blend components.

[c] Superscripted numbers refer to references at the end of this section.

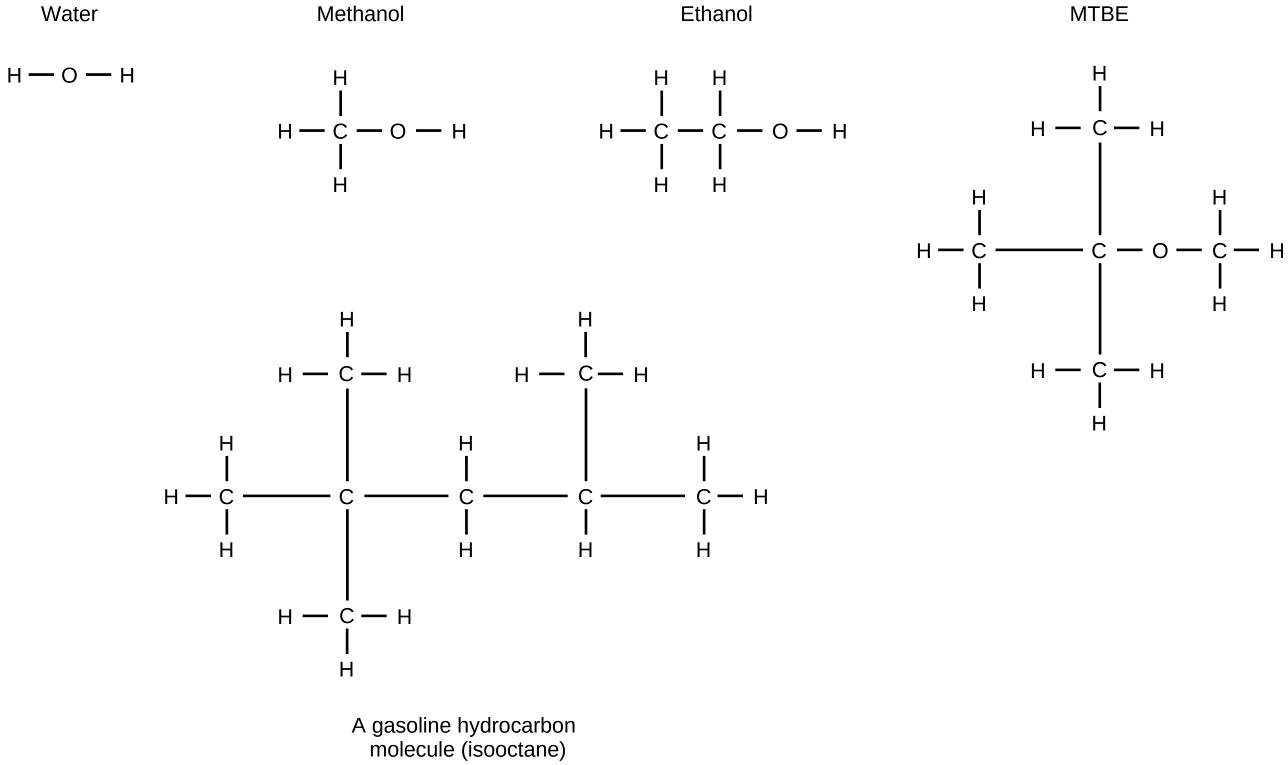

Figure 1—Molecular Structures of Water, Methanol, Ethanol, MTBE, and Gasoline

Table 4—Combustion of Alcohols, Ethers, and Hydrocarbons in Air

Fuel	Combustion Reaction Equation[a]
Methanol	$CH_3OH + 1.5O_2 + 5.64\ N_2 \longrightarrow CO_2 + 2(H_2O) + 5.64\ N_2$
Ethanol	$C_2H_5OH + 3O_2 + 11.3\ N_2 \longrightarrow 2(CO_2) + 3(H_2O) + 11.3\ N_2$
Isopropyl Alcohol	$C_3H_7OH + 4.5O_2 + 16.93\ N_2 \longrightarrow 3(CO_2) + 4(H_2O) + 16.93\ N_2$
tert-Butyl Alcohol	$C_4H_9OH + 6O_2 + 22.6\ N_2 \longrightarrow 4(CO_2) + 5(H_2O) + 22.6\ N_2$
MTBE	$C_5H_{12}O + 7.5O_2 + 28.2\ N_2 \longrightarrow 5(CO_2) + 6(H_2O) + 28.2\ N_2$
TAME	$C_6H_{14}O + 9O_2 + 33.9\ N_2 \longrightarrow 6(CO_2) + 7(H_2O) + 33.9\ N_2$
ETBE	$C_6H_{14}O + 9O_2 + 33.9\ N_2 \longrightarrow 6(CO_2) + 7(H_2O) + 33.9\ N_2$
DIPE	$C_6H_{14}O + 9O_2 + 33.9\ N_2 \longrightarrow 6(CO_2) + 7(H_2O) + 33.9\ N_2$
Gasoline or Diesel Fuel	$C_nH_{2n+2} + [(3n+1)/2]\ O_2 + 3.76\ [(3n+1)/2]\ N_2 \longrightarrow nCO_2 + (n+1)\ H_2O + 3.76\ [(3n+1)/2]\ N_2$

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[a] Based on an air mixture of 79% nitrogen, 21% oxygen.

2.4.2 If enough water is present as a second liquid phase, as a so-called "water bottom," the affinity of MeOH for the highly polar water molecules causes the MeOH to migrate from the gasoline blend to the water phase. These polarity effects are less pronounced for ethanol and may be insignificant for higher carbon number alcohols. Chapter 5 describes how this phenomenon of polarity affects vehicle operation with gasoline-oxygenate blends.

2.4.3 Another consequence of the strong polarity of MeOH, other alcohols and also water, is the need of high amounts of heat for vaporization. Alcohols with large hydrocarbon structures, such as TBA (or GTBA), have less polarity and have physical properties approaching those of hydrocarbons. Ethers vaporize, and have latent heats of vaporization similar to corresponding hydrocarbons in gasoline.

2.5 OTHER DIFFERENCES

2.5.1 Oxygenates differ from hydrocarbons significantly with respect to other properties: boiling point, vapor pressure, flammability, viscosity, flash point, and antiknock performance. As might be expected, the boiling temperatures are lowest for the lowest molecular weight alcohols and ethers. Being pure compounds, except for GTBA, all have constant boiling temperatures that generally categorize them in the more volatile, below 50% evaporated distillation temperature, fraction of typical gasoline.

2.5.2 Flammability limits, flash point and combustion characteristics of the alcohols, in particular, are much different than gasoline or diesel fuel. Ethers behave more like hydrocarbons in this regard. MeOH has a very rich flammability limit but also a somewhat rich lean limit for combustion. The antiknock performance of oxygenates cannot be measured using ASTM Research or Motor Methods. However, MeOH and EtOH are acknowledged as highly attractive engine fuels with superior knock resistance in engines, largely due to their high latent heats of vaporization and high combustion expansion ratios. Neat alcohols have relatively high flash point temperatures compared with hydrocarbons but, as discussed later, present certain safety concerns. The low luminosity of the flames of MeOH combustion causes concern about the use of MeOH as a neat fuel for vehicles as discussed in Chapter 6.

2.5.3 The freezing point of the ethers and the lower molecular weight alcohols is extremely low. However, the viscosities of alcohols at low temperature are much higher than those of light hydrocarbons. Because neat TBA approaches solidification at 78°F, it requires cosolvents for handling in refinery applications. Hence, the "Gasoline-Grade" version of TBA, termed GTBA, was developed.

2.5.4 Characteristics of oxygenates in blends with gasoline are covered in Chapter 5 and, as neat fuels for gasoline and diesel engines, in Chapter 6.

2.6 REFERENCES

1. Unless otherwise referenced, all properties listed are from American Petroleum Institute, *Alcohols and Ethers*, API Publication 4261, Second Edition, Washington, DC, July 1988.

2. L. M. Gibbs, "Transportation Fuels—Automotive Gasoline," *Encyclopedia of Energy and the Environment*, John Wiley & Sons, Inc., 1995.

3. National Institute for Petroleum and Energy Research, "Motor Gasolines," Summer 1996, Winter 1996-97, Bartlesville, OK, 1997.

4. Engine Manufacturers' Association, Alternate Fuels Committee, "A Technical Assessment of Alcohol Fuels," SAE Paper 820261 (Paper delivered at the International Congress and Exposition, Society of Automotive Engineers, Detroit, MI, February 1982).

5. T. E. Daubert, Penn State Department of Chemical Engineering, (Communication to R. L. Courtney, August 7, 1996).

6. P. Dorn, A. M. Mourao, and S. Herbstman, "The Properties and Performance of Modern Automotive Fuels," SAE Paper # 861178, Society of Automotive Engineers, 1986.

7. ARCO Chemical Company, "Product Safety Bulletin—Methyl Tertiary Butyl Ether," ARCO Chemical Company, Newtown Square, PA, February 1993.

3 Oxygenates Production Technology, Capacity, and Costs

3.1 METHANOL

3.1.1 Worldwide methanol capacity in 1998 was about 37 million metric tons, or about 12.3 billion gallons per year (802 thousand barrels per calendar day). North American capacity was about 8.3 million metric tons, or about 2.7 billion gallons per year (176 thousand barrels per calendar day).[1] Major North American producers include Methanex, Hoechst-Celanese, Borden, Lyondell, Beaumont Methanol, Edmonton Methanol, Quantum, Clear Lake Methanol, Fortier Methanol, Georgia Gulf, and Ashland.[1,2] For perspective, U.S. consumption of gasoline in 1998 was 127 billion gallons (8,253 thousand barrels per calendar day)[3] and California consumption was about 14 billion gallons (918 thousand barrels per calendar day).[4]

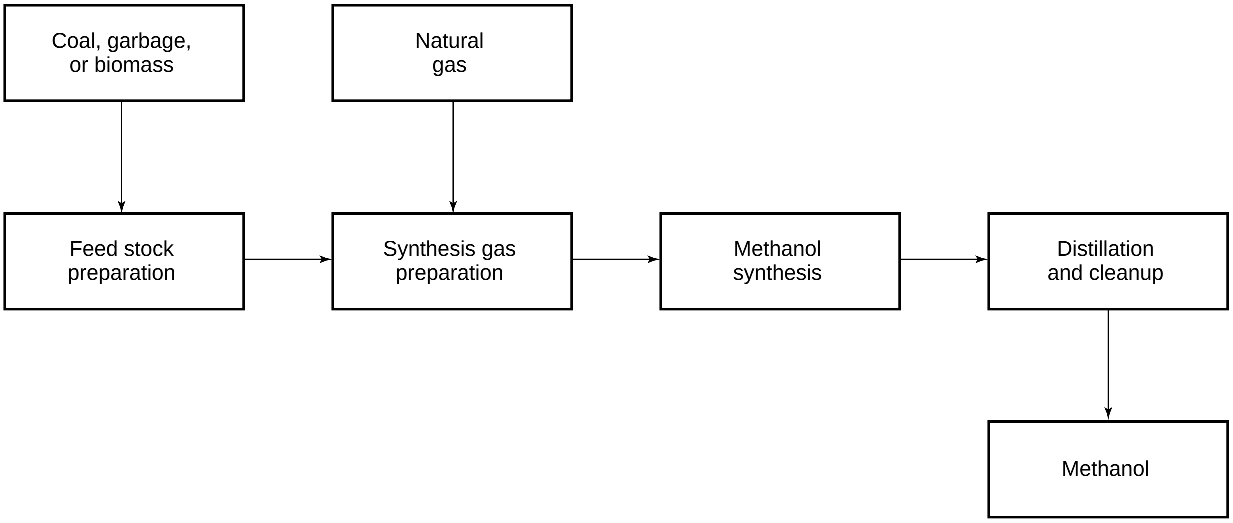


Figure 2—Methanol Production Process—Simplified Diagram

3.1.2 Essentially all methanol world wide is produced from natural gas. Technology also exists to manufacture methanol from coal, cellulosic refuse, or most types of biomass.[5] In methanol production the feedstock is used to prepare a synthesis gas, either through reforming or catalytic partial oxidation.

3.1.3 Natural gas requires little preparation for producing the synthesis gas. Other feedstocks, including coal, have to be sorted, screened and pulverized before the synthesis gas step. Feedstocks other than natural gas may also contain sulfur that has to be removed from the synthesis gas. Since natural gas often contains little sulfur, there may be no need for sulfur removal when natural gas is used as the feedstock. Figure 2 is a simplified diagram of the methanol production process.

3.1.4 Most methanol industry analysts believe that a massive methanol plant production program would be required to support supply of fuels designed to operate on 85 – 100 percent methanol,[6] i.e., the existing worldwide methanol manufacturing capacity and near term expansion will be able to supply tradition chemical markets (including formaldehyde and acetic acid) and to supply the requirements for the manufacture of MTBE for use in gasoline.

3.1.5 Estimates of methanol operating and plant capital costs depend strongly on a number of factors.[6,7,8,9] These factors include technology employed, plant size and location, infrastructure needed, return on investment required, and cost of feedstock. In every case, the capital charge is a major part of the total cost of methanol. For example, Wagner and Tatterson in 1987 estimated capital costs to build a new methanol plant that uses natural gas feedstock to be $250 – $260 million for a 300 million gallon per year plant on the Gulf Coast or in the Middle East producing methanol with state-of-the-art technology.[8] Wagner and Tatterson also estimated capital to fund a new methanol plant that uses coal as feedstock to be about $900 million. The coal plant incurs extra cost because of the additional facilities required for handling and preparing the feedstock and cleaning up the synthesis gas. Beyaert in 1988 estimated capital costs of $416 – 650 million for new plants of 292 million gallons per year capacity in remote locations producing methanol using natural gas feedstock.[6] In 1992, Hahn estimated capital costs of $339 million 1988 dollars for a 2,500 metric ton per day, or about 300 million gallon per year, methanol plant on the Texas Gulf Coast, to $418 and $590 million for similar plants in Saudi Arabia and Australia, respectively.[9] For larger plants of 10,000 metric tons per day, or about 1.2 billion gallons per year, Hahn estimated capital costs of $883 million to $1,088 million and $1,537 million for plant locations similar to those of the smaller plants.

3.1.6 Feedstock costs are also major and can be highly variable. Estimated costs for natural gas feedstock used by Wagner and Tatterson as well as by Beyaert ranged from less than $1.00 per million Btu for undeveloped remote locations (where the price of flared gas is very dependent on local factors and markets) to a market price of $2.00 per million British thermal units (MMBtu) for U.S. natural gas on the Gulf Coast. The current price is about $2.35 per MMBtu. Hahn also recognized huge uncertainties in predicting natural gas prices, and estimated natural gas prices from $0.85 to $3.08 per MMBtu for a short term scenario (2000) to $1.21 – 3.79 for medium or long term projections (2005 and beyond). In addition, Hahn estimated that an increase in natural gas prices of $1.00 results in an increase of $0.10 per gallon of methanol.

3.1.7 The return on investment (ROI) required also affects methanol production cost significantly, and most studies have assumed about 10 – 15 percent. Some methanol producers might be willing to build plants yielding lower ROI, however, others might expect at least 15 percent, depending upon the availability of alternative investments, perception of risks, and government incentives.

3.1.8 Estimates by Beyeart of long-term methanol costs delivered to the U.S. West Coast from new plants in the Middle East and Australia range from 50 cents to 97 cents per gallon.[6] Capital costs in this study were based on reported and estimated costs to build methanol plants at various locations around the world from 1981 – 1987. The costs include factors for building in developed (Middle East) and undeveloped (Australia) remote locations and assume an after tax ROI of 15 percent above inflation.

3.1.9 Wagner and Tatterson estimated future costs to produce fuel grade methanol from natural gas in plants on the U.S. Gulf Coast and a developed site in the Middle East that employ advances in steam reforming and catalytic partial oxidation technology.[8] The authors assumed a 15 percent after tax ROI (10 percent ROI above 5 percent inflation), and estimated the cost of methanol delivered to the U.S. Gulf Coast at 43 cents per gallon. Methanol costs for a coal plant were estimated at 97 cents per gallon.

Table 5—Estimated Methanol Production Costs at the Plant Gate

	Port Arthur, Texas, USA	Point Lisas, Trinidad	Jubail, Saudi Arabia	Dampier, Australia	Edmonton, Canada	Prudhoe Bay, Alaska, USA
Capital Investment	339	378	418	590	355	575
Short Term						
Investment	17	24	29	30	18	30
Depreciation	–3	–4	–4	–5	–3	–5
Non-gas oper.	10	11	13	16	10	17
Natural gas	30	15	11	11	25	8
Tax	8	11	13	14	8	13
Sum	63	58	62	66	58	63
Medium Term						
Investment	15	21	25	26	15	25
Depreciation	–3	–3	–4	–5	–3	–5
Non-gas oper.	10	11	13	16	10	17
Natural Gas	37	19	14	15	31	12
Tax	6	10	11	11	7	11
Sum	66	57	59	63	60	60
Capital Investment	883	985	1,088	1,537	925	1,498
Long Term						
Investment	10	14	16	18	10	16
Depreciation	–2	–2	–2	–3	–2	–3
Non-gas oper.	6	6	7	9	5	10
Natural gas	37	19	14	15	31	12
Tax	4	6	7	8	4	7
Sum	55	43	42	46	49	42

Notes:
1. Capital investment in million 1988 U.S. dollars.
2. Other costs in cents per gallon of methanol in 1988 U.S. dollars.
3. A 2,500 metric ton per day plant is used in the short term and medium term.
4. A 10,000 metric ton per day plant is used in the long term.
5. Cost of capital is 11 percent in the short term and 9 percent in the medium and long term for low-risk countries.
6. An additional 3 percent is added to the cost of capital for high risk countries (Trinidad and Saudi Arabia).
7. Depreciation results in a tax benefit, and thus has a negative sign.
8. Numbers may not add up due to rounding.

Source: Reference 9

3.1.10 Hahn's estimates for the cost of a gallon of methanol at the plant gates are shown in Table 5. They range from a low of 42 cents per gallon for the long term case to a high of 66 cents for the short and medium term cases. The author used an ROI of 11 percent for short term and 9 percent for the medium and long term cases for low risk locations (U.S., Canada, and Australia) and added 3 percent for high risk locations (Trinidad and Saudi Arabia). This study also reported estimated costs per gallon of methanol delivered to Dallas, Los Angeles and New York, as shown in Table 6.

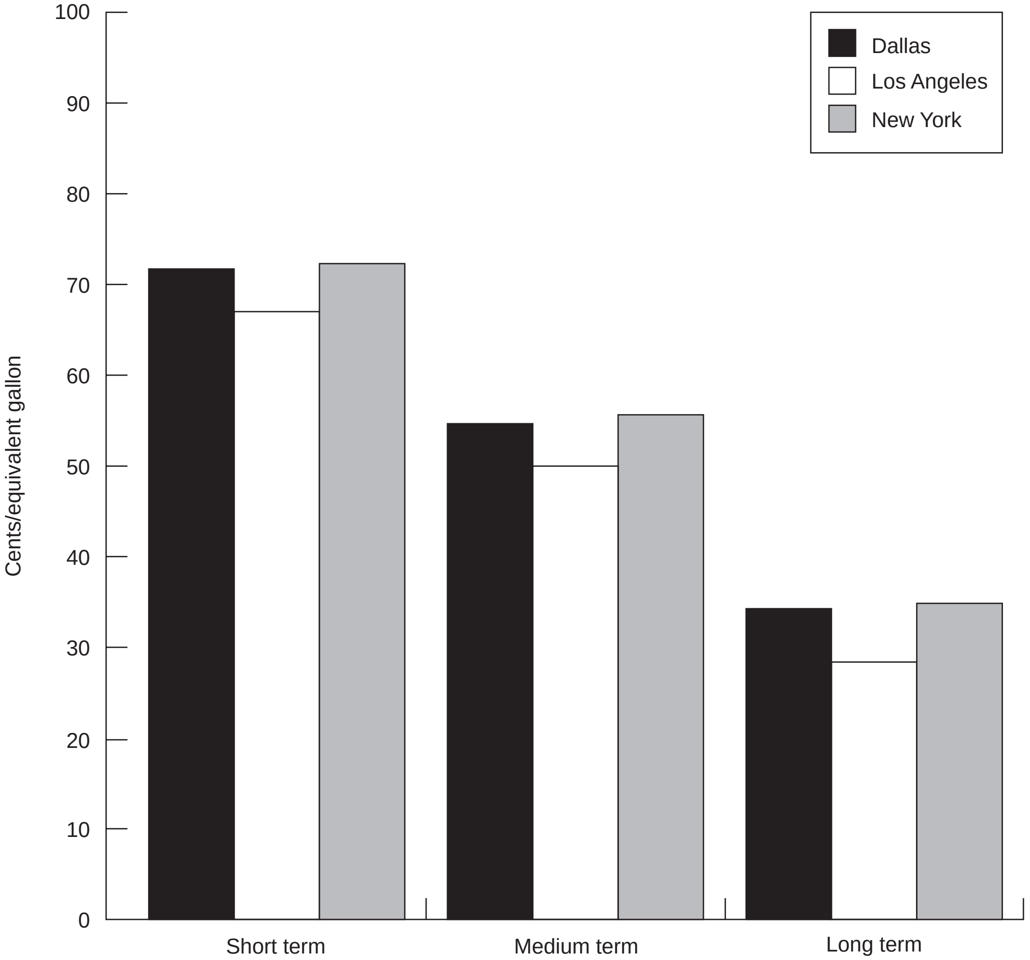
3.1.11 Whereas Beyeart and Wagner/Tatterson limited their studies to methanol delivered to the U.S. Gulf and or West Coast, Hahn went considerably further. His primary source for methanol production costs was a Bechtel study for the State of California[10] and included four cases, near term, short term, medium term, and long term, corresponding roughly to 1995, 2000, 2005, and post 2005, respectively. (Because 1995 is history, the data presented in this report will not include the near term case.) The work was based on production costs, transportation costs, distribution and marketing costs, and the incremental costs of a flexible fuel vehicle (FFV). In addition to plant gate and delivered costs, costs and prices were developed for Dallas, Los Angeles, and New York. For these cities the estimated price of M85 and the estimated "full cost," of M85 which includes the incremental costs of an FFV were compared to estimated gasoline costs. Also, instead of the 1.8 gasoline equivalency factor for 100 percent methanol (see Chapter 6), Hahn used a factor of 1.68 for M85 which includes efficiency improvements for FFVs and the gasoline portion of the fuel.

Table 6—Estimates of Delivered Methanol Costs

	Port Arthur, Texas, USA	Point Lisas, Trinidad	Jubail, Saudi Arabia	Dampier, Australia	Edmonton, Canada	Prudhoe Bay, Alaska, USA
Transport Costs						
Dallas	3	5	8	9	16	64
Los Angeles	8	5	5	4	9	52
New York	4	2	5	6	14	62
Delivered Cost						
Short Term						
Dallas	65	63	70	75	74	127
Los Angeles	71	63	67	70	66	115
New York	66	60	67	72	72	125
Medium Term						
Dallas	68	62	67	72	76	124
Los Angeles	74	62	64	67	69	113
New York	69	59	64	70	74	122
Long Term						
Dallas	58	47	50	55	65	106
Los Angeles	63	47	47	50	57	94
New York	58	45	47	52	63	104

Notes:
1. Costs in cents per gallon of 1988 U.S. dollars.
2. Total delivered cost is the sum of plant gate costs and transportation costs.
3. Numbers may not add up due to rounding.

Sources: Reference 9, also Reference 10 for transportation costs.



Source: Reference 9

Figure 3—City Comparison: Full Cost M85 Minus Gasoline Price, Base Case

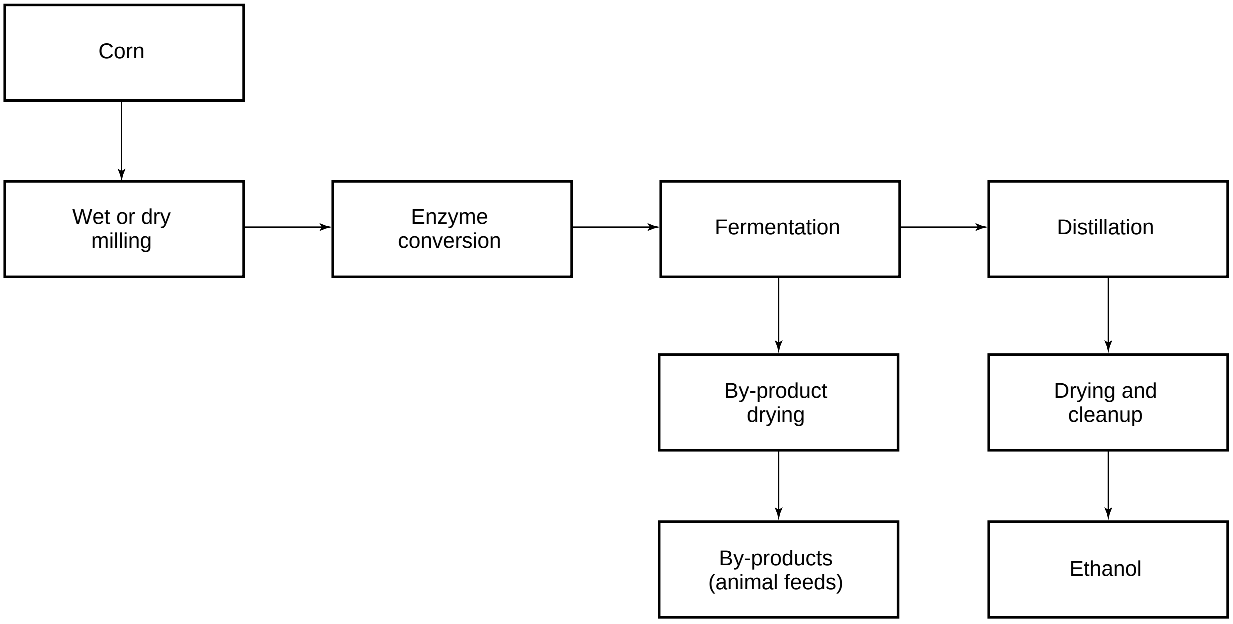


Figure 4—Ethanol Production Process—Simplified Design

3.1.12 Because of the many uncertainties associated with the costs of future motor fuels, Hahn performed sensitivity studies varying the capital charges, the real after-tax cost of capital (ROI), natural gas costs, and the FFV costs. Figure 3 is a graphic representation of Hahn's base case. It shows how the gap between the full cost of M85 and gasoline narrows substantially with time but still remains in favor of gasoline in the long term. The sensitivity studies also show that the combination of all the factors in favor of lower M85 costs still resulted in about a 45 cents higher cost for the methanol fuel per equivalent gallon of gasoline for the short term, which narrowed to about 10 cents per gallon for the long term case.

3.1.13 The energy balance for the production of methanol is shown in Table 7. In methanol manufacture, natural gas serves as both feedstock and the source of process energy; therefore, the energy balance is simple. The methanol produced contains about 65 percent of the energy contained in the natural gas consumed by the plant. The 35 percent loss of energy can be viewed as the penalty for liquefying the gas to methanol.

3.1.14 The primary economic consideration in the use of methanol is the cost. Based on the above estimates, the cost of methanol or M85 produced from natural gas that is equivalent to one gallon of gasoline remains above the price needed to be competitive with gasoline for the foreseeable future. Accordingly, unless crude prices increase significantly, or government subsidies are granted, or major advances in production technology are developed, the assessment that was made almost 10 years ago that methanol cannot compete with gasoline[11] is still valid today.

3.1.15 With today's technology, methanol from plants using cellulosic refuse of biomass for feedstocks is at least as expensive as methanol produced from coal.[12] Costs for collection and transportation of the raw materials are high and very site specific.

3.2 ETHANOL

3.2.1 U.S. Fuel Ethanol capacity in 1995 was about 7 billion gallons per year, or 111 thousand barrels per calendar day.[2] Actual production in 1998 was 1.45 billion gallons per year, or 95 thousand barrels per calendar day.[3] The major U.S. producer is Archer Daniels Midland with a capacity of about 750 million gallons per year (49 thousand barrels per calendar day). Other significant U.S. producers, but all with 110 millions per year or less capacity, are Minnesota Corn Processors, New Energy Company of Indiana, Cargill, High Plains Corporation, A. E. Staley, Midwest Grain Products, AGP, Chief Ethanol Fuels, and Nebraska Energy.[2]

Table 7—Energy Balance for Production of Methanol

	MBTU per Gallon of Methanol
Feedstock and process energy (natural gas)	88
Energy in product	57
Overall efficiency, percent	65

Source: Reference 6

3.2.2 Essentially all of the fuel ethanol in the United States is produced from corn. A bushel of corn yields about 2.5 gallons of ethanol. The remainder is produced from other grains, such as barley and waste sugars.

3.2.3 In the United States ethanol is produced by either dry milling or wet milling processes.[13] In the wet milling process water is added to the grinding step. The choice between the two processes depends largely on the ability of manufacturers to market by-products. The major by-product of the dry milling process is distillers dried grain and solubles (DDGS), which is sold in competition with soybean meal as animal feed. By-products of the wet milling process include corn gluten feed, corn gluten meal, and corn oil. Corn gluten feed is sold as livestock feed, corn gluten meal is used to make poultry feed. By-products from both processes also include carbon dioxide (CO_2).

3.2.4 After milling, starches from the corn are converted by enzymes to fermentable sugars. The sugars are then fermented with yeasts, and the by-products are separated and dried. The low-proof beer from fermentation is distilled to yield 190-proof ethanol, which is further dried and purified to yield essentially 200-proof ethanol. Figure 4 is a simplified diagram of the ethanol production process.

3.2.5 Capital employed and especially feedstock costs have a significant impact on the production costs of ethanol. Costs of ethanol from new wet and dry milling plants using an average of 1997 – 1998 corn prices of $2.25 per bushel are estimated to be $1.09 and $1.24 per gallon, respectively.[14] The production costs are summarized in Table 8 and apply to new, undepreciated plants. Without depreciation, i.e., without capital recovery from large, fully depreciated plants, ethanol costs are much lower. With favorable corn prices and by-product markets, variable costs to produce ethanol have been reported well under $1.00 per gallon, some as low as $0.50. For the past 10 years almost one half of the increase in ethanol capacity in the United States has been achieved by expanding large wet milling facilities, and these plants may carry only a small part of the initial capital charges, or may now be fully depreciated. However, even the fully depreciated plants are significantly affected by feedstock prices; a change in the price of corn of $1.00/bushel affects the variable costs of ethanol by 30 – 40 cents per gallon.

Table 8—Ethanol Production Costs in New Facilities (1998 Dollars)

	Wet Milling	Dry Milling
Capacity, million gallons per year	100	40
Capital Investment, $ million	245	98
	Dollars per gallon of ethanol	
Corn at $2.25[a] per bushel	0.90	0.90
By-product Credit	0.60[b]	(0.45)
Operating Costs	0.37[c]	0.37
Capital Recovery	0.42[d]	0.42
Total	1.09	1.24

Note: Capital recovery is based on a 10 percent real return after taxes which equates to an annual capital charge of 17.1 percent.

[a] Average of 1997 and 1998 prices.

[b] Average of 1997 and 1998 by-product credits.

[c] ERS AG Info. Bulletin No. 663, January 1993.

[d] Based on the assumptions at bottom of Table 8.

Source: Reference 14.

Table 9—Net Energy Value of Corn Ethanol, Btu per Gallon

Production Phase	Milling Process: Dry	Milling Process: Wet	Weighted Average
Corn Production	21,225	22,074	21,793
Corn Transport	1,212	1,260	1,244
Ethanol Conversion	47,425	53,273	51,343
Ethanol Distribution	3,173	3,173	3,173
Energy Losses	5,046	5,380	5,271
Total Energy Used	78,081	85,160	82,824
By-Product Credits	13,410	15,500	15,056
Net Energy Value[a]	19,290	14,301	16,193
Energy Ratio	1.30	1.21	1.24

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[a] A gallon of ethanol contains 83,961 Btu on a high heat value basis.

Source: Reference 16

3.2.6 The energy balance in ethanol manufacture is complicated because of the way feedstock energy is evaluated and because the plant uses different sources for process energy. The plant also generates by-products. The corn feed stock has calorific energy. However, since the corn is not burned directly for fuel, the plant should not be charged for the energy content of the corn as received but for the energy needed to grow the corn, i.e., the energy for fertilizer and herbicide manufacture, for cultivation and transportation, and for corn drying. Also, good land requires less energy to produce corn than land that must be irrigated (i.e., requiring additional energy to supply the water). Most large plants use coal for process fuel, but smaller plants generally use natural gas, distillate fuel or residual fuel. Finally, a credit is given for the by-products that equals the energy needed (or the replacement value) to produce the same amount of animal feed using the most efficient alternative method, which is growing soybeans. No credit is given for refinery energy savings because essentially all ethanol is added to gasoline downstream, usually at terminals. These considerations were used by Muller and Ho in 1986 with information available at that time to calculate an energy efficiency of ethanol of 95 percent.[15]

3.2.7 A more recent energy study of the production of ethanol in 1995 by Shapouri, Duffield and Graboski for the U. S. Department of Agriculture (USDA) concluded that the net energy value of corn ethanol has become positive in recent years due to technological advances in ethanol production and increased efficiency in farm production.[16] Also, corn yields have been trending higher in recent years, and the production of agricultural chemicals has become more efficient. In addition, modern ethanol production facilities conserve energy by utilizing cogeneration facilities that produce steam and electricity simultaneously. Table 9 is a summary of the USDA study on the energy efficiency of ethanol production for both the dry and wet milling processes and a weighted average taking into account that wet milling represents two-thirds of U.S. ethanol production and dry milling one-third. The calculations are also based on high heating values. The authors note that using either low or high heating values is valid for the energy balance calculations as long as the basis is consistently applied. By-product credits were based on the replacement value, and no credit was given for CO_2. The USDA study concludes that corn ethanol production is energy efficient by a ratio of 1.24 for modern facilities.

3.2.8 The primary consideration for fuel ethanol is also the cost. With the cost of ethanol produced from corn at over $1.00 per gallon in a new plant, and third quarter 1999 gasoline Gulf Coast spot prices of about $0.65 per gallon, fuel ethanol manufacture in new plants will continue to depend on subsidies. In the absence of such, only ethanol produced in fully or partially depreciated plants that primarily support variable costs may compete with gasoline or with other oxygenates.

3.2.9 Ethanol can also be produced from cellulose or biomass such as wood, corn stover, and municipal solid wastes, but the processes that use these resources have serious technical and economical problems. For example, cellulose is difficult to dissolve and hydrolyze, and the sugars produced are not fermentable with normal yeasts. Also, because of the low value density of the raw materials, supply and front-end processing must be done on a major scale. This means that processing plants must be very large and therefore would require large capital investments. Furthermore, lignin, which is partially polymerized phenolic resin, is a major by-product of ethanol from cellulose (wood), and there is no ready market for this material. Activities in this area have been limited to work in university and government facilities.[17,18] Full scale commercial production is not expected in the foreseeable future unless valuable uses for lignin and other by-products are found or there are major advances in technology.

3.3 TERTIARY-BUTYL ALCOHOL (TBA)

Worldwide capacity of TBA is estimated at 60 thousand barrels per calendar day (920 million gallons per year).[31] U.S. capacity is about 38 thousand barrels per calendar day (580 million gallons per year). Of this, Arco Chemicals (now Lyondell Petrochemical) and Texaco Chemical produce about 33 thousand barrels per calendar day and 12 thousand barrels per calendar day, respectively, as a co-product of propylene oxide production.[19] TBA can also be produced by the direct hydration of isobutylene. In the United States there is currently no market for TBA to be used as a gasoline component by itself, and all TBA available for fuel use is being converted to isobutylene for MTBE production.

3.4 OTHER ALCOHOLS

Other alcohols that could be used in gasoline include isopropyl alcohol (IPA) and butyl alcohols other than TBA. Essentially all these alcohols produced in North America are used as chemical feedstocks or as solvents. They are usually too expensive for use as a gasoline blending component; however, IPA has been used in gasoline at 2 percent or less to prevent carburetor icing.[20,21]

3.5 METHYL TERTIARY-BUTYL ETHER (MTBE)

3.5.1 Current worldwide MTBE capacity is about 523 thousand barrels per calendar day (8.0 billion gallons per year). North American capacity is estimated at 248 thousand barrels per calendar day (3.8 billion gallons per year).[22] Actual U.S. consumption is 250 thousand barrels per calendar day (about 3.8 billion gallons per year), more than 80 thousand barrels per calendar day (about 1.2 billion gallons per year) were imported.

3.5.2 Major producers of merchant MTBE in North America are Arco Chemical (now Lyondell Petrochemical), Texaco Chemical, Huntsman Corporation, Texas Petrochemical, EGP Fuels (Enron), Valero, Alberta Envirofuels, Belvieu Environmental Fuels (Enterprise/Sun/Mitchell), and Global Octane.[2,22] MTBE production has expanded explosively in recent years to meet RFG requirements, but future MTBE demand is predicted to grow slowly. World MTBE capacity appears more than adequate to cover demand through the year 2000.

3.5.3 MTBE is produced by reacting isobutylene with methanol over an ion-exchange catalyst.[22] Major sources of the isobutylene feedstock are derived from catalytic cracking and ethylene cracking; isobutylene is a refining by-product of these processes, and its supply is therefore generally limited to use in the refinery where it is produced. Merchant MTBE is manufactured from isobutylene that is produced by dehydrating tertiary butyl alcohol (TBA), or by isomerizing butane to isobutane followed by dehydrogenation.

3.5.4 Costs of MTBE produced from butanes in world scale plants have been estimated by DeWitt & Company, and are shown in Table 10. The assumptions for these costs are based on 1996 conditions and the study revealed full MTBE costs ranging from $1.07 per gallon produced in a plant on the U.S. Gulf Coast to about $1.12 for MTBE from a plant in Saudi Arabia and delivered to the U.S. The DeWitt study concluded that overall, the data indicate that these two world scale plants would be reasonable investments provided U.S. MTBE prices are at average or better levels.

3.6 TERTIARY-AMYL METHYL ETHER (TAME)

3.6.1 TAME is produced via the MTBE process using a feedstock that contains isoamylenes. Plants that produce TAME are limited to refineries for in-house use, i.e., there is currently no merchant TAME available.

3.6.2 Current U.S. TAME capacity is about 23 thousand barrels per calendar day (about 353 million gallons per year),[2] Current worldwide TAME capacity is estimated to be 47 thousand barrels per calendar day (about 721 million gallons per year).

3.7 DIISOPROPYL ETHER (DIPE)

3.7.1 Diisopropyl ether (DIPE), or isopropyl ether (IPE) has recently been under consideration as a gasoline blending component, and both Mobil[25] and UOP,[26] each with their own catalyst technology, have announced low cost processes to produce this ether. DIPE is produced from propylene and water, and in either process the propylene is hydrated to isopropyl alcohol (IPA) and further reacted to maximize DIPE and minimize IPA yields. Both processes are refinery based and do not depend on external sources of alcohol for etherification. Mobil showed costs of 78 cents per gallon of DIPE, excluding catalyst and licensing fees. The addition of an additive to the Fluid Bed Catalytic Cracker Unit (FCC) to maximize propylene yield reduced costs to 74 cents per gallon. These costs compared

Table 10—Cost of Producing MTBE

	500,000 metric tons/year (1.6 billion gallons) from butanes			
	U.S. Gulf Coast		Saudi Arabia	
Capital Costs, $ million	285		410	
	$/ton	$/gal	$/ton	$/gal
Feedstocks				
Butane	134.87	0.38	108.49	0.31
Methanol	91.54	0.26	50.92	0.14
Total Feeds	226.40	0.64	159.41	0.45
Variable Costs (Electricity, Fuel Gas, Cooling Water, Catalyst Replacement)	39.26	0.11	14.42	0.04
Fixed Costs (Labor/Overhead, Maintenance, Insurance)	30.13	0.08	44.20	0.12
Cash Costs	295.80	0.735[a]	218.02	0.61
ROI, 15% before Taxes	85.50	0.24	126.00	0.35
Full Cost	381.30	1.07	344.02	0.96

Note: Numbers may not add up due to rounding.
[a] MTBE/Oxygenates Clean Fuels, Dewitt & Co., Inc. Issue 686, August 5, 1999.
Source: Reference 22.

favorably with the costs of producing MTBE from world-scale size plants.

3.7.2 Actual use of DIPE in fuel has been limited to oil companies that are affiliated with chemical companies that produce isopropyl alcohol.[27] Special procedures are used to handle and store neat DIPE.[28]

3.8 ETHYL TERTIARY-BUTYL ETHER (ETBE)

ETBE has been proposed as a means for expanding the range of available oxygenates which have favorable octane and volatility blending characteristics, as well as the advantage of pipeline fungibility. ETBE can be made by reacting isobutylene with ethanol over a catalyst, similar to the MTBE process. Although ETBE has very good blending properties, economics currently favor MTBE production. Ethanol cost, even applying the 54 cent per gallon tax subsidy, is still considerably higher than the price of methanol.[29] However, if feedstock costs should favor ethanol, a number of MTBE plants in North America are being or have been modified for production of ETBE in addition to MTBE. It is estimated that about 53 thousand barrels per day of ETBE capacity, or about 812 million gallons per year, could be readily available,[30] if the economics turn favorable.

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4 Regulation of Alcohols and Ethers

4.1 HISTORY

4.1.1 Prior to the passing of the Clean Air Act Amendments of 1977, there were no federal or state regulations controlling the use or properties of fuels containing alcohols or ethers. Gasoline-alcohol blends were marketed in the 1930s and 1940s in Nebraska and surrounding states as Agrol, Alcoline, and Alky-Gas.[1,2] Low levels of alcohols, such as isopropyl alcohol, have been used since 1950 as carburetor antiicing additives. Beginning in 1969, Atlantic-Richfield Company (ARCO) used gasoline-grade tertiary-butyl alcohol in blends with gasoline in a number of marketing areas for about 10 years. From 1974 through 1977, a blend of 10 percent by volume ethanol and 90 percent by volume gasoline, known as gasohol, was tested in Nebraska. In 1978 the Nebraska Gasohol Commission commercially introduced gasohol, which was the beginning of widespread use of ethanol as a fuel component.[1]

4.1.2 Neat alcohols also were of interest as fuels. Henry Ford was an early proponent of neat alcohol fuels and in the 1880s he designed one of his early automobiles to run on ethanol.[2] General Motors Research investigated the use of ethanol as a fuel in the 1920s.[3] Methanol has been the fuel used to power Indianapolis 500 race cars since the 1950s.

4.2 CLEAN AIR ACT REQUIREMENTS

4.2.1 General

4.2.1.1 Attempts to achieve national goals for improved air quality and energy self-sufficiency often give rise to conflicting solutions. The Department of Energy (DOE) considers alcohols to be viable extenders of the U.S. gasoline supply and methanol as an automotive fuel for the future.[4] The EPA mandated the phasedown of lead antiknock compounds in gasoline beginning in 1980. The EPA implemented restrictions on gasoline vapor pressure beginning in 1989, which limited the use of butane, a component of high octane blending value. The implementation in 1995 of the toxics reduction requirement of the Clean Air Act Amendments of 1990 in many cases will reduce the aromatics content of gasoline, in part by dilution with oxygenates. Further, the Clean Air Act Amendments of 1990 required the use of oxygenates. The combination of these EPA regulations forces refiners and marketers of gasoline to consider new ways to restore the lost octane. One approach is to blend oxygenates into gasoline, but this is subject to certain legal and practical limitations.

4.2.1.2 The EPA is empowered to regulate fuel volatility and any other fuel property which, if uncontrolled, could contribute either directly or indirectly to air pollution. Under Section 211(f) of the Clean Air Act, as amended in 1977, unleaded gasoline marketed for use in vehicles manufactured after 1974 must be substantially similar to those fuels used during the federal emissions certification testing procedures. The EPA was concerned that oxygenated blends could adversely affect exhaust and evaporative emissions control systems. After recognizing the ad hoc commercialization of ethanol blends in 1978, the EPA began to impose restrictions.

4.2.1.3 The first potential restriction considered by the EPA eventually became a non-restriction. It dealt with gasohol, a blend of one part agriculturally-derived ethanol with nine parts finished gasoline. After the first Arab oil embargo in 1974, gasohol marketing was stimulated by a variety of tax incentives. When the “substantially similar” rule was written into the Clean Air Act Amendments of 1977, the EPA faced a dilemma. Gasohol was a politically popular fuel that could not technically be construed to be substantially similar to certification gasoline because it contained up to 3.7 percent by weight oxygen. However, the Clean Air Act Amendments of 1977 provided that the EPA could grant a waiver of Section 211(f) requirements if the applicant demonstrated that the fuel in question did not significantly deteriorate, or contribute to the deterioration of the performance of any motor vehicle emissions control system.

4.2.1.4 In 1978, gasohol interests applied to the EPA for a waiver. However, the EPA failed to render a determination of the application within the 180-day period provided for by law, and a waiver was thereby automatically granted for gasohol by operation of the Act. By permitting this automatic waiver, the EPA allowed gasohol blending but reserved its right to enforce Section 211 provisions in the future. The only restriction was the fuel consisted of 90 percent by volume unleaded gasoline and 10 percent by volume ethanol.

4.2.1.5 In 1981, the EPA ruled that unleaded fuels blended with oxygenates at concentrations of 2.0 percent by weight or less oxygen provided by aliphatic ethers and alcohols (other than methanol) qualified as being substantially similar.[5] All finished blends were required to meet at least one of the seasonal and geographical ASTM D 439 volatility class limits.[6] Some of the test procedures within the ASTM D 439 specification are considered unsuitable for use with oxygenated fuel blends. In 1991, EPA revised the “substantially similar” rule to allow fuels containing aliphatic ethers and/or alcohols (excluding methanol) to contain no more than 2.7 percent oxygen by weight. Also, the requirement involving ASTM D 439 was changed to the new specification for automotive spark-ignition engine fuel, D 4814-88.[6]

4.2.1.6 The “substantially similar” rule allowed oxygenates, such as ethanol, propyl alcohols, butyl alcohols, higher molecular weight alcohols, and ethers to be used at volume concentrations proportionate to their respective oxygen contents. Thus, compounds containing less oxygen that were more similar to hydrocarbons in chemical and physical characteristics than methanol could be used at higher volume concentrations. For example, the “substantially similar” rule nominally allows about 12 percent by volume butyl alcohol or 15 percent by volume MTBE in a typical gasoline (see Table 11). Methanol blends were excluded from the “substantially similar” rule at concentrations above 0.3 percent by volume because of questions concerning the effects of gasoline-methanol mixtures on fuel system components, water separation, and evaporative emissions.[7] Methanol was allowed at a maximum of 0.3 percent by volume, a level consistent with long-standing commercial applications as a fuel system deicer and as a cosolvent for other permitted fuel additives.

4.2.1.7 The 1978 waiver (effective December 16, 1978, but actually issued in 1979) for gasohol specified 10 percent by volume ethanol, and the original “substantially similar” rule permitted between 0 and 5.4 percent by volume of ethanol. Blends with more than 5.4 percent by volume and less than 10 percent by volume were not covered by exact language until 1982 when the EPA clarified the waiver and permitted concentrations of ethanol up to and including 10 percent by volume. The EPA does not mandate that blends containing up to 10 percent by volume ethanol must meet ASTM D 439 or D 4814 requirements. Thus, the direct addition of up to 10

Table 11—Some Oxygenated Compounds Approved by EPA for Use in Unleaded Gasoline

Compound[a]	Broadest EPA Waiver	Date	Maximum Oxygen, Weight %	Maximum Oxygenate, Volume %
Methanol	Substantially similar	July '81	—	0.3
Propyl Alcohols	Substantially similar	July '81	2.7	(9.6)[d]
Butyl Alcohols	Substantially similar	July '81	2.7	(11.5)[d]
Methyl tertiary-butyl ether (MTBE)	Substantially similar	July '81	2.7	(14.9)[d]
Tertiary-amyl methyl ether (TAME)	Substantially similar	July '81	2.7	(16.6)[d]
Isopropyl ether	Substantially similar	July '81	2.7	(17.3)[d]
Methanol and butyl alcohol or higher molecular weight alcohols in equal volumes	Substantially similar	July '81	2.7	7.4
Ethanol	Gasohol[b]	1979, 1982	(3.5)[d,e]	10.0
Gasoline grade tertiary-butyl alcohol (GTBA)	ARCO	1981	3.5	(15.7)[d]
Methanol + GTBA (1:1 maximum ratio)	ARCO (OXINOL®)	1981	3.5	(9.4)[d]
Methanol @5 volume % maximum + 2.5 volume % minimum cosolvent[f]	DuPont	1985	3.7	c
Methanol @ 5 volume % maximum + 2.5 volume % minimum cosolvent[g]	Texas Methanol (OCTAMIX)	1988	3.7	c

---

Notes:

[a] All blends of these oxygenated compounds are subject to ASTM D 439 volatility limits except ethanol. Contact the EPA for current waivers and detailed requirements, U.S. Environmental Protection Agency, Field Operations and Support Division (EN-397F), 401 M Street, S.W., Washington, D.C. 20460.

[b] See Chapter 4, Clean Air Act Requirements.

[c] Varies with type of cosolvent.

[d] Calculated equivalent for average specific gravity gasoline (0.737 specific gravity @60°F, *NIPER Gasoline Report*). Calculated equivalent depends on the specific gravity of the gasoline.

[e] Value shown is for denatured ethanol. Neat ethanol blended at 10.0 volume % produces 3.7 weight % oxygen.

[f] The cosolvents are any one, or a mixture of, ethanol, propyl alcohols, and butyl alcohols. Corrosion inhibitor is also required.

[g] The cosolvents are a mixture of ethanol, propyl, butyl, and higher alcohols up to octyl alcohol. Corrosion inhibitor is also required.

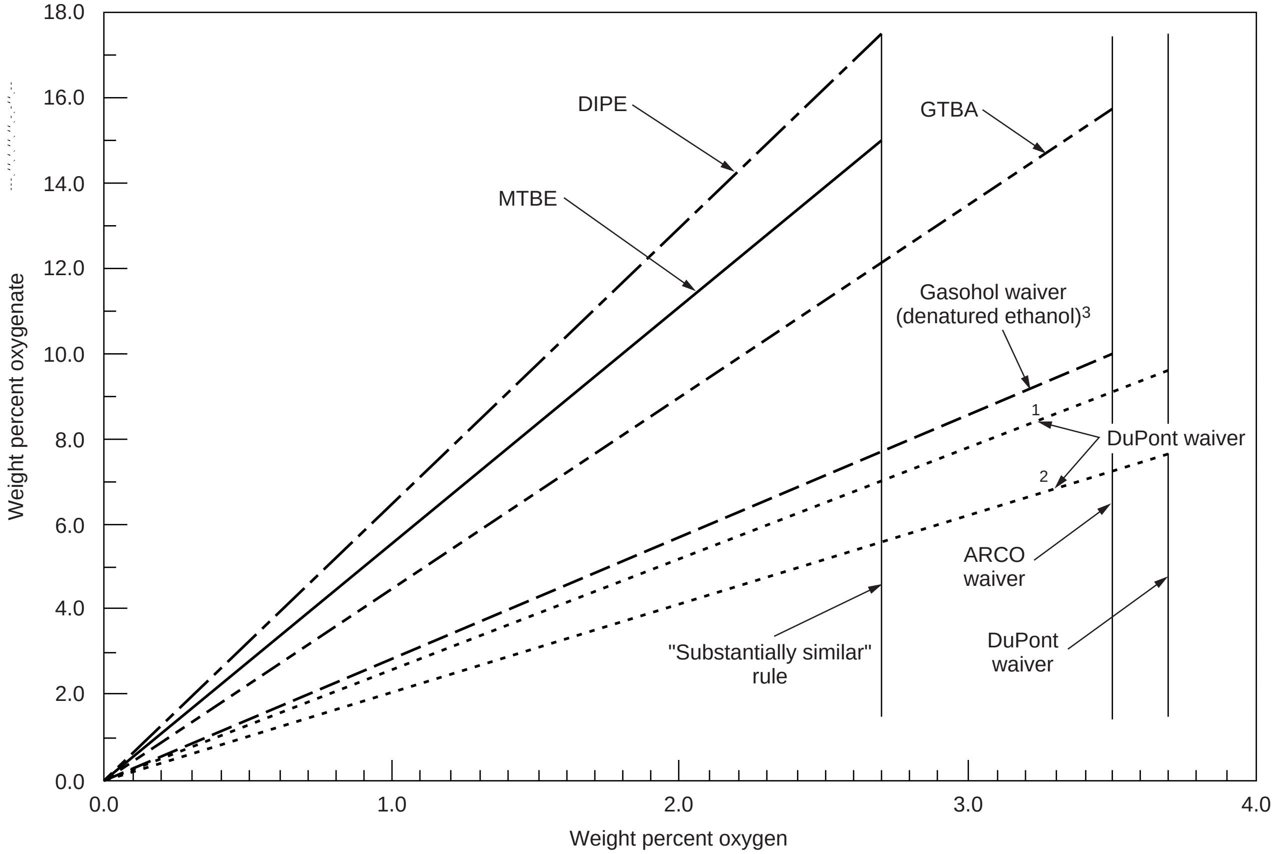
percent by volume of ethanol to unleaded gasoline can be made at distribution terminals or at other points in the distribution network. EPA allows up to 2 percent by volume of MTBE in the unleaded gasoline to which ethanol is added, if the MTBE is present only as a result of commingling in transport and storage and not purposely added as an additional component. Blending in such a manner, without regard for meeting ASTM D 4814 specifications for volatility, is commonly referred to as "splash blending."

4.2.1.8 The first waiver dealing with methanol concentrations above 0.3 percent by volume was granted to Sun Oil Company in 1979. It allowed the use of 2.75 percent by volume methanol with an equal volume of TBA up to a blend oxygen total of 2 percent by weight oxygen. Sun Oil Company demonstrated that cosolvents, namely higher molecular weight alcohols, reduced some of the adverse effects of methanol on volatility and water tolerance in blends. ARCO also received a waiver in 1979 to use up to 7 percent by volume TBA, which ARCO had marketed since 1969. These waivers were superseded by the "substantially similar" definition in 1981.

4.2.1.9 At the request of ARCO, the EPA granted a waiver in 1981 for the use of the following blends containing a maximum of 3.5 percent by weight oxygen: a) gasoline-grade TBA (GTBA), and b) OXINOL®, up to 1:1 volume ratio methanol in GTBA. At the maximum permitted level, methanol concentration in the finished gasoline blend could be as high as 4.8 percent by volume in typical gasoline. The highest allowable content of an oxygenate listed is 15.7 percent by volume GTBA. Figure 5 shows the relation between percent by weight oxygen and percent by volume oxygenate for a number of oxygenates.

4.2.1.10 The EPA granted a waiver request submitted by DuPont in 1985 for a maximum of 5.0 percent by volume methanol with at least 2.5 percent by volume cosolvent of ethanol, propyl, or butyl alcohols in the finished blend, up to a limit of 3.7 percent by weight oxygen, accompanied by specific corrosion inhibitors. In addition, the waiver incorporated a water tolerance or phase separation requirement.[8]

4.2.1.11 The EPA's concern in granting this waiver as DuPont requested was the potential effects of the combination of methanol and ethanol on evaporative emissions. Even though previous EPA waivers specified volatility limits according to ASTM D 439 for finished blends, EPA initially required that a special volatility restriction called Evaporative Index (EI) also be imposed before granting the waiver to DuPont in January 1985.[8] Upon petition the EPA subse-



Notes:

1. 5 volume percent methanol + 2.8 volume percent ethanol
2. 5 volume percent methanol + 4.7 volume percent butyl alcohol
3. Neat-ethanol blended at 10.0 volume percent produces 3.7 percent oxygen

Figure 5—Relationship Between Volume Percent Oxygenate and Weight Percent Oxygen in 0.748 Relative Density Gasoline

quently reconsidered and withdrew the EI requirement but emphasized that the ASTM standards be followed rigidly.[9]

4.2.1.12 Other waivers granted for oxygenates by EPA are summarized in Table 11.

4.2.2 Clean Air Act Amendments of 1990

4.2.2.1 The Clean Air Act Amendments of 1990 required states with carbon monoxide nonattainment areas to revise their state implementation plan (SIP) to require the use of oxygenated gasoline in the wintertime. The oxygenated gasoline programs are state administered programs and they began on November 1992 for 39 designated carbon monoxide nonattainment areas. Since then about a dozen areas have submitted requests to EPA seeking redesignation as being in attainment. Some states also are removing their requirements for oxygenated gasolines. For the current status of the oxygenated gasoline program, EPA and state officials should be contacted. EPA proposed guidelines for the program which stated the control period should be for at least four high carbon monoxide months (shorter periods would be accepted if the state can show no air quality impact). If the state chose an averaging control system, the minimum average oxygen content would be 2.7 percent by weight with a minimum oxygen content for each gallon of 2.0 percent by weight. Without averaging, each gallon must contain 2.7 percent by weight oxygen. The maximum oxygen content was 2.9 percent by weight for substantially similar oxygenates and 3.7 percent by weight for ethanol or methanol-cosolvent blends. Lower oxygen contents are allowed if a state can demonstrate that the higher oxygen levels of the EPA guidelines adversely affect air quality for pollutants other than carbon monoxide.

4.2.2.2 The Clean Air Act Amendments of 1990 also address fuel requirements for ozone nonattainment areas. The EPA classifies the ozone nonattainment areas into extreme, severe, serious, moderate, marginal, transitional, and incomplete categories. The law required reformulated gasoline (RFG) in the nine worst nonattainment areas (extreme and severe) effective January 1, 1995.

4.2.2.3 The law also allows other ozone nonattainment areas the option of choosing to have the RFG requirements apply to their areas (opt in) upon petition by the governor of their state. About 30 areas chose to opt in and of those about half have subsequently asked to opt out of the program. EPA issued a final rule on July 8, 1996, permitting opt-in areas (not required areas) to opt out of the RFG program under specified conditions. For the current status of the program, EPA should be contacted.

4.2.2.4 The final RFG rule was issued in 1994.[10] It consisted of two phases. Phase I, which became effective January 1, 1995, required a 15 to 17% reduction in both ozone forming VOC emissions during the summer and air toxics emissions throughout the year from vehicles. It specified the use of the "simple model" for 1995 through 1997, but permitted the "complex model" to be used earlier. The "complex model" had to be used after January 1, 1998. Phase II, which became effective January 1, 2000, requires a 25 to 29% reduction in ozone forming VOCs and a 20 to 22% reduction in air toxics from vehicles. It also specifies a 5 to 7% reduction in oxides of nitrogen emissions from vehicles during the summer.

4.2.2.5 Both the "simple model" and "complex model" reformulated gasoline are as of this writing required to have a minimum oxygen content. The requirement may be met on either a per gallon or average basis. The per gallon minimum is 2.0 percent oxygen by weight, which means that each and every gallon must contain at least 2.0 percent by weight. If averaging, the average minimum limit is 2.1 percent oxygen by weight and each gallon must contain at least 1.5 percent oxygen by weight. Higher limits for both per gallon and average apply to RFG areas that have been ratcheted by the EPA. The maximum allowed oxygen content for summer reformulated gasoline was originally 2.7 percent by weight with an option of 3.5 percent by weight on notice by states under specified circumstances. This was changed in 1996 to 2.7 percent by weight maximum oxygen for "substantially similar" oxygenates and to the maximum limit allowed under waivers (e.g., 10 percent by volume for ethanol). On notification by states, the maximum limit can be set at 3.2 percent oxygen by weight if the higher (waiver) level will interfere with attainment or maintenance of air quality standards.[11] The EPA still allows 10 percent by volume ethanol to be added to gasoline containing up to 2.0 percent by volume MTBE that is not purposely added, except the total oxygen content cannot exceed 4.0 percent by weight. The 4.0 percent by weight is the upper oxygen limit where "simple model" and "complex model" are applicable.

4.2.2.6 The oxygen requirements for federal RFG and for California Phase 2 RFG are summarized in Table 12. It should be noted that federal requirements take precedent over California requirements for designated federal ozone nonattainment areas.

Table 12—Oxygen Requirements for Reformulated Gasoline

Basis	Federal RFG	California Phase 2 RFG
Per Gallon, mass %		
Min.	2.0	1.8[d]
Max.	2.7[b] Substantially Similar 4.0[c] Ethanol	3.5
Average, mass %		
Min.	2.1	N/A
Cap for Average or Model[a], mass %		
Min.	1.5	0[d,e]
Max.	2.7[b] Substantially Similar 4.0[c] Ethanol	2.7

Notes:

[a] Applies to federal "simple" and "complex" models and California Predictive Model.

[b] Wintertime oxygenated RFG program for carbon monoxide nonattainment areas maximum is 2.9 mass %.

[c] Depends on relative density of base gasoline, actual maximum limit is 10 vol % ethanol. On notification of a state, the maximum limit can be set at 3.2 mass % if the higher level will interfere with attainment or maintenance of air quality standards. The 4.0 mass % is the upper oxygen limit where the "simple" and "complex" models are applicable.

[d] Federal 2.0 mass % minimum limit takes precedence in federal RFG areas.

[e] California 1.8 mass % minimum limit applies in wintertime only in specified areas.

4.2.3 Fuel and Fuel Additive Registration Regulations

4.2.3.1 Since 1975, under Section 211 (b) of the Clean Air Act, it has been unlawful to introduce into commerce any gasoline or diesel fuel and their respective additives unless they are registered with EPA. Any fuel or fuel additive, which was registered as of May 27, 1994, had to have a supplemental registration with additional data by November 27, 1994, in order to continue marketing the product. The registered products are then subject to a three-tier toxicological testing program. Tier 1 requires manufacturers to provide emissions characteristics, exposure analyses, and a literature search. If insufficient data exist, then manufacturers are required under Tier 2 to conduct a 90-day subchronic toxicity test on rodents with additional health effects testing for carcinogenicity/mutagenicity, teratogenicity, reproductive toxicity, and neurotoxicity. All Tier 1 requirements had to be submitted by May 27, 1997. Tier 2 requirements must be met by January 2004.

Tier 3 testing may be required at EPA's discretion after reviewing the Tier 1 and Tier 2 submission. A fuel or fuel additive which has not been previously registered, but is compositionally similar to a registered material can be registered as a registrable fuel or fuel additive and marketed. A new fuel or additive, which was not registered as of May 27, 1994, will not be registered until all Tier 1 and Tier 2 information is available.

4.2.3.2 To develop the information, a consortium of about 150 companies was formed. API is the agent for contracting the testing for the consortium. The oxygenates to be tested are ethanol, TBA, MTBE, ETBE, TAME, and DIPE. None of the waivered oxygenates containing methanol have undergone a supplemental registration. However, any of the previously registered waivered gasoline-methanol-cosolvent blends can be used after a supplemental registration is made and the required additional information submitted. The Tier 1 and Tier 2 requirements still must be submitted by May 27, 1997.

4.3 LEADED GASOLINE

Although the EPA established mandatory compositional limits for unleaded fuel blends, it does not regulate the use of oxygenates in leaded gasolines. A considerable range of formulations of leaded gasolines may have existed at retail outlets. However, effective January 1, 1996, the Clean Air Act Amendments of 1990 banned the use of any fuel produced with the use of lead additives in motor vehicles operating on a street or highway.

4.4 PUMP LABELING

During the wintertime oxygenated gasoline period in carbon monoxide nonattainment areas, federal law requires dispensing pumps to be labeled, "The gasoline dispensed from this pump is oxygenated and will reduce carbon monoxide pollution from motor vehicles." In addition there are state laws concerning dispensing pump labeling of gasoline-oxygenate blends. The labeling laws are not uniform. At least 29 states require labeling of the presence and type of alcohol in the fuel at the pump as a consumer protection measure. An additional 13 states require labeling for alcohols or ethers. One state requires labeling for oxygen.[12] In an attempt toward uniformity, the National Conference on Weights and Measures has issued the "Uniform Regulation For Fuels, Petroleum Products, and Automotive Lubricants" which provides model wording for states to adopt (last amended in 1991). Because of the introduction of several ethers and their variable usage, a new model labeling regulation has been developed so dispensing pump labels would not have to be changed after each fuel delivery. The new regulation changes the labeling trigger from 1.0 percent by volume of alcohols or ethers to 1.5 percent by weight oxygen. Further, the predominant type of oxygenate would be labeled (e.g., "contains ethanol" or "with MTBE"). Where mixtures of ethers are present, the label would read "contains MTBE or other ethers."

4.5 NEAT AND NEAR-NEAT ALCOHOLS FUELS

There are no federal regulations controlling the use of alcohols as fuels where the alcohol is the primary constituent of the fuel. However, under the Energy Policy Act of 1992 (EPACT), methanol, denatured ethanol, and other alcohols cannot be defined as an alternative fuel unless the alcohol concentration is 85 percent by volume or more and it is blended with gasoline or other fuels. The Secretary of DOE can allow alcohol concentrations as low as 70 percent by volume to provide for cold starting, safety, or other vehicle functions.

4.6 REFERENCES

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11. U.S. Environmental Protection Agency, "Regulation of Fuels and Fuel Additives: Revision to the Oxygen Maximum Standard for Reformulated Gasoline," *Federal Register*, Vol. 61, No. 58, 25 March 1996, pp. 12030-12041.

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5 Alcohols and Ethers Blended with Gasoline

5.1 GENERAL

5.1.1 Oxygenates provide several significant engine performance benefits particularly for older, non-computer controlled cars when used as supplements to gasolines. Major incentives for their use are reduced exhaust emissions, improved octane ratings and extension of petroleum supplies. As discussed in Chapter 2, the presence of the oxygen atom in the alcohol or ether molecule imparts properties that are quite different from those of hydrocarbons. In turn, a gasoline-oxygenate blend may have physical and chemical characteristics that are very different from either the oxygenate or the base gasoline. Many blend properties are linearly proportional to the amount of each component and are predictable.

5.1.2 Other properties of gasoline-oxygenate blends must be determined empirically. Volatility characteristics of gasoline-alcohol blends can be especially anomalous to those of neat gasoline. In turn, vehicle response to volatility properties of gasoline-alcohol blends often is different from operation on neat gasoline. Because of the strong molecular polarity of MeOH, gasoline-MeOH blends had characteristics of volatility, water tolerance and materials compatibility, which were dissimilar to those of gasoline. In an effort to offset vehicle problems posed by MeOH, mixtures of cosolvents and corrosion inhibitors with MeOH were used commercially in gasoline blends during the 1980s.[1,2,3] As indicated in Chapter 4, currently, no supplemental registration exists for a waiver to allow the use of MeOH in gasoline. As neat motor fuel, however, MeOH has distinct advantages for vehicles specifically tailored for its use. (Alcohols as neat or near-neat fuels are covered in Chapter 6.)

5.1.3 Besides oxygen content, other properties of blends that primarily affect vehicle operation are energy content, volatility and resistance to spark knock. Water tolerance characteristics also are of concern because of the effects of water on driveability should phase separation occur. Chemical compatibility of vehicle fuel system materials and blends is critical to vehicle durability.

5.2 HEATING VALUE EFFECTS

The heating value of oxygenates is less than that of gasoline. Except for MeOH, EtOH has the lowest energy content of all oxygenated hydrocarbons, one-third less than typical gasoline on a volumetric basis and 37 percent less on a mass basis. At the upper concentration of EtOH allowed by the EPA, the maximum heating value deficiency of a gasoline-EtOH blend, compared to gasoline, is 3.4 percent. Table 13 lists maximum decreases for individual oxygenates. Losses range from 2.0 percent for TAME to 3.4 percent for EtOH. Lower heating value of oxygenated blends is reflected in vehicle fuel economy, which will be discussed later in this chapter.

5.3 EFFECTS ON BLEND VOLATILITY

Volatility characteristics considered important to vehicle operation and emissions are distillation, vapor pressure, and vapor-liquid ratio (*V/L*). Alcohols have been found to influence volatility parameters of a gasoline blend to a greater degree than ether compounds.

5.3.1 Distillation

5.3.1.1 Oxygenates, except for GTBA, have constant boiling points ranging from 131°F for MTBE to 187°F for TAME. When blended with gasoline, which generally boils over a range of 80°F to 437°F temperature, oxygenates usually are located in the initial 50 percent evaporated fraction of the blend.

5.3.1.2 Adding alcohols to hydrocarbons or gasoline depresses the boiling temperature of individual hydrocarbons. The effect of alcohol addition on the shape of a distillation curve is shown in Figure 6.[4,6] Addition of 10 volume percent significantly reduces T_{50}, the temperature for the first 50 percent of the fuel to evaporate. Alcohols depress the boiling point slightly less for aromatic hydrocarbons than for aliphatic hydrocarbons. Higher molecular alcohols such as GTBA have lesser effects on boiling point depression. Ethers, such as MTBE, have the same effect on distillation as the addition of a hydrocarbon of the same volatility. Fifteen volume percent MTBE significantly lowers the distillation temperature curve of gasoline between 15 percent and 50 percent evaporated.

5.3.1.3 The depression of the mid section of a gasoline distillation curve caused by the addition of lower boiling point alcohols and ethers raised questions about the necessity for blends to match historical specifications for gasoline distillation characteristics and vapor pressure.[4,5] Traditionally, specifications for volatility of automotive gasolines have been based upon technical evidence of vehicle requirements and environmental applications. Studies of volatility effects of gasoline-oxygenate blends on vehicle driveability will be covered later in this chapter.

Table 13—Heating Value of Gasoline-Oxygenate Blends

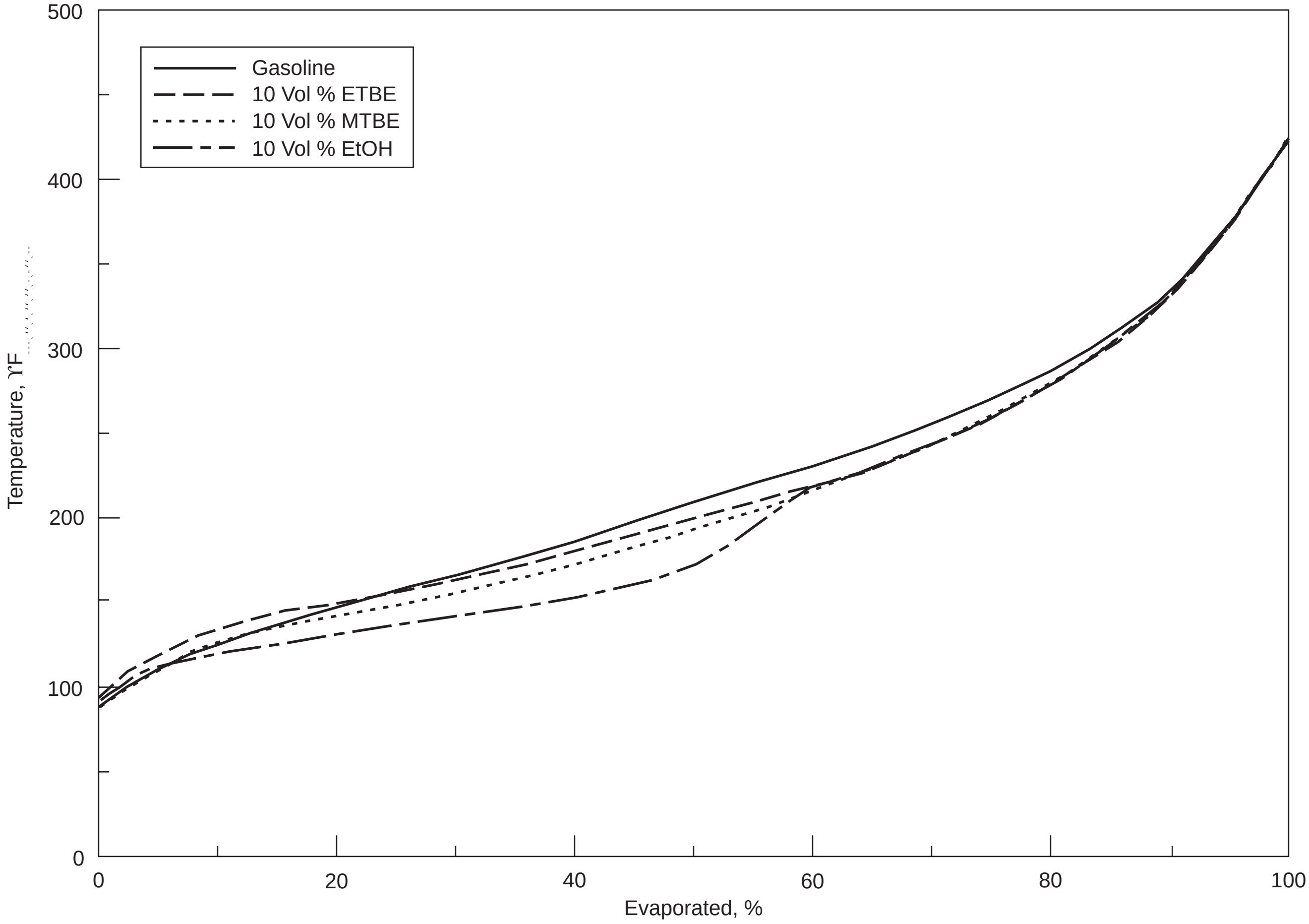
Oxygenate	Max Permitted Concentration[a] (gals/gal blend)	Lower Heating Value[b]: For max Conc. Oxygenate, Btu	Lower Heating Value[b]: Gasoline-Oxygenate Blend (Btu/gal @ 60°F)	Lower Heating Value[b]: Gasoline-Oxygenate Blend % Decrease
None	—	0	114,500[c]	0
Methanol	0.003	170	114,330	0.1
Ethanol	0.100	7,600	110,650	3.4
IPA	0.096[b]	8,390	111,900	2.3
TBA	0.157[b]	14,770	111,300	2.8
MTBE	0.149[b]	13,930	111,370	2.7
TAME	0.166[b]	16,700	112,190	2.0
ETBE	0.173[b]	16,780	111,470	2.6
DIPE	0.177[b]	17,700	111,930	2.2

Notes:

[a] See Chapter 4 for oxygenate concentrations permitted by EPA.

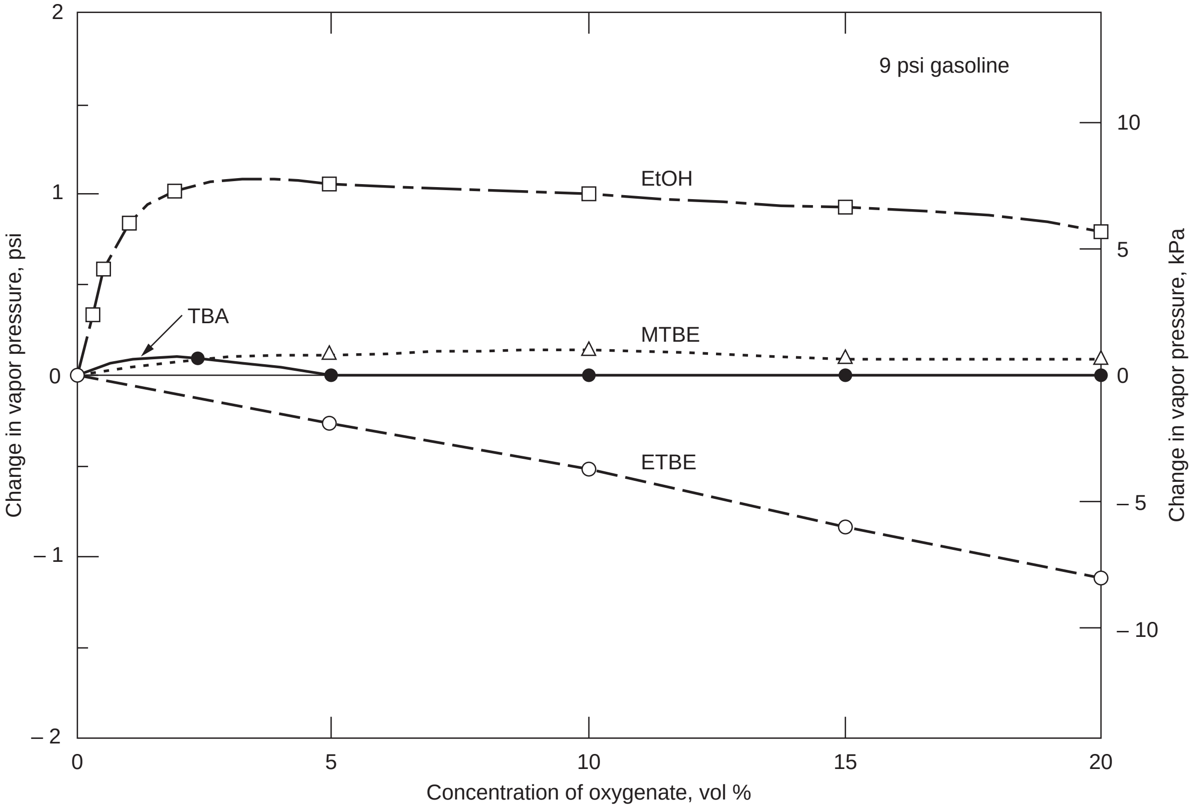
[b] Concentrations vary with density of the base fuel. This value was calculated for gasoline with 0.748 relative density at 60/60°F.

[c] For average non-oxygenated gasoline with 0.748 relative density @60°F.



Source: Reference 4.6

Figure 6—Effect of Oxygenates on Distillation



Source: Reference 4, 6

Figure 7—Effect of Oxygenates on Vapor Pressure

5.3.2 Vapor Pressure

5.3.2.1 Vapor pressure is another important volatility parameter of gasoline affected by addition of oxygenates, particularly alcohols. Aliphatic ethers have blending characteristics similar to hydrocarbons and change blend vapor pressure in linear relationship with the vapor pressure of the ether and its concentration. Ethers affect gasoline blend vapor pressure much the same as hydrocarbons of equivalent vapor pressure.[4,6] Figure 7 shows that MTBE, with a vapor pressure of 8 psi, changed the vapor pressure of 9 psi base gasoline very slightly. ETBE, with 4 psi vapor pressure, reduced the vapor pressure from that of the base gasoline in linear fashion, similar to the effect of a hydrocarbon component.

5.3.2.2 Alcohols, in contrast to ethers, always increase hydrocarbon blend vapor pressure, although not in proportion to alcohol vapor pressure or concentration. The physical phenomenon of molecular polarity is responsible for this behavior. Polar molecules have affinity for other molecules in proportion to the degree of mutual polarity. At room temperature, low molecular weight substances such as water or light alcohol such as MeOH, would be gases were they not collapsed into liquids by the highly cohesive molecular forces of hydrogen bonding. However, when MeOH is dissolved in a non-polar solvent like gasoline, its molecules become physically separated. The physical separation weakens molecular cohesion, and MeOH behaves like a gas. The release of alcohol molecules as gas causes an anomalous increase in vapor pressure that peaks at quite low concentrations of MeOH. The gaseous molecular release of EtOH from gasoline is much less pronounced, and is insignificant for higher carbon number alcohols.

5.3.2.3 As listed in Table 14, the vapor pressures of EtOH, IPA and GTBA, 2.3 to 1.8 psi, are much lower than that of gasoline, seven to 15 psi. As explained above, low molecular weight alcohol in gasoline forms a nonideal solution that does not follow linear blending relationships and causes increased blend vapor pressure. Figure 7 illustrates that, in 9 psi gasoline, 2 percent EtOH with 2.3 psi vapor pressure, increased blend vapor pressure about 1.0 psi. Additional amounts of EtOH did not further increase vapor pressure. Considering the phenomenon of molecular polarity, the plateau shape of the curve suggests that EtOH vapors exist in disproportion to alcohol concentration of the blend. Therefore, the effect of EtOH is greater in gasolines with lower vapor pressure.

Table 14—Vapor Pressure Blending Values of Oxygenates

Oxygenate	Vapor Pressure, psi	Concentration Permitted,[b] Volume %	Blending Value Vapor Pressure, psi	Maximum Vapor Pressure Change,[d] psi
MeOH	4.6	0.3	40	—
EtOH	2.3	10.0	18	+0.9
IPA	1.8	9.6[c]	14	+0.5
GTBA	1.8	15.7[c]	9	0.0
MTBE	7.8	14.9[c]	8	–0.2
TAME	1.5	16.6[c]	2	–1.2
ETBE	4.0	17.3[c]	4	–0.9
DIPE	4.9	17.7[c]	0.7	–1.5
Gasoline[a]	7 – 15		7 – 15	

Notes:

[a] Gasoline without oxygenate.

[b] See Chapter 4 for oxygenate concentrations permitted by EPA.

[c] Concentrations vary with density of the base fuel. This value was calculated for gasoline with 0.748 relative density at 60/60°F.

[d] Change for a 9.0 psi vapor pressure gasoline without oxygenate.

5.3.2.4 Figure 8 shows that the vapor pressure effect of EtOH is less in gasolines of higher vapor pressure.[6] The explanation for this result is that the partial pressure fraction generated by the alcohol mole fraction is constant for a given temperature, regardless of how much partial pressure is contributed by the gasoline. To compensate for the vapor pressure contribution of alcohol addition, gasoline-alcohol blends require special tailoring of the hydrocarbon content.

5.3.2.5 Table 14 compares blending values for vapor pressure of oxygenates that can be used for calculations of the vapor pressure for gasoline-oxygenate blends containing oxygenate near the maximum permitted concentration. EtOH has a blending value of 18 psi, approximately eight times that of its neat state. The vapor pressure of a gasoline-EtOH blend can be adjusted by removal of all of the butanes and reducing the pentanes. However, this action would produce a distillation curve with a prominent flat segment that could adversely affect vehicle driveability characteristics during cold start and drive away. Because of the impracticality of hydrocarbon adjustment of the vapor pressure of gasoline-alcohol blends containing 9 – 10 volume percent EtOH, the U.S. EPA issued Phase II volatility regulations for conventional gasoline in 1992 which permitted gasoline-EtOH blends to exceed ASTM specifications for vapor pressure by 1.0 psi during the summer. Gasoline-alcohol blends containing IPA and/or GTBA, with blending values of 14 and 9 psi, are not allowed the exemption of 1.0 psi that was granted gasoline-EtOH blends. For these blends, vapor pressure must be adjusted by means of hydrocarbon compounding.

5.3.2.6 When gasoline-alcohol blends are commingled with gasoline, as they might be in routine product handling or refueling, the effects of alcohol in the blend are the same as those described. Figure 9 shows that a mix of a gasoline-EtOH blend with gasoline of the same vapor pressure, in this case 9 psi, resulted in significantly increased vapor pressure.[7] The vapor pressure peaked to 9.8 psi for a mixture containing 20 percent gasoline-EtOH blend and 80 percent gasoline. The increase of 0.8 psi was about the anticipated amount from an addition of 2 percent EtOH (20 percent of 10 percent = 2 percent).

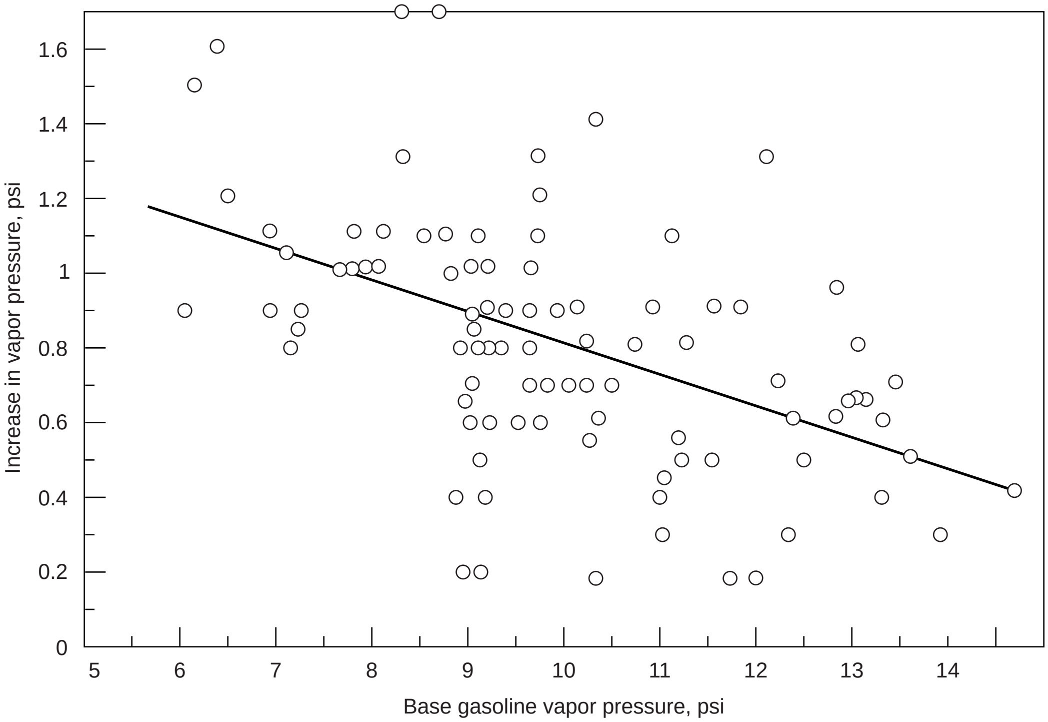
5.3.2.7 Measurement of vapor pressure of gasoline-alcohol blends requires techniques that eliminate the possibility of water contamination during heating because of the alcohol's affinity for water. New ASTM procedures[8,9,10] have been developed for use with oxygenated blends and replaces the time-honored Reid Vapor Pressure test.

5.3.3 Vapor to Liquid Ratio

5.3.3.1 At elevated operating temperatures, highly volatile fuel can cause vehicle vapor lock and increased evaporative emissions. Vehicle vapor lock is caused by excessive vapor that displaces liquid in the fuel system and results in fuel starvation and power loss. A gasoline volatility parameter, Vapor-Liquid Ratio or *V/L*, is a useful predictor of gasoline performance in a fuel system at high temperature. The temperature for a specific *V/L* either can be measured or calculated for gasoline by using a combination of distillation values and vapor pressure. Automotive engineering experience has determined that a *V/L*=20 correlates best with vapor lock protection with most cars. Temperatures for *V/L*=20 for various geographical areas and seasons are specified by ASTM and SAE.[11,12]

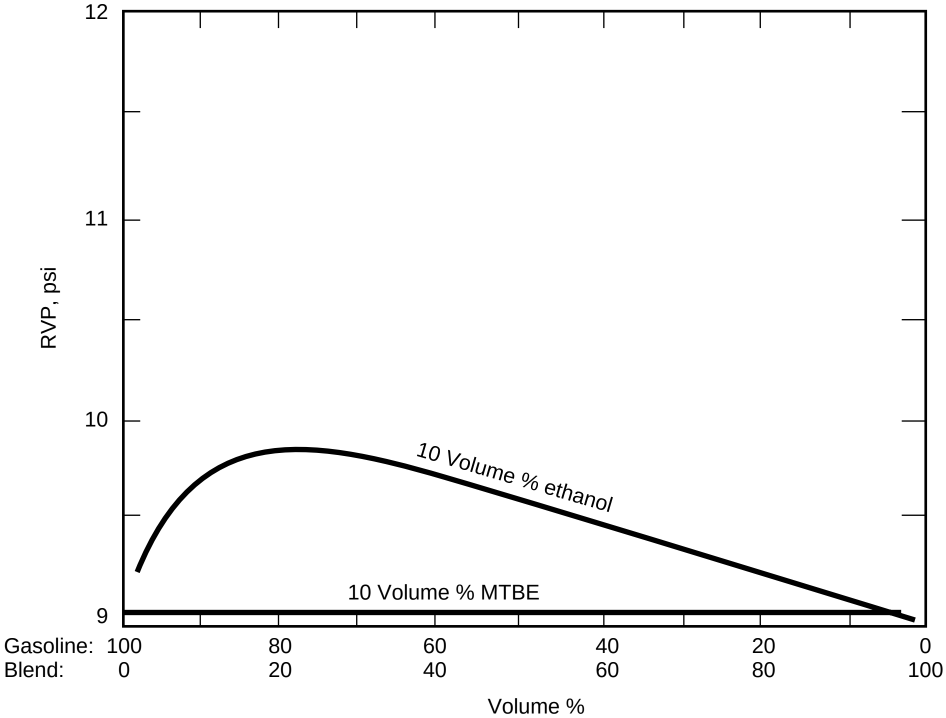
5.3.3.2 ASTM D 4814, Standard Specification for Automotive Spark-Ignition Engine Fuel, includes volatility requirements for gasolines according to geographical areas of the U.S. and seasonal periods. The schedule applies specifications for both volatility, in terms of vapor pressure and distillation, as well as for temperature for *V/L*=20. ASTM D 4814 specifications apply to all conventional gasolines and gasoline-oxygenate blends.[11] Because EtOH is splash blended, volatility requirements may not always apply. Specifications for federal and California reformulated gasolines are not included in ASTM D 4814.

5.3.3.3 Calculations of temperatures for specific *V/L* of gasoline-alcohol blends using ASTM procedures do not predict measured values. Figure 10 shows that the correlation of calculated versus measured temperatures for a *V/L*=20 for gasoline



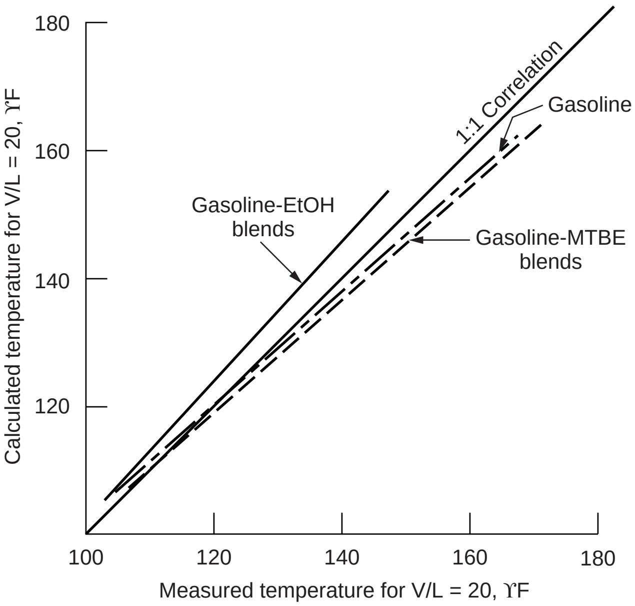
Source: Reference 6

Figure 8—Effect of EtOH Addition on Vapor Pressure of Base Gasoline



Source: Reference 7

Figure 9—Effect of Commingling a Gasoline and a Gasoline-EtOH Blend of the Same RVP



Source: Reference 13, 14

Figure 10—Calculated Versus Measured Temperature for *V/L* = 20

and for gasoline with MTBE are quite good.[13,14] The equations predicted slightly lower temperature values for gasoline-MTBE blends, and higher than measured temperature values for gasoline-EtOH blends. Obviously a higher than measured temperature predicts better vapor lock protection than can be delivered. ASTM recommends against calculations to determine temperature for *V/L* for all gasoline-oxygenate blends.

5.3.3.4 Figure 11 shows how the addition of butane and alcohols changed the temperatures at which various *V/L*s occurred.[15] Higher temperatures for a given *V/L* indicate better vehicle fuel handling at high temperature. For example, the reference gasoline reached a *V/L*=20, $T_{V/L=20}$, at a temperature of 160°F. Adding five-volume percent butane to the reference gasoline reduced the $T_{V/L=20}$ to 138°F, which, coincidentally, is the same temperature produced by the addition of 10 volume percent EtOH. The SAE and ASTM specification for $T_{V/L=20}$ for the highest temperature service in the United States is 140°F.

5.4 LABORATORY OCTANE EFFECTS

5.4.1 Oxygenates are attractive as gasoline blending components to increase antiknock performance or octane quality. Adding small percentages of oxygenates to gasoline can produce large gains in laboratory octane ratings. Each volume percent of an oxygenate added to a typical unleaded gasoline, with 87 (R + M)/2 octane, increases blend octane between 0.1 and 0.3 numbers. In higher-octane gasoline, incremental octane gains are less. Blending octane values, expressed as (R + M)/2, of oxygenates are shown in Table 15.

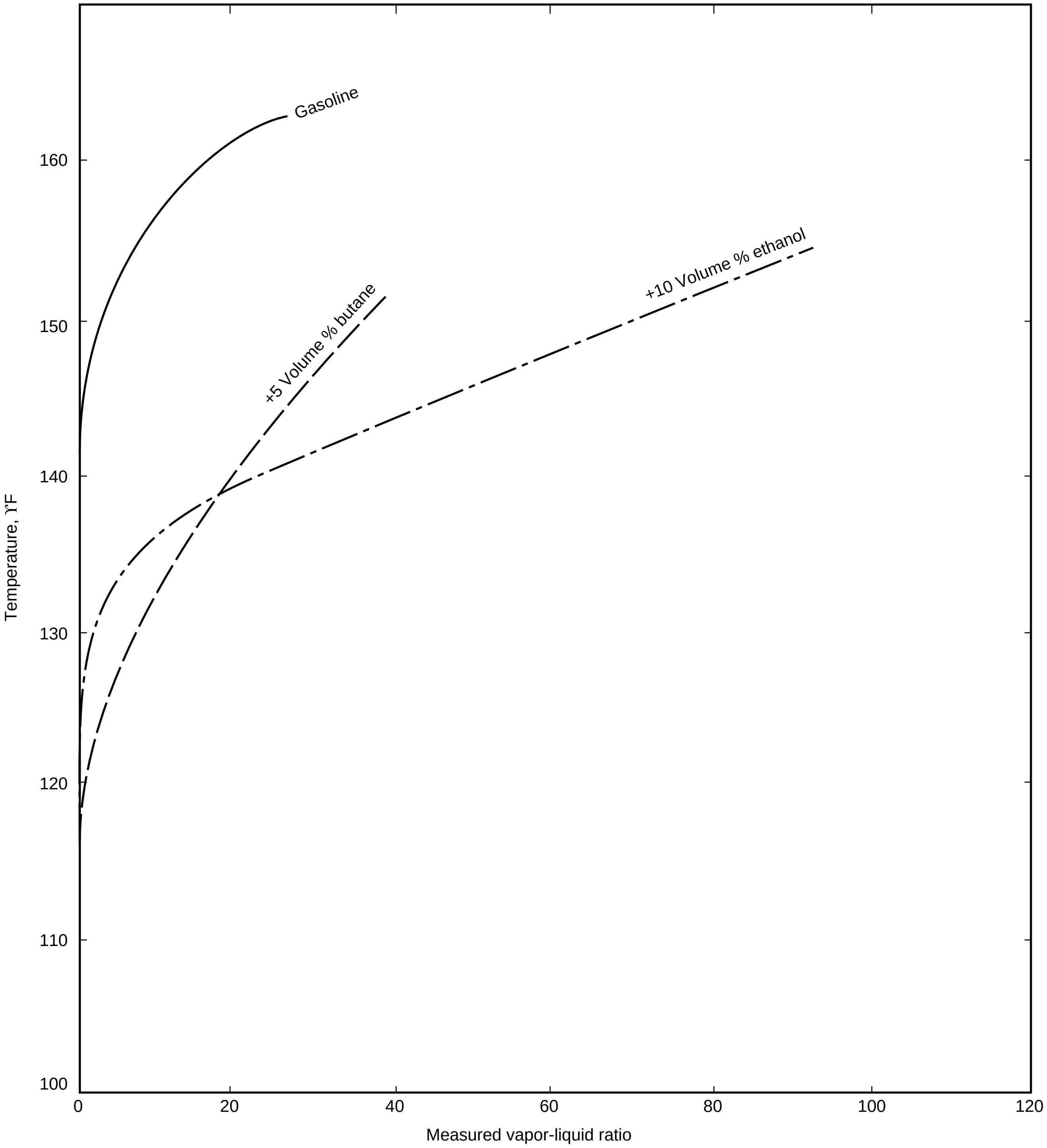
5.4.2 Of these oxygenates, MeOH has the highest octane blending value, 119 (R + M)/2, but, as discussed previously, is not currently used in blends. EtOH also offers superior blending octane value. At its permitted limit, it provides a boost of almost three numbers. Higher molecular weight alcohols have lower blending values but, nevertheless, are very attractive as octane improvers. Antiknock performance improvement from alcohol results mainly from charge cooling within the engine. The high latent heat of vaporization of alcohol reduces charge temperature well into the process of combustion and promotes cooling of the end gas.[16] A gasoline-alcohol blend with 10 volume percent EtOH has about 20 percent greater latent heat of vaporization than gasoline producing the same net combustion energy. As discussed later, however, charge cooling benefits of gasoline-alcohol blends have not been found to importantly reduce vehicle exhaust emissions of NO_X.

5.4.3 Laboratory octane improvement from ethers at maximum allowable concentration is typically three or more octane numbers. The superior antiknock performance of ethers results from combustion characteristics rather than vaporization differences. Vaporization properties of ethers are similar to those of hydrocarbons and do not appear to be responsible for antiknock benefits.

5.5 WATER SENSITIVITY AND TOLERANCE

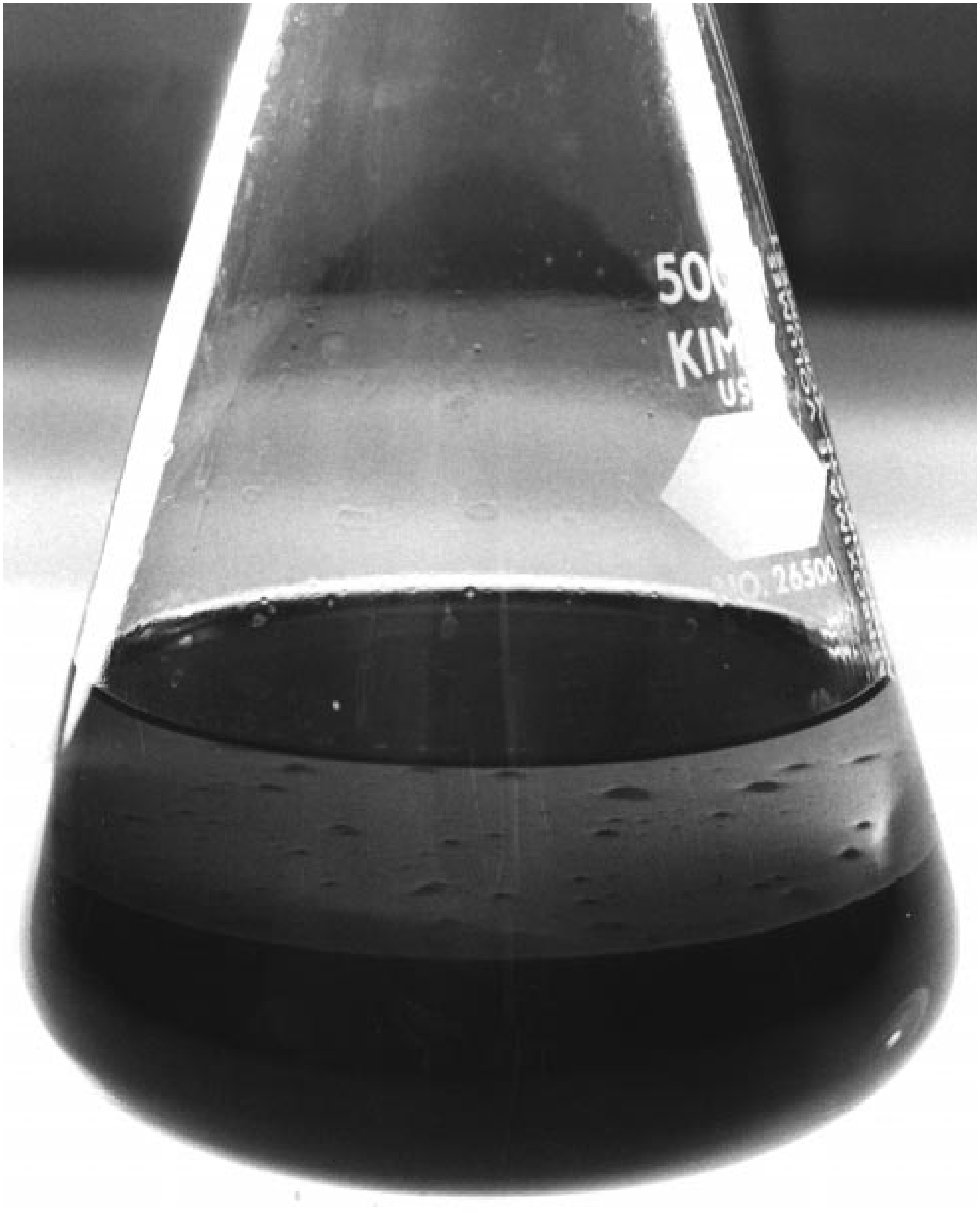
5.5.1 The solubility characteristics of alcohol in gasoline depend upon the relative influence of the hydrocarbon and the hydroxyl group of the molecule. The hydroxyl groups attached to short hydrocarbon chains, such as MeOH and EtOH, exerts more affinity for water and less for a hydrocarbon. Alcohols with longer hydrocarbon chains are more soluble in gasoline. When small amounts of water are present in a gasoline-EtOH blend, hydrogen bonds form between water and EtOH molecules and result in the separation of the water-alcohol phase from the gasoline. Higher order alcohols, such as IPA and GTBA, are more soluble in gasoline than EtOH and have less problems with water separation. Ethers also have little affinity for water and do not separate.

5.5.2 Figure 12 is a photograph showing phase separation.[17] Paraffinic hydrocarbons predominate in the upper phase, while the lower phase consists primarily of alcohol, water, and small amounts of aromatic hydrocarbons.[18] Because alcohol is less soluble in gasoline at low temperature, phase separation tendency increases as temperature decreases, as shown in Figure 13. For 10 volume percent EtOH in a blend with a gasoline containing 25 volume percent aromatics, phase separation began at 70°F with the presence of 0.7 volume percent water. At –20°F, phase separation occurred with about 0.4 volume percent water in the blend. A gasoline with a lower aromatic



Source: Reference 15

Figure 11—Effect of EtOH and Butane on Vapor-Liquid Ratio



Source: Reference 17

Figure 12—Photograph of Gasoline-Alcohol Phase Separation

Table 15—Octane Boost with Selected Oxygenates

Oxygenate	Concentration Permitted[a] (Volume Percent)	Typical Blending Value[b] (R + M)/2	Boost at Concentration Permitted[c] (R + M)/2
Methanol	0.3	119	0.1
Ethanol	10.0	115	2.8
IPA	9.6[d]	106	1.8
TBA	15.7[d]	97	1.6
MTBE	14.9[d]	110	3.4
TAME	16.6[d]	105	3.0
ETBE	17.3[d]	111	4.2
DIPE	17.7[d]	107	3.5

Notes:
[a] See Chapter 4 for oxygenate concentrations permitted by EPA.
[b] Octane blending values vary with oxygenate concentration, base fuel octane, and composition. See Glossary, Appendix A, Blending Value.
[c] Octane boost is calculated for 87 octane (R + M)/2 unleaded gasoline.
[d] Concentrations vary with density of the base fuel. This value was calculated for gasoline with 0.748 relative density at 60/60°F.

content exhibited lower water tolerance. Once separation begins, additional water will add to the water phase.

5.6 VOLUME EXPANSION OF GASOLINE-EtOH BLENDS

A small volume expansion occurs when EtOH is added to gasoline. At 10 volume percent EtOH, about a 0.1 percent increase in volume was measured in a blend with gasoline of 0.794 relative gravity. The expansion effect increased at higher EtOH concentrations, peaking at about 20 volume percent EtOH.[15] Another study reported as much as 0.6 percent increase due to 12.5 volume percent EtOH.[19] The expansion effect is greatest in gasolines of high density. In this document, no attempt has been made to adjust any values or results for possible expansion effects of EtOH in blends.

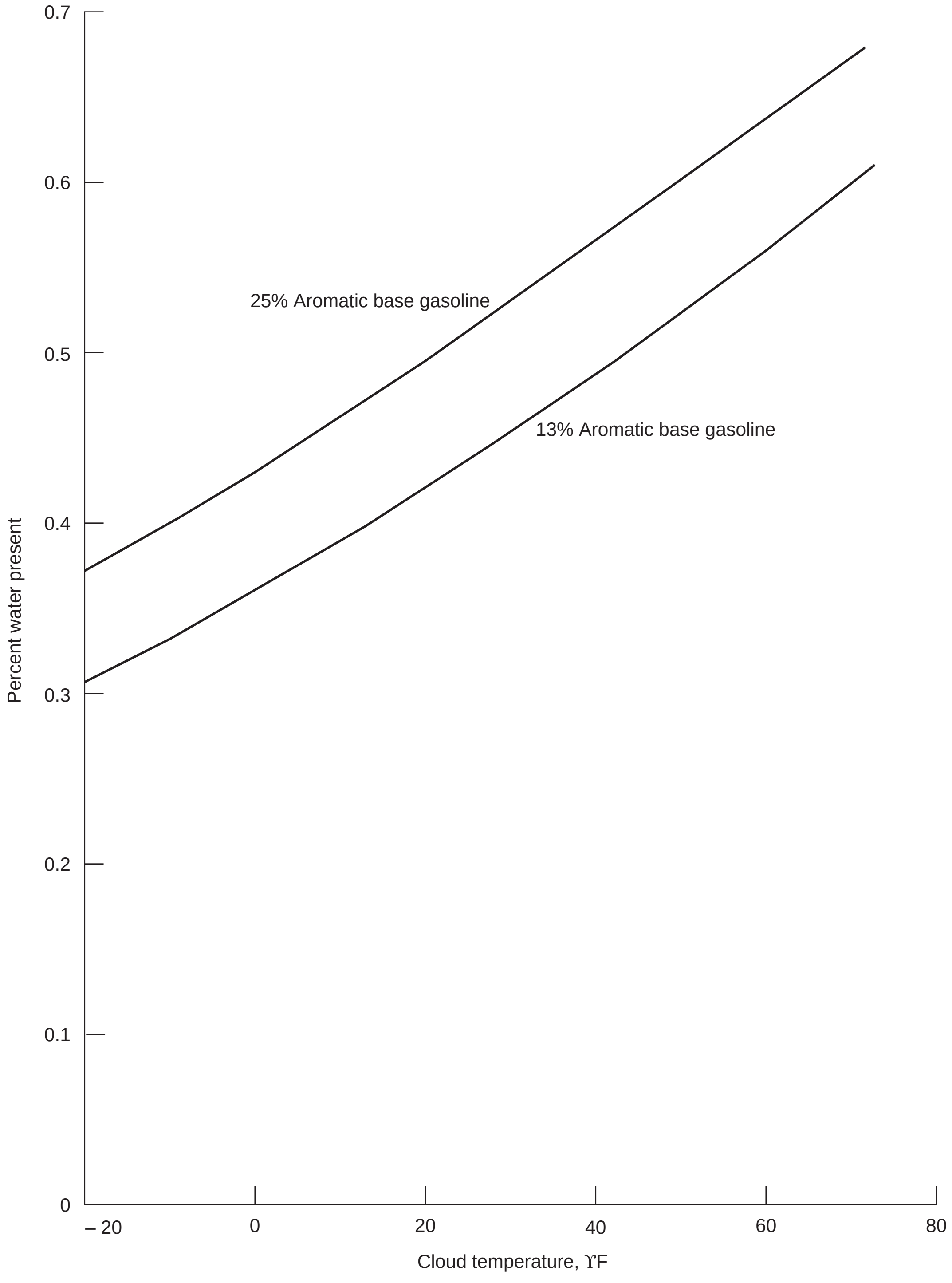
5.7 VEHICLE PERFORMANCE OF GASOLINE-OXYGENATE BLENDS

5.7.1 Acceptance of oxygenated gasolines was hindered in the 1980s by the wide variety of vehicle technology in use that had been designed to operate on gasoline. Since the 1960s, vehicle technology had been pursued as the key to eliminate automotive air pollution. During the 1970s and 1980s, in its effort to reduce national fuel consumption, the U.S. government mandated the auto industry to increase vehicle fuel economy and encouraged gasoline suppliers to use alcohol as a gasoline extender. Concurrently, Federal and California timetables for reduced vehicle emissions pressured the auto industry to expedite new technology to the marketplace. Many vehicles that were engineered to run on gasoline simply were not suitable for operation on gasolines blended with alcohol.

5.7.2 Gasoline blends containing either MeOH or EtOH were found to have caused swelling of certain fuel system elastomers.[20,21,22,23] Phase separation problems with gasoline-ethanol blends were reported to have caused corrosion of vehicle fuel tanks and supply lines.[20,24] Engines of older vehicles without computer controls encountered fuel mixture enleanment with gasoline-oxygenate blends, and often had problems of misfiring, surging and stalling. As late as 1987, most auto manufacturers remained cautious about possible side effects of oxygenated gasolines on driveability and fuel system durability. Nine of ten auto manufacturers surveyed by EPA in 1987 cautioned new car customers that, if driveability problems occurred with the use of gasoline containing 10 percent EtOH, gasoline should be used.[25] The tenth manufacturer specifically recommended against the use of any oxygenated gasoline.

5.8 VEHICLE TECHNOLOGY FACTORS

5.8.1 Table 16 summarizes the variety of vehicle emission control devices generally found on vehicles of several model years. Closed crankcase ventilation, initiated in 1960 models and employed currently to control emissions of blow-by gases, ranks as the most cost-effective control for hydrocarbon emissions. Control of evaporative hydrocarbon emis-



Source: Reference 18

Figure 13—Water Tolerance of Gasoline—10% EtOH Blend

Table 16—Light Duty Vehicle Emission Control Technology

Emission Control Device	Model Year Generally Available 1973	1983-5	1989	1994	1998
Closed Crankcase Vent	X	X	X	X	X
Open Loop Carburetor	X	X			
Open Loop Port Fuel Inj.	X				
Exhaust Gas Recirculation	X	X	X	X	X
Exhaust Air Injection	X	X	X	X	
Evap.Emission Trap	X	X	X	X	X
Closed Loop Carburetor		X			
Closed Loop TBI		X	X		
Closed Loop Port Fuel Inj.		X	X	X	
Closed Loop Sequential Port FI		X	X	X	
Adaptive Learning Control		X	X	X	
Transient Adaptive Learning				X	X
Exhaust Oxidation Catalyst	X				
Three-Way Catalyst (3WC)	X	X	X	X	
Oxidation + 3WC	X	X	X	X	
Secondary Oxygen Sensor			X	X	X
Warm-up Catalyst				X	X

sions, by means of a simple charcoal trap, also has continued to prove satisfactory. Exhaust gas recirculation, introduced in the early 1970s primarily to provide NO_x control, remains useful in several variations on current vehicles.

5.8.2 Prior to the emphasis on emissions reduction, changes of gasoline composition were motivated by needs expressed by the auto industry, usually for higher octane performance or controlled volatility. A milestone change in gasoline occurred with the widespread voluntary introduction of unleaded regular grade gasoline in 1971. Unleaded gasoline helped increase the durability of EGR systems and, more important, allowed exhaust oxidation catalysts to become commercial reality. Government mandates required that unleaded gasoline with 91 RON be generally available by July 1974. Elimination of the use of lead antiknock compounds stressed refinery capabilities for high-octane hydrocarbons. The high octane blending value of certain oxygenates was very attractive to gasoline suppliers.

5.8.3 Under certain conditions, oxygenates in gasoline reduce exhaust emissions of HC and CO. Older vehicles with open loop carburetors calibrated with richer than stoichiometric air-fuel ratios on gasoline, have been found particularly responsive.[5,26,27,28,29,30,31] In those vehicles, increased oxygen content of the fuel leaned the air-fuel mixture of the engines and produced less HC and CO. In late model cars, the benefit of oxygenates on reducing emissions is nil. Also, it has been common engineering practice to calibrate air-fuel mixtures for rich operation during warm up of an engine. Emissions of CO and HC, which are highest during low temperature starting and driveaway, have been reduced by the addition of oxygenate to gasoline. Oxygenated gasoline also leans rich mixtures that result from operation of open loop carburetors at a high altitude.[30] The effectiveness of oxygenates in older cars in the reduction of CO resulted in regulations (discussed in Chapter 4) that necessitate the addition of oxygenate to winter gasolines in certain areas of the U.S.

5.8.4 Technical summaries of available data concerning alcohols and ethers as fuels were published by API in 1971, 1976 and 1988.[32,33,34] The 1988 assessment included exhaust emissions findings from several sources, which indicated that, oxygenates reduced, or did not increase, average HC and CO emissions from vehicles with either open or closed loop fuel control. Oxygenate effects on NO_x ranged from decreases to increases, without regard for the fuel control system. It was reported that gasoline blends with either EtOH or MeOH caused vehicles with conventional non-closed loop fuel control systems to have poor starting and driveability at low, moderate and high temperature conditions.[26,31,35] The available documentation of driveability on gasoline-alcohol blends did not show any clear superiority of closed loop fuel control systems over open loop systems.[31,36,37]

5.8.5 Several vehicle models of circa 1973-4 were equipped with EGR for NO_x reduction, and open loop fuel control calibrated for lean mixtures for low HC and CO. In vehicles calibrated with very lean mixtures, the additions of oxygenate caused mixtures that were too weak and frequently resulted in driveability problems. Those vehicles generally drove poorly on gasoline-alcohol blends due to mixture enleanment. Exhaust oxidation catalysts (OC), introduced for HC and CO control on many 1975 models, allowed richer fuel mixture calibrations and greatly improved driveability. Three-way catalysts (3WC), introduced around 1980 for control of HC, CO and NO_x, required a computer-controlled closed loop system to maintain engine operation at stoichiometric air-fuel ratio. The closed loop fuel control fortuitously provided automatic fuel mixture compensation for oxygenated gasolines but also removes most if not all of the emissions benefit of oxygenates. The 3WC-control system response to operating factors, such as ambient environment, engine conditions and fuel properties, was further enhanced by adaptive transient learning, sequential fuel injection and selective ignition.

5.8.6 As control technology has advanced and been refined, design diversity of vehicle fuel systems has narrowed. Automotive News estimated that, of the 193 million cars and trucks in use during 1995, more than 50 percent of them were newer than 7.4 years.[38] Although many vehicles with outmoded technology remain in use, 95 percent of the passenger cars sold during the past 12 model years have closed loop fuel control systems. This chapter reviews the progress made to understand the response of vehicle emissions control and driveability to gasoline-oxygenate blends. Another area of prior concern, the compatibility of fuel system materials, also has been reviewed.

5.9 THE AUTO/OIL AIR QUALITY IMPROVEMENT RESEARCH PROGRAM

5.9.1 It was obvious that information was needed to define the benefits and disadvantages of oxygenates, particularly with respect to vehicle emissions. In October 1989, the U.S. automotive and oil industries launched a landmark cooperative research program as the first comprehensive emissions research effort to consider vehicles and the fuels they use as a total system.[39,40] The Auto/Oil Air Quality Research Program (AQIRP) was funded jointly by 14 oil companies and the "big three" automakers, Chrysler, Ford, and General Motors. The program developed a substantial database of vehicle emissions using a variety of real or potential fuels, including oxygenates. The AQIRP employed the best talent and contemporary instrumentation and, as a result, produced the largest, most technically correct study of gasoline-oxygenate blends. Federal test procedures and protocol for measuring exhaust and evaporative emissions were used throughout the program. The AQIRP database and conclusions have been used as the primary resource for the definition of federal and state regulations for reformulated gasolines. This chapter summarizes the AQIRP findings for gasoline-oxygenate blends. Chapter 6 includes the AQIRP results from "future" vehicles designed to operate on neat or near neat alcohols.

5.9.2 Because of the variety of vehicle emissions control technology in service, two fleets of well-maintained vehicles were designed to represent "current" and "older" technology. The "current" fleet included ten pairs of 1989 model cars and light duty trucks which were equipped with state-of-the-art exhaust emissions controls. Seven pairs of 1983-5 model year vehicles comprised the "older" fleet. Table 17 lists the emissions controls of the test vehicles. Mass and speciated emissions of both exhaust and vapors were measured using a wide range of fuels. Fuel factors other than oxygenates, such as hydrocarbon type, sulfur, and volatility parameters, were varied.

5.10 EFFECTS OF GASOLINE-OXYGENATE BLENDS ON VEHICLE EMISSIONS

5.10.1 General

5.10.1.1 The AQIRP "current" fleet was used to measure the emissions effects of three oxygenates at their maximum allowable concentrations: EtOH at 10 volume percent, MTBE at 2.7 mass percent oxygen and ETBE at 2.7 mass percent oxygen. Four "base" gasolines were tested without and with splash blended 10 volume percent EtOH. Two of the four "base" gasolines were blended with 15 volume percent MTBE and were also tested. One of the four "base" gasolines was blended with 16 volume percent ETBE and was also tested. At least two exhaust and evaporative emissions tests were run on each of 11 test fuels.[41]

5.10.1.2 The effects of the three oxygenates on mass exhaust and evaporative emissions are plotted in Figure 14 as percentage increase or decrease from the emissions from non-oxygenated base fuels. All three oxygenates significantly reduced, at 95 percent confidence level (CL), emissions of total HC, non-methane HC and CO. EtOH significantly increased NO_x by 5 percent. The effect of MTBE and ETBE on NO_x appeared insignificant at 95 percent CL, probably because fewer comparisons were available for statistical analysis.

5.10.1.3 Evaporative emissions were measured under diurnal and hot soak conditions. The diurnal phase emulates ambient daily temperature cycling, and the hot soak phase simulates shut down following a driving cycle. The ethers had no effect on diurnal emissions. However, EtOH increased diurnal evaporative emissions by 30 percent, and hot soak emissions by 50 percent. MTBE increased hot soak emissions by 13 percent. AQIRP found that, for either gasolines or gasoline-EtOH blends, diurnal emissions were lowered by 50 percent by a vapor pressure reduction of one psi (the magnitude of vapor pressure increase caused by splash blending 10 volume percent EtOH). Hot soak emissions were not reduced.

5.10.1.4 Toxic air pollutants are defined by the Clean Air Act as benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter (POM). In the AQIRP, each of these species was measured except POM. The effect of oxygenates on toxic exhaust emissions is shown in Figure 15. All three oxygenates reduced benzene emissions, almost the same magnitude as their dilution effect on the fuel. No significant effects on 1,3-butadiene and formaldehyde were observed. However, both EtOH and ETBE more than doubled the emissions of acetaldehyde, but MTBE had no significant effect.

5.10.2 Exhaust Emissions from Vehicles with High Emissions

AQIRP obtained seven, poorly maintained, 1986-7 model year automobiles and measured the effect of several fuel factors on exhaust emissions.[42] The vehicles were equipped with closed loop (CL) fuel injection and 3WC, technology similar to that of the "current" fleet, but had accumulated between 50,000 and 73,000 miles. All cars were running excessively rich and emitted from five to 60 times the FTP CO standard of 3.4 grams/mile for that model year. Test

Table 17—AQIRP Test Vehicle Fleets

14 Older Model Fleet Vehicles (42,000 to 79,000 Miles)

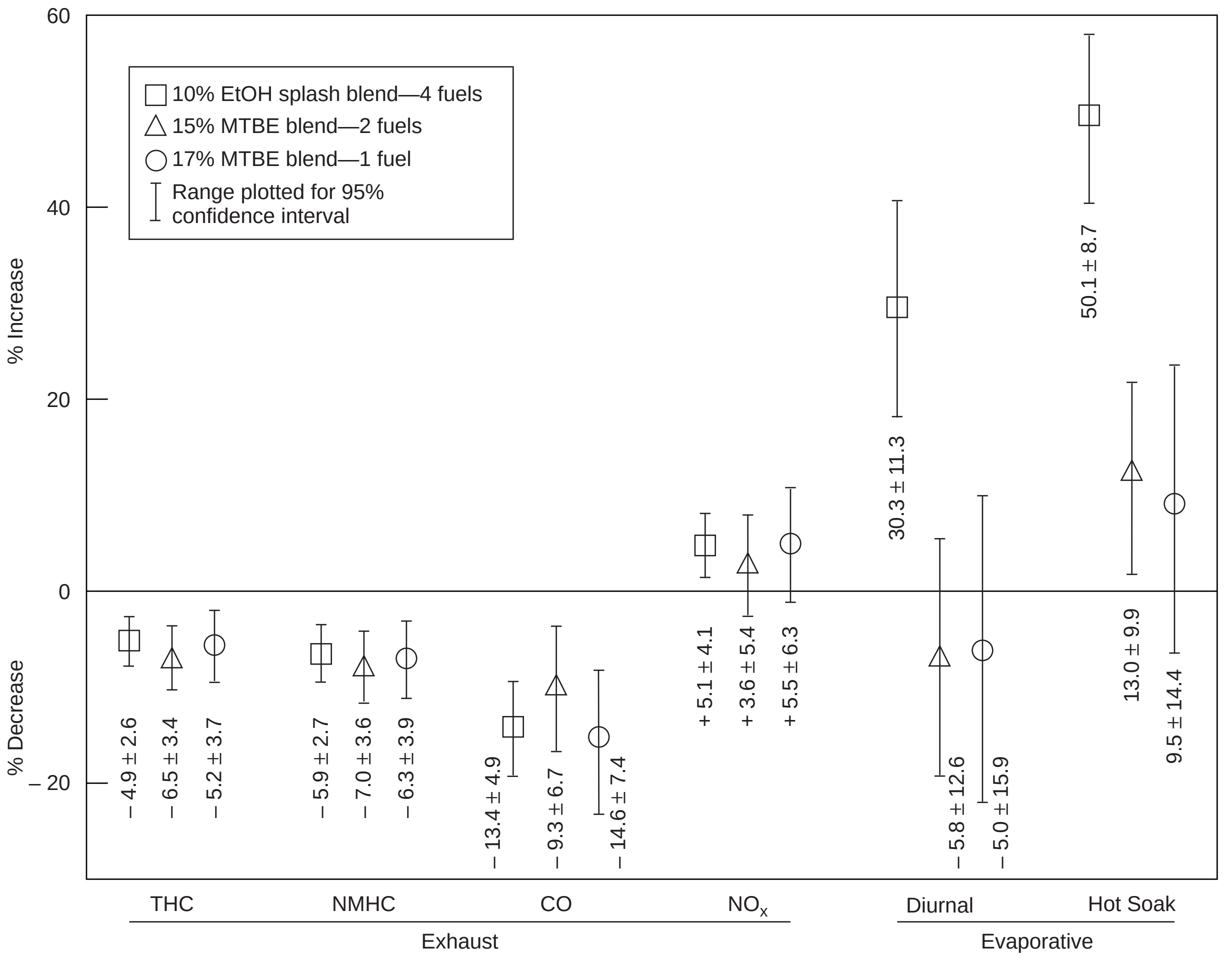
Number	Vehicle Model	Fuel System	Exhaust Emission Control System
2	1985 Plymouth Reliant 2.2L	CL Carb.	EGR, Air, 3WC/OC, CC
2	1985 Ford Tempo 2.3L	CL TBI	EGR, Air, 3WC/OC, UF
2	1983 Ford F150 Pickup 4.9L	OL Carb.	EGR, Air, OC, UF
2	1985 Honda Accord 1.8L	CL Carb.	EGR, Air, 3WC, UF
1	1984 Pontiac Grand Prix 3.8L	CL Carb.	EGR, Air, 3WC/OC, UF
1	1984 Oldsmobile Cutlass 3.8L	CL Carb.	EGR, Air, 3WC/OC, UF
1	1985 Chevrolet Caprice 5.0L	CL Carb.	EGR, Air, 3WC/OC, UF
1	1985 Chevrolet Impala 5.0L	CL Carb.	EGR, Air, 3WC/OC, UF
2	1984 Chevrolet Suburban 5.7L	OL Carb.	EGR, Air, OC, UF

20 Current Model Fleet Vehicles (10,000 to 29,000 Miles)

Number	Vehicle Model	Fuel System	Exhaust Emission Control System
2	1989 Plymouth Sundance 2.5L	CL TBI	EGR, 3WC, CC
2	1989 Dodge Shadow 2.5L TC	CL PFI	3WC, UF
2	1989 Ford Mustang 5.0L	CL SFI	EGR, Air, 2(3WC/OC), UF
2	1989 Ford Taurus 3.0L	CL PFI	3WC, CC
2	1989 Ford Aerostar 3.0L	CL PFI	2(3WC), UF
2	1989 Toyota Camry 2.0L	CL PFI	EGR, 3WC, CC
2	1989 Honda Accord 2.0L	CL Carb.	EGR, Air, 3WC, UF
2	1989 Chevrolet Suburban 5.7L	CL TBI	EGR, 3WC, UF
2	1989 Pontiac Grand Am 2.3L	CL PFI	3WC, UF
1	1989 Oldsmobile Delta 3.8L	CL PFI	EGR, 3WC, UF
1	1989 Pontiac Bonneville 3.8L	CL PFI	EGR, 3WC, UF

Codes:

Air = Air injection
Carb. = Carburetor
CC = Close coupled
CL = Closed loop
EGR = Exhaust gas recirculation
L = Liters
OC = Oxidation catalyst
OL = Open loop
PFI = Port fuel injection
SFI = Sequential fuel injection
TBI = Throttle body injection
TC = Turbocharged
3WC = Three way catalyst
UF = Underfloor



Source: Reference 41

Figure 14—Effect of Oxygenates on Mass Emissions RVP/Oxygenate Matrix, Current Fleet

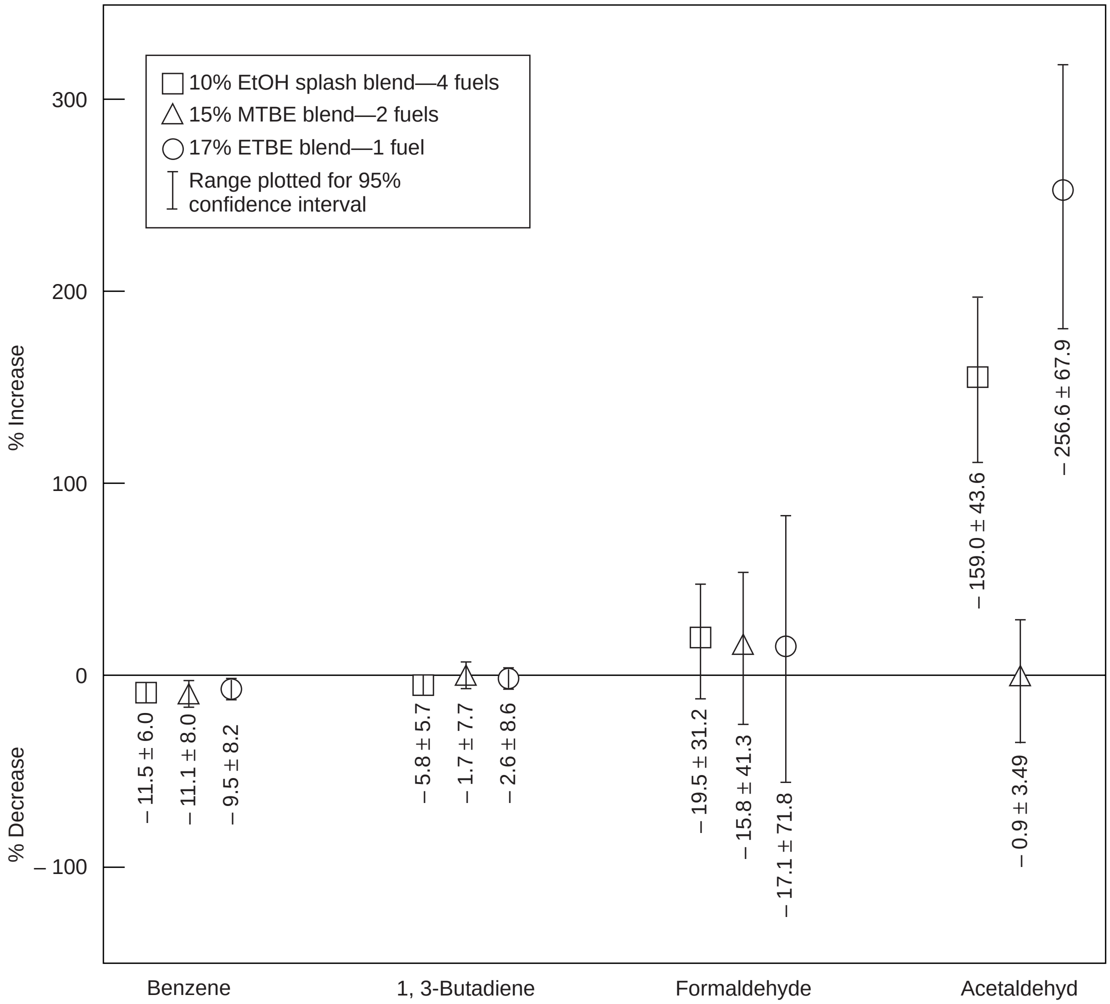
fuels were four non-oxygenated gasolines: one blend with 10 volume percent EtOH, and six gasoline blends containing between 11 and 15 volume percent MTBE. These same fuels also had been tested previously in the 20 vehicles of the "current" fleet.

Figure 16 shows that the gasoline-EtOH blend reduced HC emissions from the high emitters 24 percent. The gasoline-EtOH blend also reduced CO emissions 26 percent. The gasoline-MTBE blends reduced both HC and CO by 33 percent. However, NO_x increased by 21 percent with the EtOH blend, and by 33 percent with the MTBE blends. The extraordinary reductions in HC and CO were found to be a result of the rich, oxygen-deficient, air-fuel mixtures of the high emitters. This hypothesis was proven by normalizing the emissions data for air-fuel equivalence ratio. The normalized means, plotted as asterisks in the figure, are moderate and approach the emissions changes that resulted from EtOH and MTBE blends tested in the "current" fleet.

5.10.3 Comparison of MTBE and TAME Effects on Emissions

5.10.3.1 The effect of MTBE on mass exhaust emissions was studied further in the "current" and "older" AQIRP fleets.[43] Ten fuels without MTBE were compared with eight of the ten that were blended with 15 volume percent MTBE. As Figure 17 shows, the results confirmed those reported above. MTBE significantly reduced HC, NMHC and CO emissions and had no significant effect on NO_x emissions from either fleet.

5.10.3.2 Changes in speciated emissions caused by MTBE in this program are shown in Figure 18.[44] MTBE did not significantly change benzene emissions in the "current" fleet, but did reduce emissions of 1,3-butadiene. In the "older" fleet, MTBE reduced benzene emissions, but did not significantly change emissions of 1,3-butadiene. No change of acetaldehyde emissions due to MTBE was observed in either fleet. In



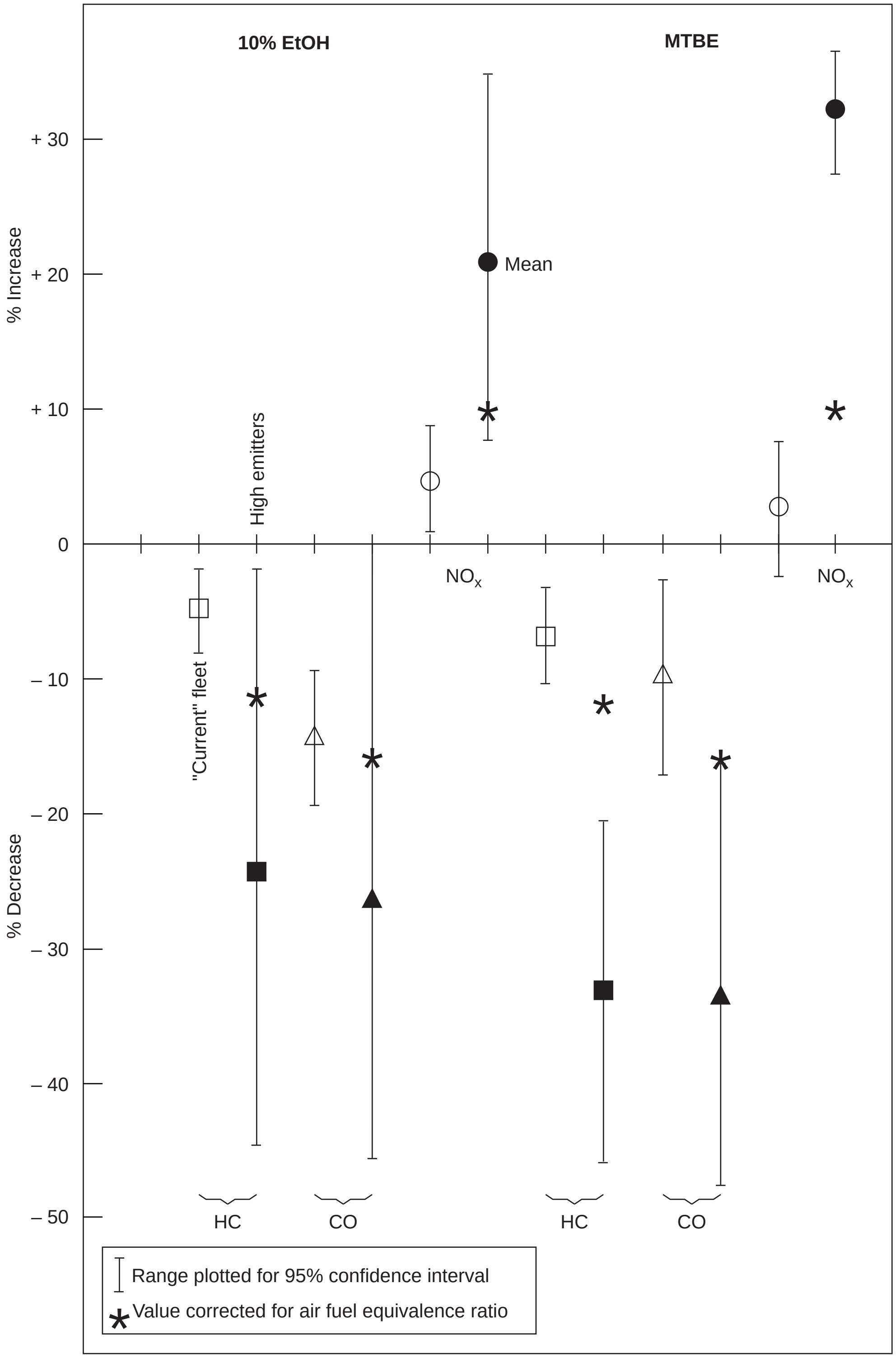
Source: Reference 41

Figure 15—Effect of Oxygenates on Toxic Exhaust Emissions RVP/Oxygenate Matrix, Current Fleet

this study, MTBE increased emissions of formaldehyde from both fleets. The absolute level of formaldehyde emissions from the "older" fleet was an average of about four times that from the "current" fleet. AQIRP analysis concluded that the trucks of the "older" fleet accounted for a large share of the increase of formaldehyde emissions. It was postulated that the higher levels of exhaust emissions from the trucks, and/or the reactions of their oxidation catalytic converters, were responsible. Analysis of data from the "current" fleet did not identify the trucks of the "current" fleet to be responsible for the observed increase of formaldehyde emissions.

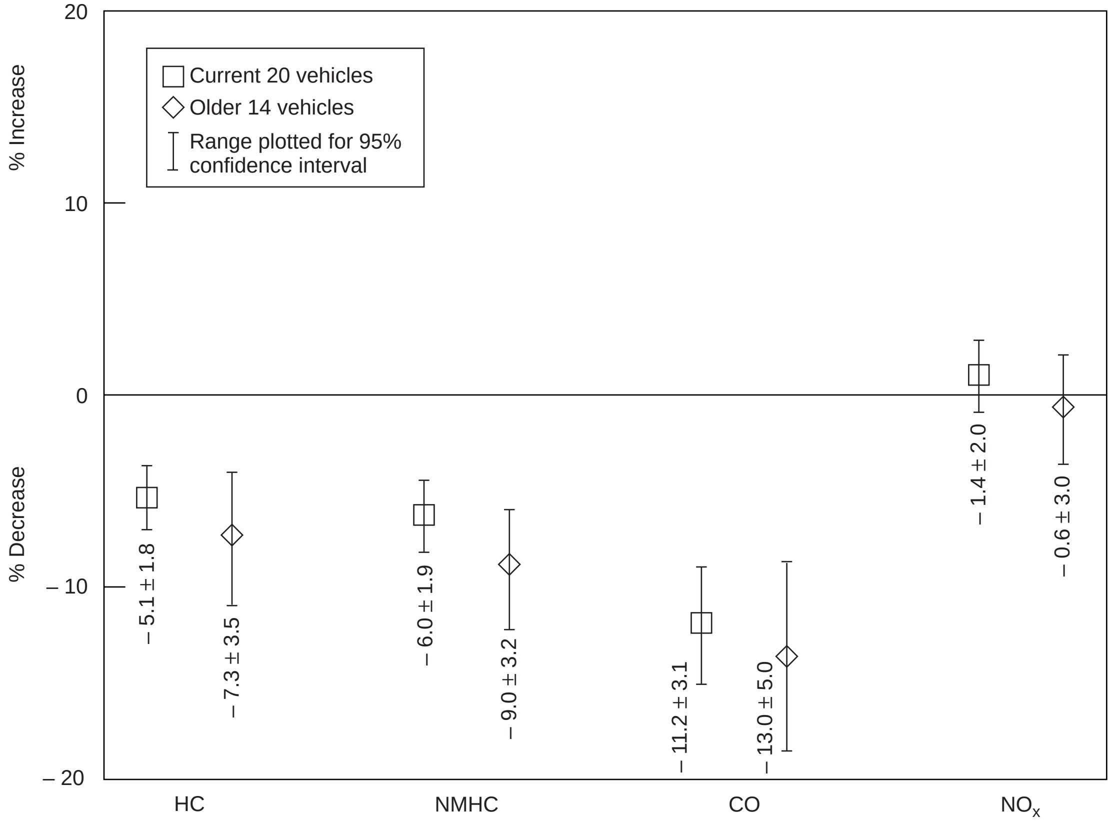
5.10.3.3 The AQIRP compared the emissions performance of TAME with that of MTBE in the same gasoline.[45] The comparison was made using ten vehicles, one-half of the "current" fleet. Mass and speciated exhaust emissions, and evaporative emissions were measured. The results are listed in Table 18. No statistically significant difference was observed between TAME and MTBE for HC, CO, or NO_x either ahead of the exhaust catalyst, "engine-out", or at the tailpipe. TAME produced 24 percent fewer diurnal evaporative emissions than MTBE. Nine of the ten test vehicles had lower diurnal emissions with TAME. There was no significant difference between the ethers with respect to hot soak emissions.

5.10.3.4 The only statistically significant difference between the ethers was between formaldehyde emissions which were 28 percent higher with TAME. Higher formaldehyde content was observed in the exhaust emissions during a cold start. It was postulated that the lower volatility of TAME may have been the cause.



Source: Reference 42

Figure 16—Effect of Oxygenates on Mass Exhaust Emissions from High Emitting Vehicles



Source: Reference 43

Figure 17—Effect of MTBE on Mass Exhaust Emissions

5.10.4 Mixtures of Ethers and Effects on Emissions

The possibility of interactions or commingling effects of ether mixtures on emissions was studied extensively in a group of 1989 – 1991 passenger cars listed in Table 19.[46] Ether concentrations in the gasolines were controlled to full limit 2.7 weight percent oxygen, as opposed to 2.0 percent of the AQIRP program previously discussed. No significant differences in exhaust emissions were observed between the ethers or mixtures of the ethers, as shown in Table 20. This finding indicates that no interactions exist between the ethers. With respect to emissions of toxics, the ethers produced similar types and levels of hydrocarbon species, with the exception of DIPE. DIPE produced higher emissions of acetaldehyde, a known product of incompletely oxidized DIPE. The emissions of formaldehyde were not found to be significantly greater than the reference gasoline or any other ether, in deference to the AQIRP finding. Evaporative emissions of hydrocarbons and benzene were significantly lower from the gasoline-ether blends than those from the reference gasoline. TAME produced significantly greater amounts of benzene during hot soak than other ethers as presented in Table 21.

5.11 EFFECTS OF GASOLINE-OXYGENATE BLENDS ON DRIVEABILITY

5.11.1 General

5.11.1.1 The mandates for stringent control of vehicle emissions brought about the demise of carburetor and atmospheric pressure fuel systems, a combination that, historically, intensified driveability problems and vapor lock. Closed loop feedback fuel management, in addition to being essential to exhaust emissions control, provides precise fuel quantity delivery for excellent driveability. Feedback systems include on-vehicle computers, and sensors of mass air flow, ambient temperature, barometric pressure and exhaust oxygen content. Electronic controls, accompanied by fuel systems which operate at higher pressure and lower peak temperatures, has helped widen the tolerance of vehicle driveability to volatility and oxygenated blends. Modern engine fuel management systems, coupled with three-way catalysts, are optimized for lowest exhaust emissions, and automatically control air-fuel mixture to stoichiometric ratios within excursion limits. Although stoichiometric air-fuel ratio provides best emissions control, it may not provide optimum driveability because it is usually about 10 percent lean from the ratio that provides best power. Thus

Table 18—Fleet Average Emissions from Fuels Containing MTBE or TAME[45]—Current Vehicle Fleet

	MTBE	TAME	Difference, % TAME vs. MTBE
Exhaust (g/ml):			
HC	0.21	0.21	0
NMHC	0.17	0.17	0
CO	2.48	2.57	4
NO_x	0.63	0.64	2
Exhaust Toxics (mg/ml):			
Benzene	6.6	6.5	–2
1.3-Butadiene	0.7	0.7	5
Formaldehyde	1.5	1.9	28*
Acetaldehyde	0.6	0.7	17
Total	9.4	9.9	5
Evaporative HC (g/test):			
Diurnal	0.54	0.41	–24*
Hot Soak	0.37	0.39	7
Evaporative Benzene (mg/test):			
Diurnal	2.2	2.5	11
Hot Soak	3.8	4.1	8

Note: % Difference = $\frac{\text{TAME} - \text{MTBE}}{\text{MTBE}} \times 100$

*Difference is significant at the 95% confidence level.

Table 19—Test Vehicles for Study of Ether Mixture Effects on Emissions (All Closed Loop Fuel Control)

Vehicle Model	Fuel System	Exhaust Emission Control System
1990 Pontiac Bonneville 3.8L	SFI	EGR, 3WC, UF
1989 Pontiac Grand Am 2.3L	PFI	3WC, UF
1991 Ford Crown Victoria 5.0L	SFI	EGR, 3WC, OC, Air
1990 Ford Taurus 3.0L	PFI	3WC, CC
1990 Chrysler New Yorker 3.3L	PFI	3WC
1990 Honda Accord 2.2L	SFI	EGR, 3WC, UF
1990 Nissan Sentra 1.6L	TBI	EGR, 3WC, P-Air

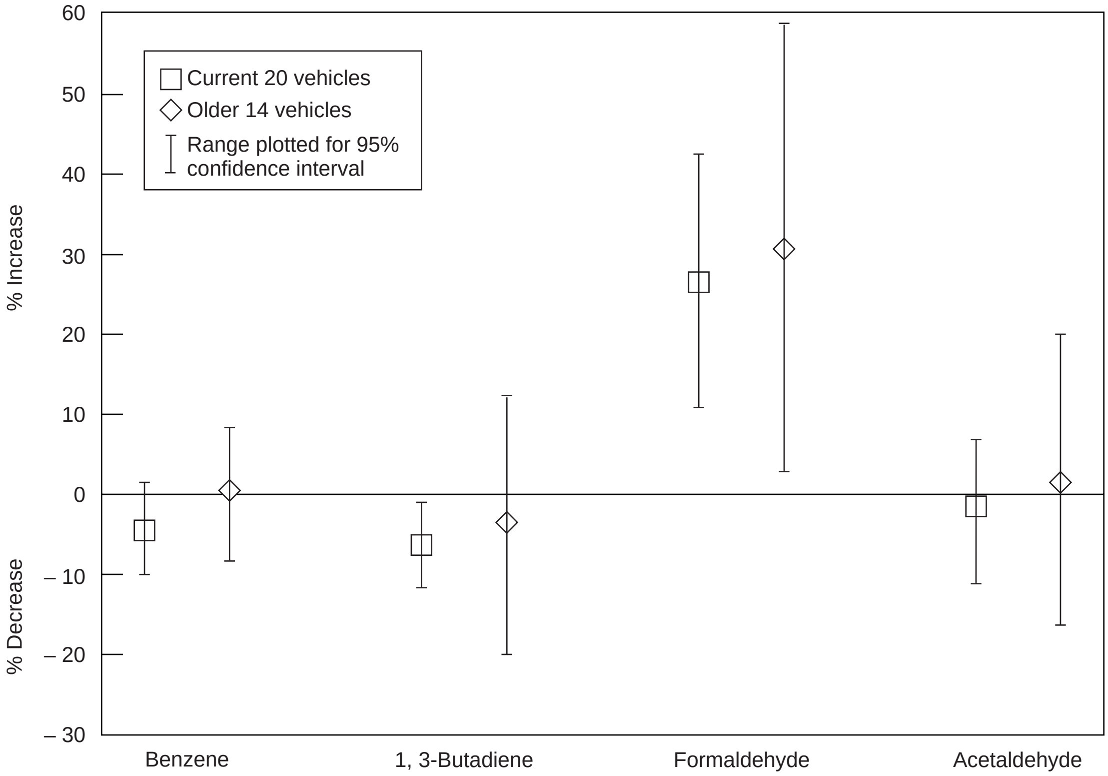
Codes: Air = Air injection
CC = Close coupled
EGR = Exhaust gas recirculation
L = Liters
OC = Oxidation catalyst
P-Air = Pulsed air injection
PFI = Port fuel injection
SFI = Sequential fuel injection
3WC = Three way catalyst
TBI = Throttle body injection
UF = Underfloor

under some driving conditions, mixture enrichment is programmed electronically to optimize driveability.[47]

5.11.1.2 For decades, gasoline volatility interactions with carbureted fuel systems at low and high temperatures have motivated countless studies for engineers and chemists of the auto and oil industries. The Coordinating Research Council, a nonprofit corporation supported by the petroleum and automotive equipment industries, has conducted many programs to quantify oxygenate effects on driveability at various ambient temperatures. CRC driveability test procedures and terminology provide a means for the automotive and oil industries to technically describe an extremely subjective measurement.

5.11.1.3 The CRC test procedure requires skilled raters to start engines, drive prescribed modes, and record observations.[48] Starting time is measured, and driveability is rated during idle, acceleration and cruise conditions. The driving cycle is repeated several times, and demerits are assigned for substandard operation in any phase of the cycles. A composite driveability rating is determined by applying weighing factors to the observed demerits according to the severity of the event. For example, engine stalling is regarded as extremely serious and is given a very high weighting multiple. Duplicate tests are conducted. The composite rating for each fuel/vehicle/ambient combination is termed Total Weighted Demerits, TWD. Statistical differences between TWD ratings are analyzed and correlations between fuel factors and vehicle performance may be derived. Such methodology has been applied to driveability studies with oxygenated blends at various ambient temperatures.

5.11.1.4 A combination of weighted distillation values for T_{10}, T_{50} and T_{90}, termed “Driveability Index” (DI) has been correlated with driveability TWD measured in CRC tests, particularly at moderate ambient temperatures. Historically, DI has been a total of (a)T_{10} + (b)T_{50} + (c)T_{90}.[49] As vehicle and fuel technology shifted, it was found that DI correlated better with increased emphasis on the more volatile 50 percent fraction of the fuel. At the time of this publication, SAE J312, SAE Recommended Practice for Automotive Gasolines, states DI = (1.5)T_{10} + (3)T_{50} + (1)T_{90}.[12] ASTM D4814 has included DI as a standard specification for motor gasoline beginning in 1998.[11] DI changes are being studied to provide better, perhaps more linear, correlation with driveability TWDs observed in late model vehicles operating on gasoline-oxygenate blends.[50,51] CRC driveability test procedures also are being revised to increase TWD differentiation between fuels observed in vehicles with less sensitivity to volatility.[52]



Source: Reference 44

Figure 18—Effect of MTBE on Mass Toxic Emissions

Table 20—Vehicle Exhaust Emissions from Gasoline-Ether Blends[46]

	Grams per Mile			Milligrams per Mile			
Ether	HC	CO	NO_x	Benzene	1,3 Butadiene	Formaldehyde	Acetaldehyde
None	0.29	4.34	0.81	12.3	1.1	2.4	0.9
15.0% MTBE	0.23	3.22	0.82	7.1	0.8	2.2	0.8
18.6% DIPE	0.24	3.13	0.82	7.6	0.8	2.4	1.4
18.4% TAME	0.24	3.29	0.81	7.9	0.8	2.5	0.8
7.5% MTBE + 9.3% DIPE	0.24	3.32	0.85	8.3	0.8	2.4	1.3
7.5% MTBE + 9.2% TAME	0.23	3.27	0.83	8.2	0.8	2.7	0.9
5.0% MTBE + 6.2% DIPE + 6.1% TAME	0.24	3.21	0.82	7.9	0.8	2.5	1.1
95% confidence interval	±0.02	±0.41	±0.05	±1.1	±0.1	±0.5	±0.1

Table 21—Vehicle Evaporative Emissions from Gasoline-Ether Blends[46]

	Evaporative Emissions			
	Hydrocarbons, grams/test		Benzene, milligrams/test	
Ether	Diurnal	Hot Soak	Diurnal	Hot Soak
None	0.20	0.25	6.4	11.2
15.0 vol% MTBE	0.15	0.22	5.1	8.5
18.6 vol% DIPE	0.16	0.23	5.1	8.3
18.4 vol% TAME	0.15	0.22	5.7	9.9
7.5% MTBE+ 9.3% DIPE	0.14	0.23	4.6	8.4
7.5% MTBE+ 9.2% TAME	0.15	0.23	4.9	9.1
5.0% MTBE+ 6.2% DIPE + 6.1%TAME	0.15	0.22	3.9	8.2
95% confidence interval	±0.02	±0.02	±1.0	±1.1

5.11.2 Cold Start Driveability at Low Ambient Temperatures

To start a cold engine, the mixture of fuel vapor and air must be sufficiently rich to be ignited and to support combustion. Gasolines with higher vapor pressure and lower front-end distillation temperatures usually vaporize better and exhibit improved cold starting and drive away. To a large extent, CRC and other studies have found this generality holds true for gasoline-oxygenate blends.

5.11.3 Low Temperature Driveability

5.11.3.1 CRC conducted extensive low temperature driveability programs during 1986-8 to quantify the effects of gasoline blends made with EtOH or MTBE. In one program, cold start driveability of five gasoline-EtOH blends was compared with that of five gasolines with matched volatility in twenty-seven 1986 model vehicles equipped with closed loop fuel control and either carburetor, TBI or PFI.[53] Controlled volatility parameters were T_{10}, T_{50} and vapor pressure. The test vehicles are listed in Table 22. Prior to evaluating startup and driveability on each fuel, each vehicle was run on the fuel to be tested, and soaked overnight at an average temperature of 18°F. The test procedure measured the time for engine starting, and rated driveability during drive away, cruising, acceleration, maneuvering and idling. The TWDs for each combination of fuel and vehicle are listed in Table 23.

5.11.3.2 In terms of TWDs, gasoline-EtOH blends performed significantly worse than gasolines with the same volatility. Higher volatility of either gasoline or the gasoline EtOH blends provided better driveability. The fuel injected vehicles drove significantly better than the carbureted vehicles on all fuels. With the exception of one fuel/vehicle group combination, the fuel injected vehicles statistically performed the same with EtOH blends as they did with gasolines of matched volatility. Lower sensitivity of fuel injected vehicles to volatility and oxygenate has been observed in other CRC driveability programs.

5.11.3.3 Another large CRC low temperature driveability program was conducted at high and lower altitude test sites.[54] Six 1978-9 vehicles without computer control, and fifteen 1987 model vehicles with closed loop fuel control were included as described in Table 24. Three sets of gasoline-oxygenate blends were compared with base gasolines of high, medium and low volatility. Volatility parameters, T_{10}, T_{50} and vapor pressure, were matched for three gasoline-EtOH blends that contained 10 volume percent EtOH and three gasoline-MTBE blends that contained 11 volume percent MTBE. Three additional gasoline-EtOH blends were splash blends of 10 volume percent EtOH with the three base gasolines.

5.11.3.4 Because the altitude effect was not significant, the TWD values in Table 25 are the average results obtained at both altitudes. Driveability ratings were significantly better with gasolines than with gasoline-oxygenate blends. Matched volatility blends with MTBE were not significantly better than the EtOH splash blends. However, matched volatility blends with EtOH performed worse than other oxygenated blends. These effects were observed in all four categories of vehicles.

5.11.3.5 Higher distillation temperatures, T_{10} and T_{50}, deteriorated cold driveability with either oxygenated fuels or gasoline. Vehicles with open loop carburetion performed poorly on all fuels, but performed better, to a significant

Table 22—Test Vehicles for Low Temperature Driveability Program[53]

Fuel System	Vehicle Description (All 1986 Model Year)
Carburetor	Chevrolet Caprice 5.0L
	Chrysler Fifth Avenue 5.2L
	Ford Bronco 4.9L
	Ford Escort 1.9L
	Honda Accord 2.0L
	Oldsmobile Ciera 2.8L
	Plymouth Horizon 2.2L
	Pontiac Grand Prix 3.8L
	Toyota Corolla 1.6L
Throttle Body Injection	Chevrolet Astro Van 4.3L
	Chevrolet Cavalier 2.0L
	Dodge Aries 2.2L
	Dodge Aries 2.5L
	Ford Tempo 2.3L
	Ford Thunderbird 3.8L
	Oldsmobile Ciera 2.5L
	Pontiac Sunbird 1.8L
	Renault/AMC Alliance 1.7L
Port Fuel Injection	(2) Chevrolet Camaro 2.8L
	Chrysler LeBaron 2.2L Turbocharged
	Lincoln Continental 5.0L
	Mercury Sable 3.0L
	Oldsmobile Delta 88 3.0L
	Oldsmobile Delta 88 3.8L
	Toyota Camry 2.0L
	Volkswagen Jetta 1.8L

degree, with hydrocarbon fuel than with any of the oxygenated blends. Port fuel injected vehicles outperformed those with other fuel system technology but, statistically, were not significantly better than other vehicles with closed loop fuel control.

5.11.4 Cold Starting

5.11.4.1 Cold starting quality was determined in these CRC programs by measuring the length of time required to start the engine. If an engine did not start within two seconds, demerits were assigned for each additional second. Table 26 lists the average cold start demerits from both low temperature CRC programs. The older vehicles with open loop fuel systems were difficult to start on all fuels, regardless of oxygenate. Splash blends with EtOH, which had higher vapor pressures than the other fuels, provided shorter starting times than EtOH blends with matched volatility. Both test programs found poorer starting with gasoline-EtOH blends than with gasolines of matching volatility.

5.11.4.2 Vehicle fuel system technology differences overshadowed the fuel composition effects. All vehicles with closed loop fuel systems received fewer demerits than the older vehicles. The vehicles with throttle body injection had poorer cold starting only with gasoline-EtOH blends with matched volatility. Port fuel injected vehicles had more demerits on oxygenated blends than vehicles with closed loop carburetor or TBI systems. Port fuel injectors release fuel in close proximity to the engine's cylinders, allowing less vaporization time than does a carburetor or TBI.

5.11.5 Driveability at Intermediate Ambient Temperatures

5.11.5.1 Many studies of the effects of oxygenated gasolines on driveability have been conducted at moderate ambient temperatures, typically between 34 and 80°F. CRC compared driveability performance of a gasoline-EtOH blend with volatility matched to that of a high volatility gasoline with a that obtained using a blend with $T_{V/L=20}$ matched to the gasoline.[55] All 12 test vehicles, listed in Table 27, were 1985 models, equipped with closed loop carburetors, TBI and PFI control fuel systems. Within each vehicle group, all fuels performed without significant difference from each other at 90 percent confidence level, as shown in Table 28. However, combination of the car groups showed the gasoline-EtOH blend with matched $T_{V/L=20}$ to be significantly better than the hydrocarbon gasoline, possibly because the vapor pressure of the gasoline was higher than that of the blend.

5.11.5.2 The previously mentioned CRC program that was conducted at low ambient temperatures included a second fleet of 27 vehicles that were tested for cold start driveability at intermediate ambient temperatures.[53] The test vehicles, with closed loop fuel control for carburetors, TBI and PFI, are

Table 23—Cold Start Driveability at Low Ambient Temperature[53]
(–8 to 31°F Soak Temperature, 23°F Average Run Temperature)

		Average Vehicle Total Weighted Demerits		
Volatility	Oxygenate Content	Carburetor	Throttle Body Injection	Port Fuel Injection
HI/LO/LO	HC Only	97	77	51
	10 vol% EtOH[1]	152	85	104
LO/HI/LO	HC Only	147	78	73
	10 vol% EtOH	163	77	80
LO/HI/HI	HC Only	187	126	111
	10 vol% EtOH	244	132	113
HI/LO/HI	HC Only	126	99	80
	10 vol% EtOH	150	101	92
MED/MED/MED	HC Only	148	103	78
	10 vol% EtOH	151	83	69
FUEL AVERAGE	HC Only	141	97	79
	10 vol% EtOH	172	96	92

Notes:
[1] Matched Volatilities by blending components

VOLATILITY CODE: Vapor Pressure/ T_{10} /T_{50}

Vapor Pressure, psi:	HI = 11.0 – 13.3	MED = 9.4 – 10.3	LO = 8.0 – 9.0
T_{10}, °F:	HI = 36 – 144	MED = 127 – 129	LO = 110 – 113
T_{50}, °F:	HI = 228 – 234	MED = 211 – 214	LO = 194 – 204

Table 24—Test Vehicles for Low Ambient Temperature Driveability Program[54]

Fuel System	Vehicle Description	Fuel System	Vehicle Description
Open Loop Carburetor	1978 Dodge Van 5.9L	Closed Loop Throttle Body Injection	1988 Chevrolet Astro 4.3L
	1979 Ford Fairmont 2.3L		1987 Mercury Cougar 3.8L
	1979 Plymouth Volare 5.2L		1987 Chrysler LeBaron 2.5L
	1979 Dodge Pickup 5.9L		1987 Buick Century 2.5L
	1979 Pontiac LeMans 3.8L		
	1979 Ford Van 5.0L		
Closed Loop Carburetor	1987 Chevrolet Caprice 5.0L	Closed Loop Port Fuel Injection	1987 Buick LeSabre 3.8L
	1987 Plymouth Horizon 2.2L		1987Ford Aerostar 3.0L
	1987 Chrysler Fifth Avenue 5.2L		1987 Ford LTD Crown Victoria 5.0L
	1987 Honda Civic 1.5L		1987 Chrysler LeBaron 2.2L Turbocharged
	1987 Ford Escort 1.9L		
	1987 Nissan Sentra 1.6L		1987 Toyota Camry 2.0L (4 valves/cyl)

Table 25—Cold Start Driveability at Low Ambient Temperature[54]
(17 – 36°F Average Temperatures)

		Total Weighted Demerits, Average Two Altitudes			
Volatility	Oxygenate	O-L Carb.	C-L Carb.	TBI	PFI
HIGH	None	264	60	55	50
	EtOH/MV	336	79	63	66
	MTBE/MV	310	69	57	43
	EtOH/SPL	312	59	56	41
MEDIUM	None	363	104	75	57
	EtOH/MV	408	107	90	65
	MTBE/MV	360	84	64	49
	EtOH/SPL	400	88	74	44
LOW	None	394	108	102	64
	EtOH/MV	452	138	126	70
	MTBE/MV	425	114	103	74
	EtOH/SPL	418	119	92	62

Volatility Code:	Vapor Pressure, psi	T_{10}%, °F	T_{50}%,°F
HIGH	13 – 14	106 – 111	170 – 204
MEDIUM	13 – 14	107 – 114	193 – 234
LOW	10 – 11	133 – 142	224 – 238

Oxygenate Code:
EtOH/MV = 10 vol% EtOH Matched Volatility Blend
MTBE/MV = 11 vol % MTBE Matched Volatility Blend
EtOH/SPL = 10 vol % EtOH Splash Blend

Vehicle Fuel System Code:
O-L Carb. = Open Loop Carburetor
C-L Carb. = Closed Loop Carburetor
TBI = Throttle Body Injection
PFI = Port Fuel Injection

listed in Table 29. The test fuels with matched volatility EtOH blends were the same as those evaluated in the low temperature cold start program.

5.11.5.3 As found at low ambient temperatures, gasoline-EtOH blends with matched volatility caused significantly higher driveability demerits than gasolines. Table 30 shows that driveability was better with higher volatility gasoline and gasoline-EtOH blends. Both TBI and PFI vehicles drove significantly better than carbureted vehicles on all fuels.

5.11.5.4 In another large program with 1988-9 model vehicles, CRC measured the driveability performance of gasolines and splash blends containing 10 volume percent EtOH or 15 volume percent MTBE at ambient temperatures ranging from 30°F to 56°F.[56] Five different volatility levels were tested. T_{10} and T_{50} were varied and T_{90} was held constant by adjustment of base gasoline composition. Vapor pressures of the 15 test fuels were controlled by the addition of butane. Twenty-four vehicles with closed loop fuel control were included as shown in Table 31. Standard CRC test procedures for rating driveability were followed.

5.11.5.5 Driveability ratings, reported as total weighted demerits, are listed in Table 32. At the moderate ambient temperatures of this program, cold starting was not a problem with any of the fuels, even with vapor pressures as low as 6.5 psi. Driveability of the vehicles equipped with carburetors was best with the gasoline or gasoline-MTBE blend with the highest vapor pressure and front end volatility. For the collective fleet, gasoline-MTBE blends provided the best driveability. Gasoline-EtOH blends, with volatilities that matched those of the gasolines or gasoline-MTBE blends, caused the poorest driveability.

Table 26—Effect of Oxygenates on Low Temperature Starting[53,54]

[CRC Program] Fuel	Average Initial Cold Start Demerits 1978-9 Open Loop Carburetor	Closed Loop Carburetor	Throttle Body Injection	Port Fuel Injection
[CRC 569] Gasoline Only	4.5	1.2	0.1	1.1
EtOH/MV	5.1	1.3	0.4	1.6
MTBE/MV	4.8	0.4	< 0.1	1.2
EtOH/SP	4.0	0.7	< 0.1	0.8
[CRC 568] Gasoline Only	No Vehicles	1.6	1.6	3.2
EtOH/MV	No Vehicles	2.8	2.2	4.2

Data Source

CRC 569: Values are average of fuels of three volatilities and two altitudes. Ambient air test temperature 17 – 36°F. See Table 21 for vehicle description

CRC 568: Values are average of fuels of five volatilities. Ambient air test temperature –8 to 31°F. See Table 19 for vehicle description.

Oxygenate Code:

EtOH/MV = 10 vol% EtOH Matched Volatility Blend
MTBE/MV = 11 vol % MTBE Matched Volatility Blend
EtOH/SPL = 10 vol % EtOH Splash Blend

Table 27—Test Vehicles for Intermediate and High Temperature Driveability Program[55]

Fuel System	Vehicle Description (All 1985 Model-Year)
Closed Loop Carburetor	Buick Century 3.0L
	Buick Skylark 2.8L
	Chevrolet Camaro 5.0L
	Chrysler Reliant 2.2L
	Ford LTD Wagon 3.8L
	Nissan Pulsar 1.6L
Closed Loop TBI	Renault/AMC Alliance 1.7L
	Buick Skylark 2.5L
	Ford Tempo 2.3L
Closed Loop PFI	Buick Park Avenue 3.8L
	Chrysler New Yorker 2.2L Turbocharged
	Toyota Supra 2.8L

5.11.5.6 Without exception, port fuel injected vehicles had better driveability with all fuels than vehicles with carburetors or TBI. Also, driveability of the PFI vehicles seemed to respond little to fuel front end volatility, T_{10} and vapor pressure, but exhibited somewhat poorer performance with fuels with high T_{50} level. The driveability of PFI vehicles on the least volatile gasoline-EtOH blend was as good as carbureted vehicles on the most volatile blend. As observed here, and in other programs, vehicle fuel system technology was a stronger influence on driveability than fuel volatility.

5.11.5.7 Refined CRC test procedures and demerit calculation techniques are under development to improve the detection of driveability problems of vehicles with port fuel injection. During early 1991, CRC conducted a large driveability program to evaluate consumer satisfaction with driveability of contemporary vehicles using gasolines and gasoline-10 volume percent EtOH blends of a wide range of volatility.[51] Over 8,000 driveability performance assessments were made using 1985 to 1991 model year vehicles, equipped with carburetor, PFI and TBI systems. Test temperatures ranged from 40 to 68°F. The program concluded that gasoline-EtOH blends produced malfunctions that were distinctly different from those observed using gasolines or a gasoline-14 volume percent MTBE blend. With fuels of high DIs, customers were most critical of "hesitation" with the EtOH blends, and found "stumble" to be associated with gasolines. The program indicated that the current CRC test procedure did not correlate very well with customer satisfaction, and that the TWD system and/or the driving cycle needed revision. Figure 19 shows the customer satisfaction as a function of the DI that is currently used.[57] The CRC conducted

Table 28—Intermediate Temperature Driveability[55]
(Ambient Temperature 67 – 80°F)

	Total Weighted Demerits			
Fuel	Carburetor Vehicles	TBI Vehicles	PFI Vehicles	Combined Fleet
Gasoline T_{10}, °F = 94 T_{50}, °F = 210 Vapor Pressure, psi = 16 $T_{V/L=20}$, °F = 104	89	39	16	58*
Gasoline + 9.1 vol% EtOH Matched T_{10},T_{50}, Vapor Pressure T_{10}, °F = 100 T_{50}, °F = 211 Vapor Pressure, psi = 16 $T_{V/L=20}$, °F = 102	64	20	3	38
Gasoline + 9.4 vol% EtOH "Splash Blend" Matched $T_{V/L=20}$ T_{10}, °F = 104 T_{50}, °F = 184 Vapor Pressure, psi = 15 $T_{V/L=20}$, °F = 105	64	12	4	36*

*Statistically different from gasoline at 90% confidence level.

a comprehensive 3-year, three ambient temperature program (1995 – 1997) investigating cold start driveability using hydrocarbon-only fuels, 10 vol % EtOH blends, and 15 vol % MTBE blends.[69] The results show that the current Driveability Index (DI), which was originally developed in the 1980s based on data primarily from carbureted vehicles, continues to be a good predictor of cold start and warm-up performance of gasolines in vehicles equipped with fuel injection. However, the study also shows that the current DI equation does not accurately predict the performance of gasoline-oxygenate blends. The presence of oxygenates can cause increased driveability problems due to leaning of the air/fuel mixture. Driveability problems can also be manifested through increased intake charge cooling caused by the higher latent heat of vaporization in the case of alcohols. To more accurately predict vehicle performance of oxygenate blends, the CRC results show that an adjustment must be made to the DI formula. The resulting modified DI equation based on all the data is as follows:

$$\text{DIMOD} = 1.5\text{T}10 + 3.0\text{T}50 + 1.0\text{T}90 + x$$

where

x = 86 for 10 vol % EtOH blends or 43 for 15 vol % MTBE blends when T is expressed in °F.

Further analysis of the data shows that the oxygenate offset varies with ambient temperature and uncorrected DI level. The offset decreases with increasing ambient temperature and decreasing DI levels. At this time, the CRC is planning an intermediate ambient temperature program to address the effect of intermediate concentrations of EtOH and MTBE on vehicle cold-start and driveaway performance.

5.11.5.8 MTBE effects were measured, using test procedures with amplified warmup events, in (24) 1989-94 model year vehicles including 18 port-fuel injected vehicles as listed in Table 33.[52] Tests included eight fuels, five of which were gasoline-MTBE blends with nominally 11 volume percent MTBE. Three hydrocarbon-only fuels were included with vapor pressure, T_{50}, and T_{90} that matched three of the gasoline-MTBE blends. It was observed that driveability was a non-linear function of volatility factors for both hydrocarbon-only fuels and gasoline-MTBE blends. Also, as earlier programs found, the presence of MTBE statistically did not affect driveability. The results of this study led to exploration of different DI calculations that combined percents evaporated at 200°F and 300°F.[49]

Table 29—Test Vehicles for Intermediate Temperature Driveability Program[53]

Fuel System	Vehicle Description
Carburetor	1985 Buick Regal 3.8L
	1985 Chevrolet Caprice 5.0L
	1986 Chevrolet Sprint 1.0L
	1987 Chrysler Fifth Avenue 5.2L
	1985 Dodge Aries 2.2L
	1986 Honda Accord 2.0L
	1986 Mercury Lynx 1.9L
	1987 Nissan Sentra 1.6L
	1986 Toyota Corolla 1.6L
Throttle Body Injection	1986 Chevrolet Astro Van 4.3L
	1986 Chevrolet Cavalier 2.0L
	1986 Chrysler LeBaron 2.5L
	1986 Dodge 600 2.2L
	1986 Mercury Topaz 2.3L
	1986 Oldsmobile Ciera 2.5L
	1986 Oldsmobile Ciera 2.8L
	1986 Pontiac Sunbird 1.8L
	1986 Renault/AMC Alliance 1.7L
Port Fuel Injection	1986 Chrysler LeBaron 2.2L Turbocharged
	1986 Ford Aerostar Van 3.0L
	1986 Mercury Cougar 5.0L
	1986 Oldsmobile Calais 3.0L
	1986 Oldsmobile Delta 88 3.8L
	1986 Pontiac 6000 2.8L
	1985 Toyota Camry 2.0L
	1986 Volkswagen Golf 1.8L

5.11.5.9 Sun Company, Inc. conducted a study of consumer response to driveability during cold start and warmup using gasolines and gasoline-MTBE blends of various volatilities.[58] Forty-one participants with vehicles of model years that varied from 1977 to 1992 rated the driveability of ten fuels encompassing a broad range of DIs, expressed as $DI = (1.5)T_{10} + (3)T_{50} + (1)T_{90}$. Five fuels were all-hydrocarbon gasolines and five fuels were gasoline-15 percent MTBE blends. Evaluations were made during a period of intermediate ambient temperatures. This study found that when a gasoline was splash blended with MTBE, consumer satisfaction was greater. Of more importance, the study revealed that for fuels with equivalent DI, a blend with MTBE gave less customer satisfaction than neat gasoline. As an example, splash blending 15 percent MTBE reduced the DI of a gasoline with 1254DI by about 61 units, and increased driver satisfaction from 70 percent to 80 percent. The same reduction of DI with all-hydrocarbon gasoline, increased satisfaction from 70 percent to 95 percent. As the curves of Figure 20 show, an all hydrocarbon gasoline with 1193 DI satisfied 95 percent of the test participants, whereas a gasoline-MTBE blend with the same DI satisfied only 70 percent of the drivers. The observed DI debit of 54 to 64 units due to MTBE was explained by the transient vaporization characteristics of MTBE in engines. Laboratory studies concluded that although MTBE increases fuel evaporation, the resultant air-vapor mixture is richer in MTBE and thus leaner in energy content than mixture achieved with all-hydrocarbon fuel.[59] This research also found that among descriptors of fuel volatility, T_{50} was the best predictor of engine torque response time in an engine. Measurements in a non-PFI engine indicated that a gasoline-15 volume percent MTBE blend increased response time the same amount as a 20°F increase of gasoline T_{50}. In the equation for DI that is currently specified, 20°F greater T_{50} increases DI by 60 units, approximately the same degree of MTBE debit reported from the consumer satisfaction study. In the Sun test, vehicles with port fuel injection showed least driveability response to DI changes of gasoline-MTBE blends. Seventy-seven percent of the drivers of PFI vehicles had no complaints using the gasoline-MTBE blend with the highest DI, contrasted with only 29 percent of the drivers of vehicles that did not have PFI.

5.11.5.10 In a similar Sun program involving 47 vehicles, consumer driveability evaluations of gasoline-16 volume percent ETBE blends were compared with those of gasoline-15 volume percent MTBE blends.[60] Driver satisfaction with gasoline-MTBE blends was found to be nearly the same as in the previous study. Gasoline-ETBE blends and gasoline-MTBE blends with the same DI provided similar consumer satisfaction. A single gasoline-MTBE/ETBE blend that contained 7.6 percent MTBE and 8.0 percent ETBE and had 1162DI was also evaluated in this program. Driveability satisfaction was about the same as the average satisfaction of the MTBE and

Table 30—Cold Start Driveability at Intermediate Ambient Temperature[53]
(36 – 61°F Ambient Air Run Temperature)

Volatility	Oxygenate Content	Average Vehicle Total Weighted Demerits		
		Carburetor	Throttle Body Injection	Port Fuel Injection
HI/LO/LO	HC Only	46	20	8
	10 vol% EtOH[1]	43	40	30
LO/HI/LO	HC Only	53	15	18
	10 vol % EtOH	75	45	18
LO/HI/HI	HC Only	86	52	30
	10 vol % EtOH	100	89	47
HI/LO/HI	HC Only	71	28	15
	10 vol % EtOH	85	39	29
MED/MED/MED	HC Only	70	40	26
	10 vol % EtOH	87	37	29
FUEL AVERAGE	HC Only	65	31	19
	10 vol % EtOH	78	50	31

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[1] Matched Volatilities by blending components

VOLATILITY CODE: Vapor Pressure/ T_{10} /T_{50}

Vapor Pressure, psi:	HI = 11.0 – 13.3	MED = 9.4 – 10.3	LO = 8.0 – 9.0
T_{10}, °F:	HI = 136 – 144	MED = 127 – 129	LO = 110 – 113
T_{50}, °F:	HI = 228 – 234	MED = 211 – 214	LO = 194 – 204

Table 31—Test Vehicles for Intermediate Temperature Driveability Program[56]

Fuel System	Vehicle Description	Fuel System	Vehicle Description
Closed Loop Carburetor	1989 Chevrolet Caprice Wagon 5.0L		1988 Ford Taurus 2.5L
	1988 Chevrolet Spectrum 1.5L		1989 Honda Civic 1.5L
	1988 Chevrolet Sprint 1.0L		1989 Plymouth Acclaim 2.5L
	1989 Chrysler Fifth Avenue 5.2L		1989 Plymouth Sundance 2.5L
	1988 Dodge Ram Pickup 2.0L		
	1988 Ford Festiva 1.3L	Closed Loop Port Fuel Injection (PFI)	1989 Chevrolet Celebrity 2.8L
	1989 Honda Prelude 2.0L		1989 Chrysler New Yorker 3.0L
	1989 Jeep Wrangler 4.2L		1989 Ford Aerostar 3.0L
			1989 Ford F-150 Pickup 4.9L
Closed Loop Throttle Body Injection (TBI)	1989 Buick Century 2.5L		1988 Ford Mustang 5.0L
	1988 Chevrolet Cavalier 2.0L		1988 Nissan 200SX 2.0L
	1988 Dodge Ram LE350 Van 5.2L		1989 Oldsmobile Cutlass Calais 2.3L
	1989 Ford Escort 1.9L		1988 Oldsmobile 98 3.8L

Table 32—Cold Start Driveability at Intermediate Ambient Temperature[56] (37 – 51°F Average Run Temperature)

Volatility[1]	Oxygenate Content	Average Vehicle Total Weighted Demerits[2]		
		Carburetor	Throttle Body Injection	Port Fuel Injection
HI/LO/LO	HC Only	52	28	24
	15 vol% MTBE	51	39	24
	10 vol% EtOH	66	27	17
LO/HI/LO	HC Only	63	39	27
	15 vol % MTBE	58	31	26
	10 vol % EtOH	71	47	34
LO/HI/HI	HC Only	98	75	38
	15 vol % MTBE	82	55	31
	10 vol % EtOH	112	92	60
HI/LO/HI	HC Only	86	59	27
	15 vol % MTBE	66	44	29
	10 vol % EtOH	101	67	34
MED/MED/MED	HC Only	72	41	26
	15 vol % MTBE	53	33	22
	10 vol % EtOH	59	35	25

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[1] Matched Volatilities by blending components

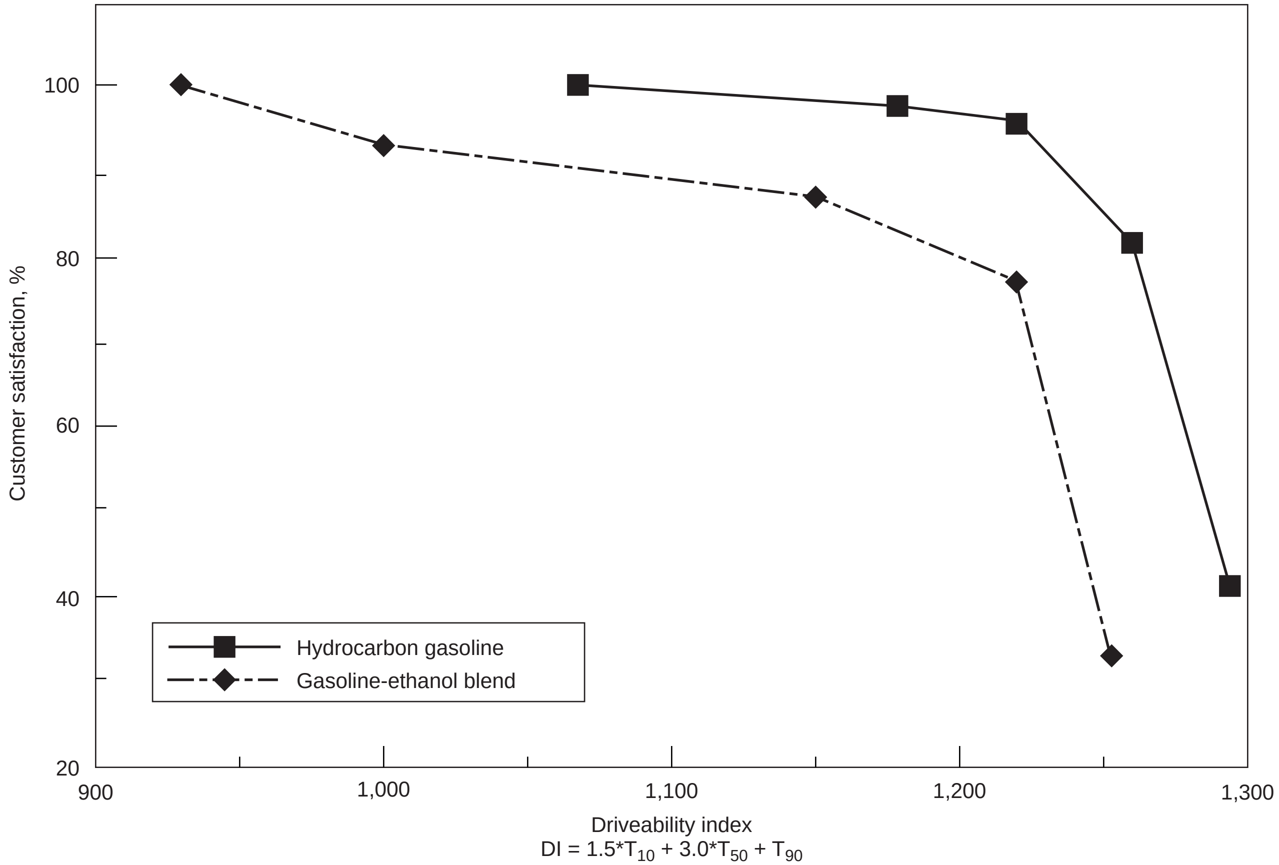
VOLATILITY CODE: Vapor Pressure/ T_{10} /T_{50}

Vapor Pressure, psi: HI = 10.9 – 11.3 MED = 8.6 – 9.0 LO = 6.5 – 6.9
T_{10}, °F: HI = 134 – 147 MED = 122 – 127 LO = 113 – 120
T_{50}, °F: HI = 217 – 246 MED = 199 – 222 LO = 170 – 204

[2] Uncorrected TWD Values

Table 33—Test Vehicles for Intermediate Ambient Temperature Driveability Program[52]

Fuel System	Vehicle Description	Fuel System	Vehicle Description
Carburetor	1989 Honda Accord 2.0L		1989 Dodge Shadow 2.5L TC
	1989 Nissan Sentra 1.6L		1989 Ford Aerostar 3.0L
			1991 Ford Explorer 4.0L
Throttle Body Injection	1992 Chevrolet Lumina Van 3.1L		1989 Ford Mustang 5.0L
	1989 Chevrolet Suburban 5.7L		1989 Ford Taurus 3.0L
	1994 Dodge Spirit 2.5L		1991 Ford Taurus 3.0L
	1989 Plymouth Sundance 2.5L		1993 Nissan Maxima 3.0L
			1994 Plymouth Voyager 3.0L
Port Fuel Injection	1994 Buick LeSabre 3.8L		1989 Pontiac Grand Am 2.3L
	1991 Chevrolet Lumina 3.1L		1989 Pontiac Bonneville 3.8L
	1994 Chevrolet Cavalier 2.2L		(2) 1989 Toyota Camry 2.0L
	1992 Dodge Caravan 3.0L		1993 Toyota Camry 2.2L
	1988 Dodge Grand Caravan 3.0		



Source: Reference 57

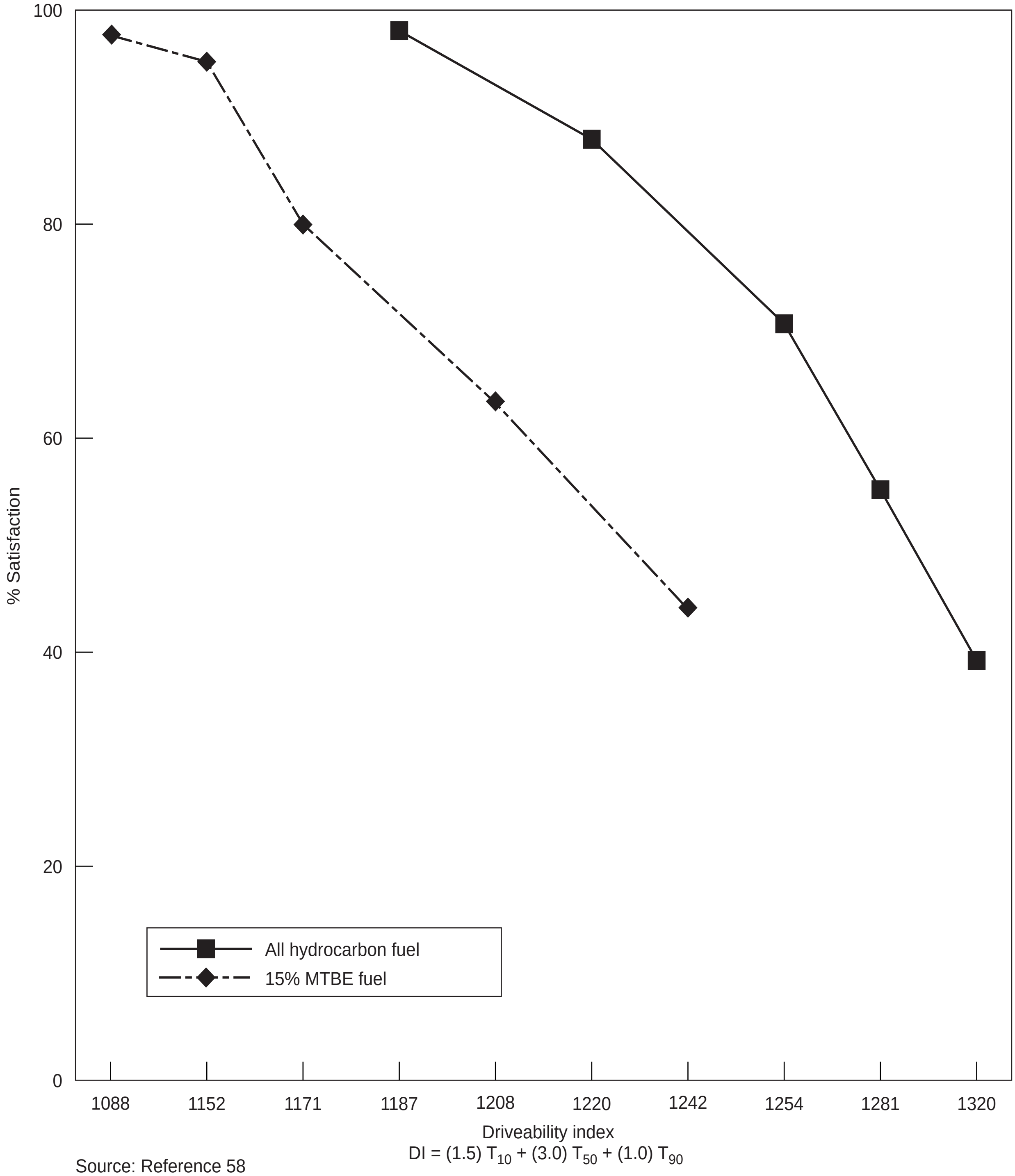
Figure 19—Customer Satisfaction as a Function of Driveability Index

ETBE blends at the same DI level, which indicated there was no commingling effects.

5.11.6 High Temperature Driveability

5.11.6.1 Under conditions of demand for full power, the existence of vapors within the fuel transport system can reduce fuel delivery and starve the engine. Traditionally, automakers have determined the occurrence of vapor lock by vehicle acceleration capability at high ambient temperatures. Vehicle tolerance of gasoline volatility and vapor lock often was expressed in terms of the increase in time to accelerate from low to high speed. Fourteen years ago, CRC ran vapor lock tests of gasoline-EtOH blends on a chassis dynamometer at 100°F in fourteen 1980 model cars, half of which had closed loop fuel control. Splash blended gasohol increased acceleration time by 26 percent in vehicles with open loop carburetors. Gasoline-EtOH blends with matched RVP did not significantly increase vapor lock. The vehicles with closed loop fuel control in this program were insensitive to the EtOH blends.

5.11.6.2 CRC driveability test techniques, similar to those used for evaluations at low and moderate temperatures, have been adapted to measure fuel volatility effects at high temperatures. As fuel systems and control technology improved, CRC refined driveability test procedures for sharpened definition of volatility effects. Twelve 1985 model automobiles with closed loop fuel control, listed in Table 27, were tested at high ambient temperatures using road test procedures to compare effects of gasoline-EtOH blends. Two volatility levels of gasoline were compared with gasoline-EtOH blends with matched T_{10},T_{50} and vapor pressure, and gasoline-EtOH blends with matched $T_{V/L=20}$. In these tests, even though PFI cars provided better driveability than either TBI or carbureted cars on all fuels, the PFI vehicles experienced much poorer driveability with both versions of the high volatility matched EtOH blends, significant at 90 percent confidence level. As Table 34 also shows, driveability of the carbureted cars was significantly degraded by the low volatility EtOH blend with matched T_{10},T_{50}, and vapor pressure. It might be noted that although this blend was more volatile than the matching gasoline, it had no important effect on performance of the TBI and PFI vehicles.



Source: Reference 58

Figure 20—Driver Satisfaction vs. DI for All-Hydrocarbon and 15% MTBE Fuels

Table 34—High Temperature Driveability[55]
(Ambient Temperature 90 – 92°F)

Fuel	Total Weighted Demerits			
	Carburetor Vehicles	TBI Vehicles	PFI Vehicles	Combined Fleet
Low Volatility Gasoline T_{10}, °F= 128 T_{50}, °F = 226 Vapor Pressure, psi = 10 $T_{V/L=20}$, °F = 136	52	17	5	32
Low Volatility Blend Gasoline + 9.1 vol% EtOH Matched T_{10},T_{50}, Vapor Pressure T_{10}, °F=131 T_{50}, °F = 238 Vapor Pressure, psi = 13 $T_{V/L=20}$, °F = 124	101*	32	7	60*
Low Volatility Blend Gasoline + 9.4 vol% EtOH "Splash Blend" Matched $T_{V/L=20}$ T_{10}, °F=131 T_{50}, °F = 211 Vapor Pressure, psi = 9 $T_{V/L=20}$, °F = 133	63	22	14	40
High Volatility Gasoline T_{10}, °F= 94 T_{50}, °F = 210 Vapor Pressure, psi = 16 $T_{V/L=20}$, °F = 104	163	39	3	92
High Volatility Blend Gasoline + 9.1 vol% EtOH Matched T_{10},T_{50}, Vapor Pressure T_{10}, °F=100 T_{50}, °F = 211 Vapor Pressure, psi = 16 $T_{V/L=20}$, °F = 102	178	46	19*	105
High Volatility Blend Gasoline + 9.4 vol% EtOH "Splash Blend" Matched $T_{V/L=20}$ T_{10}, °F=104 T_{50}, °F = 184 Vapor Pressure, psi = 15 $T_{V/L=20}$, °F = 105	120	50	32*	80

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*Statistically different from gasoline at 90% confidence level.

Table 35—Test Vehicles for High Temperature Driveability Program[61]

Fuel System	Vehicle Description
Carburetor	1985 Chevrolet Impala 5.0L
	1986 Dodge Colt 1.5L
	1983 Ford F-150 Truck 4.9L
	1985 Honda Accord 1.8L
	1986 Plymouth Grand Fury 5.2L
	1985 Plymouth Reliant 2.2L
Throttle Body Injection	1992 Chevrolet Caprice Classic 5.0L
	1991 Chevrolet Cavalier 2.2L
	1992 Geo Metro 1.0L
	1985 Ford Tempo 2.3L
	(2) 1992 GMC Jimmy 4.3L
	1992 GMC Safari Van 4.3L
Port Fuel Injection	1992 Ford Tempo 2.3L
	1992 Mercury Grand Marquis 4.6L
	1992 Nissan Sentra 1.6L
	1991 Oldsmobile Cutlass Ciera 3.3L
	1992 Plymouth Voyager Van 3.3L
	1992 Pontiac Gran Prix LE 3.1L
	1992 Toyota Camry LE 2.2L

5.11.6.3 CRC conducted a gasoline-oxygenate blend study to provide more information concerning the effects of T_{50} and vapor pressure on driveability. In addition to fuel factors, environmental parameters of high and low altitude, and high and intermediate ambient temperatures were included.[61] Fuel control technology of the 20 test vehicles embraced a range of 1983 to 1992 models, with and without closed loop systems. Table 35 lists the test vehicles. Test procedures were modified from those used in prior programs in an effort to improve fuel discrimination.

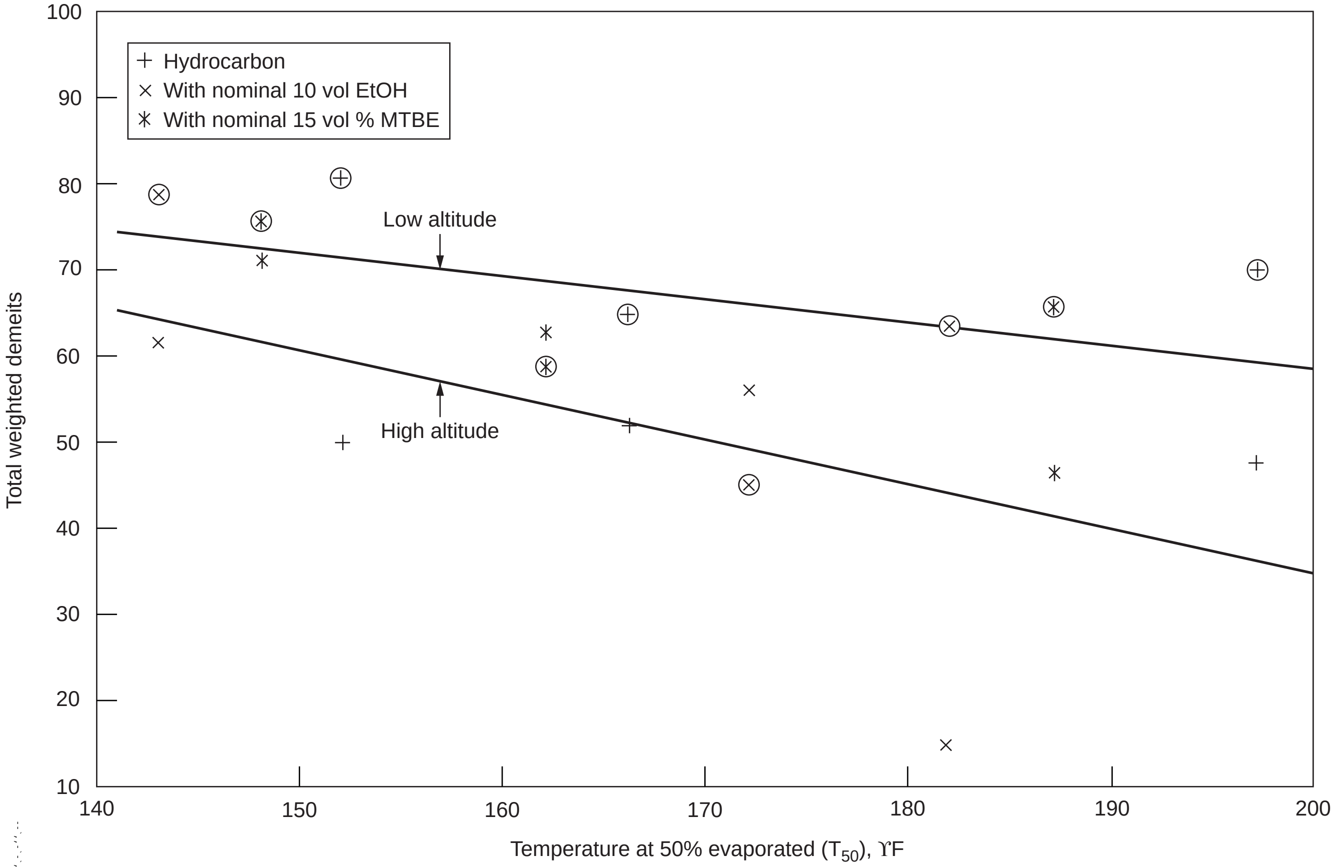
5.11.6.4 At the lower altitude, no effect of T_{50} or vapor pressure of the fuels was distinguished. At the higher test site at high ambient temperatures and with high vapor pressure fuels, the carbureted vehicles had significantly better driveability on the blends with either EtOH or MTBE than on gasoline blends. Both blends gave the same driveability. At lower ambient temperature, under the other aforementioned conditions, the MTBE blend gave significantly better driveability than gasoline or the EtOH blends.

5.11.6.5 For the carbureted vehicles, significant correlations between TWD and T_{50} were developed for the combination of the low vapor pressure fuels for the high altitude, high temperature conditions. Figure 20 shows this correlation and one for the carbureted vehicles at the low altitude. At the high altitude, driveability was improved by 0.43 TWD for each degree increase of T_{50}. At the lower altitude, TWDs decreased 0.28 for each degree increase of T_{50}. These data suggest that the effect of a depression of the distillation curve at T_{50} of 12°F, typically resulting from the addition of 10 volume percent EtOH, could cause a 10 percent driveability penalty, ~5 TWDs, operating at the high altitude and high temperature. The penalty at the lower altitude could be about one-half of that at the high altitude. A blend's distillation curve can be compensated for T_{50} depression. However, as several CRC programs have demonstrated, matched volatility gasoline-EtOH blends may cause inferior driveability. Driveability offsets are major considerations in setting volatility specifications for blends.

5.12 EFFECTS OF GASOLINE-OXYGENATE BLENDS ON FUEL ECONOMY

5.12.1 Volumetric fuel economy is reduced by the addition of oxygenates to gasoline. The extent of the decrease depends upon the reduction of heating value due to the oxygenate, and the vehicle response. As Table 13 indicated, the maximum reduction of heating value resulting from 10 volume percent EtOH in typical gasoline is 3.4 percent. However, internal combustion engines do not necessarily experience losses in fuel economy in direct proportion to fuel heating value. This was demonstrated in a group of 256 fuel-paired 1973-1980 model vehicles that ran on 10 volume percent EtOH and only lost an average of 1.7 percent miles-per-gallon.[62] In this study, fuel metering technology was a strong influence. It was observed that forty-one 1973-4 model vehicles, pre-catalyst and calibrated very lean, lost an average of 3.8 percent fuel economy. Presumably, the "gasohol" caused mixture enleanment beyond flammability limits that resulted in misfiring occasionally. The majority of 1975 to 1979 model vehicles incorporated exhaust oxidation catalysts and carburetors that were calibrated richer than prior year models for improved driveability. This group lost only between 0.6 and 1.7 percent fuel economy. Closed loop fuel control technology became widespread with the 1980 models and regulated fuel metering at stoichiometric mixture, within limits, regardless of fuel oxygenate. This group lost 5 percent fuel economy.

5.12.2 In terms of energy consumption or heat value, the 1975-1979 model year vehicles experienced improved economy ranging from 1.7 to 2.8 percent. The observed improvement in energy specific fuel economy with gasoline-EtOH blends relates to oxygen enhancement of engine thermal efficiency. With oxygenated fuels, the combustion process needs less air and, thus, less nitrogen that is inert and does not contribute to the combustion process. The thermal efficiency advantage, coupled with that of increased volumetric efficiency from cylinder cooling, favor neat alcohols attractive as



Source: Reference 61

Figure 21—Effect of Volatility Parameter T_{50} on Driveability

fuels for high performance engines. Chapter 6 covers neat alcohol as motor fuel. Tables 2 and 3 list stoichiometric ratios, and ratios for moles of combustion product to moles of oxygen plus nitrogen.

5.12.3 Recent fuel economy studies of Federal and California reformulated gasolines have generated much information about oxygenated gasolines. Unfortunately, any effect of oxygenate was obscured in these studies because of the large influence of hydrocarbon composition differences. However, in the Auto/Oil Air Quality Improvement Research Program, the effect of oxygenates as an independent variable was measured using the Federal EPA City Driving Cycle.[63] The effect of EtOH on fuel economy of the AQIRP fleets was found to be similar to that observed in earlier model vehicles.

5.12.4 Volumetric fuel economy was obtained on the fleets of the AQIRP vehicles, described in Table 17, during exhaust emissions testing on the Federal Test Procedure. In one AQIRP test matrix of 11 fuels, the fleet of twenty 1989 model vehicles lost 2.6 percent volumetric fuel economy, significant at the 95 percent confidence interval, when it used gasoline-EtOH blends with 10 volume percent EtOH. Energy specific fuel economy, however, was significantly better by 1.0 percent. The same vehicles when operated on gasoline-MTBE blends, with 15 volume percent MTBE, and gasoline-ETBE blends, with 17 volume percent ETBE, also produced significantly less volumetric fuel economy, 2.3 and 1.7 percent respectively. However, there was no significant difference in energy specific fuel economy. Table 36 summarizes these results. One explanation for the improved energy specific fuel economy, and apparently increased thermal efficiency, with the gasoline-EtOH blends is that the EtOH blends contained 30 percent more oxygen than the blends with MTBE or ETBE.

5.12.5 Another test matrix of 16 test fuels compared fuel economy with, and without, MTBE in both vehicle fleets. Gasoline-MTBE blends in the fleet of older, 1983 – 1985 models, significantly reduced volumetric fuel economy 1.6 percent.

Energy specific fuel economy significantly improved by 0.8 percent. In the fleet of 1989 models, volumetric fuel economy with MTBE significantly decreased by 2.3 percent, about the same as observed with the other test fuel matrix. There was no significant change in energy specific fuel economy.

5.13 COMPATIBILITY OF FUEL SYSTEM MATERIALS WITH OXYGENATED GASOLINES

5.13.1 Automobile manufacturers have cautiously approached endorsement of oxygenated blends from standpoints of customer satisfaction with vehicle driveability and durability. Prior to "gasohol", manufacturers assured the durability of fuel system materials with the use of hydrocarbon-only fuels. Some of the material compatibility problems with "gasohol" in older vehicles directly impaired vehicle operability. During the mid-1980s, steel vehicle fuel tanks and supply lines were found corroded by long term use of "gasohol" in mid-northwestern U.S. Nitrile elastomers and foamed plastics used in carburetors became swelled or saturated by gasoline-alcohol blends. Acrylonitrile-butadiene rubber, commonly used as hose material for gasoline, swelled, softened and lost tensile strength with use of gasoline-alcohol blends.

5.13.2 With the exception of corrosion problems associated with water contaminated blends, currently approved oxygenated gasolines have not caused distinct field problems of vehicle or engine durability. Although phase-separated water-ethanol has been most frequently identified as cause of steel corrosion, chemical attack of aluminum carburetor parts with "dry" gasoline-ethanol blends by has been observed. Test methods are available to screen fuel system metals for "dry" corrosion resistance.[64]

5.13.3 An area of continuing concern is the compatibility and selection of nonmetallic materials for fuel systems. Elastomers and plastics that retain shape and strength with hydrocarbons or neat alcohol occasionally perform poorly with gasoline-alcohol blends. When alcohol and hydrocarbon are combined, polar groups from the alcohol are set free and seek polar compounds of plastics and elastomers. Many elastomers with high resistance to hydrocarbons have polar compounds that are vulnerable to displacement by polar groups from alcohol. Gasoline blends with MeOH and EtOH are especially susceptible to loss of hydrogen bonding of polar groups. Blends with higher molecular weight alcohols or ethers do not have large solubility and polar effects on elastomers.[65]

5.13.4 Fuel system elastomers and plastics must retain adequate dimension, flexibility, and strength after extended exposure to fuel. Permeability and leakage of fuel system components can contribute significantly to increased evaporative emissions. Most all elastomers change characteristics to different degrees when soaked in gasoline.[66] Table 37 lists properties of several elastomers after soaking in gasoline and gasoline blends containing 10 volume percent of either EtOH or 15 volume percent MTBE. The blend containing EtOH caused somewhat more change in most materials than the blend with MTBE. Fluorocarbons, such as Viton A, which exhibit excellent resistance to swelling and hardness change in gasoline and blends, have broadly replaced nitrile elastomers.

5.13.5 Some plastic materials, such as Nylon 66, are essentially impervious to gasoline but swell and lose tensile strength in gasoline-alcohol blends, similar to their behavior in water. GM conducted other long term compatibility bench tests of elastomers and plastics used in vehicles.[67] Some tests were conducted at high temperatures and pressure, as necessary, to accelerate materials deterioration. Table 38 summarizes test results of eight materials that were pertinent to EtOH and MTBE. From these results, GM concluded that, except for deterioration of polybutene terephthalate in the

Table 36—Effect of Oxygenates on Fuel Economy[63]

AQIRP Fleet, FTP City Driving Cycle			
		Percent Change from Non-Oxygenated Fuel	
Test Vehicles	Oxygenate	Volumetric Fuel Economy	Energy Specific Fuel Economy
(20) 1989 Model Year			
11 Test Fuel Matrix	10 vol% EtOH Splash Blend	–2.63, ±0.44*	0.97, ±0.44*
11 Test Fuel Matrix	15 vol% MTBE	–2.30, ±0.58*	No Signif. Diff.
11 Test Fuel Matrix	17 vol% ETBE	–1.71, ±0.80*	No Signif. Diff.
16 Test Fuel Matrix	15 vol% MTBE	–2.39, ±0.21*	No Signif. Diff.
(14) 1983-5 Model Year			
16 Test Fuel Matrix	15 vol% MTBE	–1.61, ±0.54*	0.84, ±0.55*

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* 95% Confidence level.

gasoline-EtOH blend, the property changes were not sufficient to cause concern. The plastic in-tank filter materials that were tested, and the foamed urethane and nitrophyl floats were unchanged.

Table 37—Effects of Gasoline Oxygenate Blends on Some Elastomers (After 72 Hour Immersion)

	Elastomer					
FUEL	Fluorocarbon	Polyester Urethane	Epichloro-hydrin homopolymer	Butadiene-acrylonitrile	Chloro-sulfonated Poly-ethylene	Ethylene-propylenediene terpolymer
Tensile Strength, MPa						
None*	18	23	13	15	17	9
Gasoline	14	18	10	8	13	4
+10% EtOH	12	12	11	7	8	4
+15% MTBE	14	19	10	8	22	4
Elongation, %						
None*	175	477	180	350	222	217
Gasoline	145	348	140	222	97	80
+10% EtOH	153	272	238	195	132	80
+15% MTBE	138	380	135	198	120	83
Hardness, Durometer Shore A, points						
None*	74	70	89	70	87	67
Gasoline	74	64	75	56	66	39
+10% EtOH	—	—	42	49	—	50
+15% MTBE	72	64	72	57	58	40
Volume Change, %						
Gasoline	1	1	3	2	45	137
+10% EtOH	3	37	28	51	56	124
+15% MTBE	3	13	17	35	46	132

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* New Material

5.13.6 Historically, vehicle fuel system components subject to elastomer failures in high mileage, older vehicles have been hoses, carburetors, and mechanical fuel pumps. In early 1995, Chevron monitored fuel system failures of privately owned vehicles that were operated on oxygenated gasolines over a six month period. A fleet of 118 vehicles was fueled by a test blend that contained 11.4 volume percent MTBE and conformed with specifications for California Phase 2 RFG. A companion fleet of 117 vehicles was operated on conventional California wintertime gasoline that had different properties. The vehicles ranged in age from older than 1981 models to newer than 1989 models. In both fleets, about 60 percent of the vehicles had odometer readings greater than 100,000 miles. A combined total of seven possibly fuel related failures, involving fuel pumps, hoses and a carburetor, were observed in the fleets. All incidents occurred in high mileage, older vehicles.[68]

5.13.7 Newer vehicles with fluorocarbon elastomers have not been found to experience problems with oxygenated gasolines. Fuel hoses of domestic automobiles have been lined with fluoroelastomers since about 1982 model-year. Port fuel injection systems, which operate at higher fuel pressures than carbureted and most TBI systems, have incorporated premium materials that are completely compatible with oxygenated fuels. Currently, all auto manufacturers guarantee trouble-free fuel system performance on approved oxygenated fuels, and complete compatibility with California Phase 2 RFG (Reformulated Gasoline) and Federal RFG.

5.13.8 The choice of materials for engines and fuel systems for operation with neat and near-neat alcohol is covered in Chapter 6.

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Table 38—Durability of Plastic and Elastomeric Fuel System Materials

		Percent Change in Weight after Reflux Test		
		1000 hour	24 hour	
Fuel	Plastics:	Saran	Foamed Urethane	Nitrophyl (Foamed nitrile)
Reference Gasoline RFA		–2	–2	–1
CaRFG with 11 % MTBE		–2	–1	–1
CaRFG with 11 % EtOH		–2	–1	–1

PERCENT CHANGE AFTER TESTING [1,2]

	Polybutene Terephthalate	Polyphenylene Sulfide	Fluorocarbon V-A		Epichlorohydrin		Fluorosilicone		Nitrile	
FUEL	Parr[1]	Parr[1]	Parr[1]	Reflux[2]	Parr[1]	Reflux[2]	Parr[1]	Reflux[2]	Parr[1]	Reflux[2]
Tensile Strength										
RFA	–25	9	–29	–25	–24	–12	–39	–17	–20	–69
EtOH	–76	2	–45	–35	–45	–14	–49	–41	–31	–12
MTBE	–21	6	–32	–30	–32	–4	–45	–33	–24	–13
Elongation										
RFA	9	16	–14	–21	–52	–36	–38	–31	–44	–59
EtOH	–77	12	–13	–7	–42	–37	–22	–24	–51	–27
MTBE	2	–5	–5	–14	–50	–26	–35	–33	–51	–30
Hardness										
RFA	—	—	–13	–10	–22	–24	–21	–9	6	–26
EtOH	—	—	–19	–17	–27	–24	–38	–29	–4	1
MTBE	—	—	–14	–12	–12	–17	–28	–23	17	–10
Volume										
RFA	4	2	15	12	16	15	17	15	5	21
EtOH	4	1	20	14	17	15	18	17	6	8
MTBE	3	1	16	13	8	12	25	21	1	15

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[1] Parr Sealed Bomb Test @100°C for 500 hours.
[2] Reflux Test at 37 to 41 °F for 500 hours.

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6 Neat and Near-Neat Alcohols for Fueling Automotive Vehicles

6.1 GENERAL

6.1.1 Gasoline and diesel engine technology advanced during the past century in step with the availability of fuels of increased performance and efficiency. The focus on low vehicle emissions and national energy independence accelerated compositional changes of gasolines and diesel fuels, and renewed interest in neat oxygenates as automotive fuels. The most widely used neat oxygenates as automotive fuels have been MeOH and EtOH. In the United States, and other countries such as Germany and New Zealand, most attention has focused on optimizing vehicles for MeOH rather than EtOH because of considerations discussed in Chapter 3. Long range studies of future low emissions vehicles, beyond the scope of this report, have proposed the possibility of on-vehicle production of hydrogen from MeOH to supply a fuel cell power plant.[1]

6.1.2 Advances in gasoline-powered vehicle technology helped ease the acceptance of gasoline-oxygenate blends. However, with neat alcohols, additional engine and vehicle modifications have been necessary to attain customarily acceptable operation. Spark ignition engines have readily accommodated the combustion of neat alcohols. However, diesel engines were found difficult to compromise for operation on neat alcohols because of the resistance of alcohols to compression ignition.

6.2 ALCOHOL COMBUSTION CHARACTERISTICS

6.2.1 As fuels for passenger car engines, neat MeOH and EtOH can provide excellent performance and efficiency, and potential for low exhaust emissions. For low temperature duty, however, they pose major problems of cold starting. Also, because of their low energy densities, neat MeOH and neat EtOH render shorter vehicle driving range compared to the range obtained from the same amount of gasoline or diesel fuel. Volumetric fuel economy or miles per gallon obtained with MeOH would be about half of that obtained with gasoline or diesel fuel. Nevertheless, on a basis of specific energy consumption, MeOH has been observed to increase fuel efficiency 3 to 4 percent over that obtained with gasoline, even in unmodified vehicles.[2,3,4,5]

6.2.2 Neat alcohols have combustion characteristics and physical properties that differ distinctly from those of gasoline and diesel fuel. The design and development of engines must recognize and accommodate the differences in order to achieve the greatest performance and efficiency. Specifically, MeOH and EtOH differ from hydrocarbon fuels in the following attributes:

a. Have lower energy density; require greater weight or volume for given energy.

b. Require more heat for vaporization.

c. Have constant boiling point temperature.

d. Have wider limits of flammability.

e. Require higher temperature for autoignition and have longer ignition delay (lower cetane, higher octane).

f. Require less air for complete combustion.

g. Produce larger combustion product volume per unit input of oxygen and nitrogen.

h. Burn faster, once ignited, allow optimal piston engine torque development.

i. Burn smoke-free.

j. Burn with lower flame luminosity; less rejected radiant energy of combustion.

k. Produce lower engine exhaust gas temperature.

l. Produce more consistent engine cycle-to-cycle power pulses, once warmed-up.

m. Have lower viscosity in liquid state.

6.2.3 MeOH provides greater engine thermal efficiency than gasoline or diesel fuel because it requires less air to complete combustion. For stoichiometric combustion, one molecule of MeOH is accompanied by 5.64 molecules of nitrogen, and one molecule of gasoline is accompanied by 47 molecules of nitrogen. Nitrogen in the air moves through the combustion process merely “for the ride”, except for occasionally reacting with oxygen at very high temperatures producing small amounts of NO_X. Nitrogen is heated during the combustion process but does not produce power. For stoichiometric combustion of one pound of typical gasoline, as shown in Table 2, 14.7 pounds of air are needed, which contain 11.3 pounds nitrogen. For stoichiometric combustion of the amount of MeOH necessary to match the heating value of gasoline, nitrogen throughput is 10.7 pounds, or 5 percent less than that with gasoline. To lesser degrees, other oxygenates need less air for the same power as from gasoline.

6.2.4 Values cited for autoignition temperature depend upon the laboratory equipment and test procedures used for measurement. Of the compounds assessed here, MeOH has the highest temperature for autoignition, being about 300°F higher than that for diesel fuel and about 400°F higher than that for gasoline. In order to initiate combustion of MeOH in compression ignition engines by autoignition, very high in-cylinder surface temperatures must be developed in the presence of very rich mixtures of alcohol vapor and air during cranking. Bench tests found that the lowest temperature for autoignition or spontaneous combustion of MeOH was 790°F with a fuel to oxygen ratio of 0.05, equivalent to an air-fuel mixture ratio of 2.6.[6,7] For EtOH, measured under similar conditions, the minimum autoignition temperature was about 50°F lower, at 740°F, and occurred at a 0.48 fuel to oxygen ratio, equivalent to an air-fuel ratio of 3.0.[8] In engine applications, the cylinder temperature required for autoignition of alcohols is considered to be as much as 300°F higher than laboratory values because of the cooling effect from vaporization.[9]

6.3 SPARK-IGNITION ENGINE OPERATION WITH NEAT ALCOHOL

6.3.1 General

6.3.1.1 As a fuel for high performance race cars, MeOH historically has been widely used and identified with the annual Indianapolis 500. To take advantage of the superior knock resistance of MeOH, racing engines commonly either had high compression ratios or intake air supercharging and ran very rich mixtures.[10] Typically, such engines were designed to burn MeOH mixtures 40 percent richer than stoichiometric, and devour masses of fuel about three times as fast as possible with gasoline.[11] Theoretically, as shown in Table 2, MeOH is capable of combustion with mixture richness four times its stoichiometric ratio.

6.3.1.2 Until vehicle emissions became an issue, higher power output was a key attraction of alcohols in spark ignition engines. Without major engine changes, neat MeOH generally can increase engine power output by 10 percent over that obtained with gasoline due to increased charge density and engine breathing.[12,13] MeOH has a very high latent heat of vaporization, and it can burn very rich mixtures. This combination results in lower temperatures of the engine’s working fluid during intake, combustion and exhaust and effectively increases engine breathing (improved volumetric efficiency).[14] For racing purposes, MeOH might be preferable to EtOH because of its potential for lower mixture temperatures and higher volumetric efficiency. MeOH offers the same antiknock benefits as EtOH but requires 71 percent more heat for vaporization for each unit of combustion heat generated. This can be considered either an advantage or a disadvantage.

6.3.1.3 Additional thermal efficiency benefits of MeOH can be derived through engine modification. Increased compression ratio is the most common route for either improved power or economy.[6] Alcohol-fueled engines improve performance with increased compression ratio and respond with gains in fuel economy comparable to that observed in gasoline engines.[15,16] MeOH, EtOH and some ethers may allow significant increases of engine compression ratio for maximum thermal efficiency. For several years, 85 to 90 percent of the new cars in Brazil were built with engines with ~12:1 compression ratio to use a mixture of 95 percent denatured EtOH and 5 percent water.[3,17] Higher compression ratio allows greater power output and fuel economy, although benefits become incrementally less at higher compression ratios due to increased engine friction and combustion chamber geometry effects.[18,19] In a single cylinder engine optimized for MeOH, Brinkman observed that an increase of compression ratio from 8:1 to 18:1 improved engine efficiency by 16 percent.[20] Generally fuel economy of spark-ignited engines increases between 2 and 4 percent for each ratio number increase between 8 and 12:1.[6,21] Higher gains in fuel economy are possible if the increased engine power output achieved with the higher compression ratio engine is traded off for maximum fuel economy.[22]

6.3.1.4 An indirect approach to vehicle fuel economy improvement entails the use of superchargers or turbochargers that allow increased engine power output similar to aircraft engine practice.[23,24] Supercharging or turbocharging is not generally regarded as a means to increase engine thermal efficiency, but it can allow fuel economy to be improved through reduced vehicle weight made possible by the use of smaller, lighter weight engines.

6.3.2 Exhaust and Evaporative Emissions with Neat Oxygenates

6.3.2.1 Current knowledge concerning the characteristics of exhaust and evaporative emissions of alcohol-powered vehicles designed to meet U.S. emissions standards is based on data from a limited number of experimental and prototype vehicles. Brazil operates more than one million vehicles on neat EtOH but has no emissions standards. In the United States there is little widespread interest in EtOH as a neat motor fuel due to the economics described in Chapter 3. Of all oxygenates, MeOH, both neat and adulterated, has received most of the attention as a potential means to reduce regulated vehicle emissions for both spark-ignition and compression-ignition engines.

6.3.2.2 Neat MeOH offers potential for lower evaporative and exhaust emissions of hydrocarbons. It has lower photochemical activity than most hydrocarbons in the reactions that result in "smog" and may offer advantages for regions that have severe urban air pollution problems.[25,26,27,28,29] Additionally, hydrocarbons that might be formed by combustion of MeOH may have lower reactivity than those formed by gasoline combustion.[30] The differences between the reactivity of emissions from vehicles using alcohols and those using gasoline led to changes in the specifications for hydrocarbon emissions. California initiated a consistent "fuel neutral" specification, applicable to both alcohol or gasoline vehicles, to replace the familiar term HC. It adopted NMOG, Non-Methane Organic Gas, for TLEV and LEV emissions standards. In turn, fuel reactivity factors could be applied for use in air quality modeling studies of the impact of vehicle emissions on air quality. The concept led to a complicated system that adjusted the mass emissions of individual organic species according to their estimated ozone forming potential.[31] In this system, MeOH was given a Maximum Incremental Reactivity (MIR) factor of 0.56 grams potential ozone per gram NMOG emissions, EtOH had 1.34 MIR, and conventional gasoline had 3.42 MIR. U.S. EPA chose to replace HC in its emissions standards with OMCHE, Organic Material Hydrocarbon Equivalent. It should be noted, however, that data available for estimating the air quality impact of methanol vehicle emissions is limited. Multi day smog episodes may give adequate time for methanol to react to form ozone. The EPA and automakers have acknowledged that the air quality benefits of methanol substitution are uncertain and that estimates of the potential benefits have to be updated as more data become available.[32,33] Appendix A includes some of the jargon used to describe vehicle organic emissions and their contribution to atmospheric ozone. The subject of projecting air quality benefits due to vehicle use of alcohol fuels is beyond the scope of this assessment.

6.3.2.3 Exhaust emissions of CO and NO_X from optimized methanol vehicles have been found to be substantially the same as those from vehicles powered by gasoline.[18,34] Theoretical benefits of reduced emissions of NO_X due to lower peak combustion temperatures when MeOH is used instead of gasoline have not necessarily been realized from optimized MeOH vehicle calibrations. Engine compression ratio increases, which are desirable to take advantage of the high octane of MeOH and improve fuel economy, increase production of NO_X and unburned fuel emissions.[19]

6.3.2.4 Exhaust emissions control systems were required to lower exhaust emissions of prototype engines designed to operate on either neat or near-neat MeOH blends. Most systems employed three-way catalysts, closed loop control, and

Table 39—Aldehydes From Partial Oxidation of Oxygenates

MeOH	
	$CH_3OH + {}^1/_2\,O_2 \rightarrow$ HCHO (formaldehyde) + H_2O
EtOH	
	$C_2H_5OH + {}^1/_2\,O_2 \rightarrow CH_3CHO$ (acetaldehyde) + H_2O
MTBE	
	$C_5H_{12}O + 2{}^1/_2\,O_2 \rightarrow$ 5(HCHO) (formaldehyde) + H_2O
TAME, ETBE, DIPE	
	$C_6H_{14}O + 3O_2 \rightarrow$ 6(HCHO) (formaldehyde) + H_2O

Note: See Table 4 for Products of Complete Combustion Reactions.

exhaust-gas recirculation as developed for gasoline engines.[4,35,36,37,38] Unburned MeOH and CO was lowered effectively by either oxidation-only catalysts or by three-way catalyst. However, due to lower exhaust-gas temperature with MeOH, three-way catalytic converters did not operate as efficiently on MeOH vehicle exhaust as on gasoline vehicle exhaust, particularly with respect to NO_x reduction.[39] Most of the unburned MeOH and CO emissions observed on the FTP procedure were generated during the cold start portion of the test.

6.3.2.5 Neat MeOH generally produced less evaporative losses from fuel-injected vehicles than gasoline.[32] Evaporative emissions of MeOH appeared to be controllable in a manner similar to the conventional charcoal canisters used for gasoline. However, the working capacity of a canister with MeOH was found to be less,[40] and there were some questions about long term MeOH effects on canister durability.[41,42,43] Emissions of evaporated MeOH are toxic as discussed in Chapter 10 and their control has implications other than "smog" formation.

6.3.3 Aldehyde Emissions

6.3.3.1 Although MeOH vehicles may produce less reactive hydrocarbon emissions than gasoline vehicles, they can generate large amounts of formaldehyde. Formaldehyde, in addition to being an eye irritant and a probable human carcinogen, has been identified as being highly active in photochemical smog reactions. The MIR value for formaldehyde is 7.15 compared with a MIR for conventional gasoline of 3.42. The EPA currently considers a molecule of formaldehyde to be 4.83 times as reactive atmospherically as a molecule of (non-methane) hydrocarbon.[33] California LEV standards currently limit tailpipe emissions of formaldehyde to 15 milligrams per mile.

6.3.3.2 Aldehydes are reactive and difficult to measure in vehicle exhaust.[44,45,46] Table 39 shows the partial oxidation reactions that produce aldehydes from some oxygenates. Aldehydes result from partial combustion of overly rich mixtures, such as during starting and warmup, when insufficient oxygen is available to completely combine with the hydrocarbon remaining after hydrogen oxidation to form water. They are not a unique result of oxygenate combustion but also occur in combustion gases of gasoline engines, usually when mixture ratios are richer than stoichiometric.[5] Partial oxidation of MeOH is prone to produce formaldehyde, while EtOH is likely to produce acetaldehyde. Further incomplete oxidation of formaldehyde or acetaldehyde produces formic acid or acetic acid, respectively. Partial oxidation of MTBE has the potential to form five times the amount of formaldehyde as MeOH on equal consumption basis and three times that of MeOH on a basis of equivalent heating value. Tailpipe emissions from experimental vehicles operating on neat-MeOH or near-neat MeOH on the FTP driving cycle have contained as much as ten times the amount of formaldehyde observed from gasoline vehicles.[39,45,48,49] Vehicle exhaust catalysts, either oxidation or three-way, can effectively control aldehyde and formaldehyde emissions from engines using either gasoline or MeOH, especially at lean or stoichiometric air-fuel mixtures.[39,49] CRC testing showed that three-way exhaust catalyst systems lowered aldehydes from neat MeOH by over 90 percent. However, the level of aldehyde after treatment was not as low as attainable with gasoline.[45] Much development work remains to optimize catalyst formulations for application to MeOH vehicles. One automobile manufacturer was able to optimize a catalyst formulation and size, and lower aldehydes to the same levels obtained from gasoline with a three-way catalyst.[48] Another observed that certain base metal catalysts are as effective on MeOH vehicles as noble metal catalysts used in three-way systems.[39] Formaldehyde emission control remains to be demonstrated for high mileage vehicles.

6.3.3.3 Exhaust catalyst requirements for controlling formaldehyde emissions from MeOH engines appear to be dictated primarily by the lean-operating capability of the engine during warm-up.[39,48] Through very lean operation, the production of NO_x can be minimized in the combustion process and allow low NO_x without exhaust-gas recirculation or a reduction catalyst. Although formaldehyde emissions were higher in lean-burn systems, they have been successfully lowered through oxidation catalysts.

6.3.4 Experiments with Neat Ethers

6.3.4.1 Neat ethers have been technically considered as automotive fuels because they have high knock resistance, and require less heat to vaporize and have higher energy densities than alcohols. Also, they have been widely used commercially as blending agents for reformulated gasoline. A vehicle experiment, worthy of note, demonstrated that neat MTBE could be an alternative fuel for vehicles designed for gasoline. Springer et al, compared FTP exhaust emissions and fuel economy of neat MTBE with EPA certification gasoline in a 1988 model Buick at both 70°F and 20°F.[50] No modifications were made to the car to accommodate the use of neat MTBE. At "normal" 70°F FTP test temperature, HC, CO, and NO_x were lower with MTBE by 36 percent, 44 percent and 9 percent, respectively. At 20°F, with MTBE, emissions of HC were 31 percent lower than with gasoline, CO emissions were not different, and NO_x emissions were 8 percent greater with MTBE. The HC and CO differences were greatest during the cold start phase of the test. Formaldehyde emissions also were observed to be greater than those with gasoline at the lower temperature, as might be expected. Cold starting and driveability at 20°F with neat MTBE was reportedly "without stalling, hesitation or apparent driveability problems." As discussed later, engine starting at 20°F with neat MeOH is a moot point, and large quantities of unburned MeOH and formaldehyde would be emitted during starting attempts. Volumetric fuel economy with MTBE was 20 percent lower than with gasoline, due to MTBE's 17 percent lower energy density. Specific energy consumption was the same for both fuels at 70°F, but was better with MTBE, 2.6 percent lower, than with gasoline at 20°F.

6.3.4.2 Dimethyl Ether reportedly has cetane quality comparable to diesel fuel and burns without forming soot. Significant reductions in NO_x emissions have been achieved through increased EGR rates. Fleish, et al, reported that use of neat Dimethyl Ether allowed a Navistar V-8 truck diesel engine to meet 1998 California ULEV regulations for medium-duty vehicles without need for exhaust treatment. Dimethyl Ether provided slightly better energy efficiency that diesel fuel but about 80 percent poorer volumetric fuel economy due to its lower energy density.[51]

6.3.4.3 AVL List GmbH conducted a feasibility study of Dimethyl Ether as neat fuel for a direct injection diesel passenger car engine and demonstrated low NO_x emissions but that an oxidation catalyst would be needed to reduce HC and CO to meet ULEV standards.[52] Although the results of these experiments were highly encouraging from a technical viewpoint, ethers have not received much commercial attention as neat automotive fuels, likely due to considerations of manufacturing capacities and product costs, as discussed in Chapter 3. Technically, ethers, such as MTBE, offer high octane performance for spark-ignition engines that is comparable with MeOH and EtOH, but they do not have combustion features as thermodynamically unique as those of neat alcohols.

6.3.5 Neat MeOH Passenger Vehicle Demonstration Programs

6.3.5.1 During 1981 through 1983, in Sacramento, California, the California Energy Commission field tested 39 Volkswagens calibrated for either neat EtOH or neat MeOH.[53] All of the vehicles were equipped with The Volkswagen "Changeable Methanol Concept" (CMC) system which incorporated a 12.6:1 compression ratio engine, and a complex dual fuel supply system to allow emergency downgraded operation on gasoline.[38] With the CMC system, operation on MeOH produced maximum power with minimum energy consumption, but emergency operation on gasoline produced only 83 percent of the power and 73 percent of the efficiency obtained using MeOH. The isolation of gasoline from MeOH in the fuel system of the CMC eliminated the potential problems of excess vapor pressure caused by commingling fuels in a single fuel tank system. The Volkswagen test program lasted two years and was judged a technical success. During that time frame, the California Energy Commission also deployed 20 MeOH Ford Escorts that were successfully operated in Los Angeles.

6.3.5.2 Based on the technical success of the Sacramento and Los Angeles test programs with the Volkswagens and Ford Escorts, in 1983, California embarked on testing 500 dedicated MeOH Escorts on a wider geographic scale. Initially, the MeOH was dosed with pentanes to aid starting, and later, premium-grade gasoline was used. A network of about 15 MeOH dispensing stations were set up so that the vehicle could be driven between northern and southern California. At Los Angeles International Airport, 150 units were allotted through a car rental agency to state employees for airport transportation. However, "consumer acceptance" problems were encountered due to driver perceptions of an inadequate availability of fuel from the limited distribution network. The lessons learned, concerning driving range with MeOH vehicles and fuel availability, provided additional encouragement for the development of gasoline-tolerant MeOH vehicles, and flexible fuel vehicles.[54] By the end of 1987 six hundred thirty Ford-built MeOH vehicles were on the road in various feasibility demonstration programs.[55] California also has neat-MeOH demonstration projects for heavy-duty diesel vehicles, which will be mentioned later.

6.3.6 Emissions of Experimental Neat MeOH Vehicles—Spark-Ignition Engines

6.3.6.1 The wide flammability limits of MeOH permit spark-ignited engines to operate with very lean combustion and allow improved fuel economy and lower engine NO_x emissions. In 1985, Toyota developed an experimental lean-burn engine that operated at mixtures 40 percent leaner than stoichiometric.[48] When operated lean-burn, a vehicle with the engine produced less than 0.7 grams NO_x per mile and 9 percent better fuel economy than it did when it was operated at stoichiometric mixture.[56] Toyota's second generation lean-burn MeOH vehicle incorporated intake swirl control valves and high turbulence combustion chambers with 11.0:1 compression ratio. It also incorporated a lean mixture sensor, sequential PFI, air injection and dual oxidation exhaust catalysts for HC and CO control.[57] Toyota discovered that compression ratios above 11.0:1 produced more power, but increased brake specific fuel consumption at low NO_x emissions and promoted high speed knock and preignition.

6.3.6.2 AQIRP measured emissions and fuel economy of three experimental vehicles: a second generation Toyota lean-burn MeOH Corolla, a MeOH Nissan Sentra and a Chevrolet Lumina developed for exclusive operation on M85, a mixture of 85 percent MeOH and 15 percent gasoline.[58] The vehicles were not evaluated for low temperature starting or driveability. Exhaust emissions and fuel economy results are shown in Table 40. For the Toyota, exhaust emissions of CO and NO_x met requirements for California TLEV emissions. However, NMOG emissions, which include oxygenated hydrocarbons, exceeded the TLEV limit. Formaldehyde emissions were well below the LEV standard, and even met the more stringent ULEV standard of 8 mg/mile. FTP fuel economy was 17.4 miles per gallon MeOH. Table 40 also lists AQIRP measurements of emissions from a Nissan lean-burn MeOH Sentra with 12:1 compression ratio, PFI, oxygen sensor and three way catalyst. The vehicle had lower CO emissions and better fuel economy than the Toyota but failed to meet TLEV standards for other pollutants.

6.3.6.3 Volkswagen developed an experimental spark-ignited engine with direct cylinder fuel injection for operation on neat MeOH. The engine was operated unthrottled and power output was regulated by control of the fuel injection

Table 40—FTP Exhaust Emissions of Experimental MeOH Passenger Cars

					Comparative Reference Values		
	Volkswagen Jetta[1]	Nissan Sentra[2]	Toyota Corolla[2]	Chevrolet Lumina[2]	1989 Models[3]	1989-91 Models[4]	California TLEV/LEV/ULEV Standards[5]
FTP Fuel Economy, MPG MeOH:							
	15.1	18.4	17.4	11.8	—	—	—
Emissions, Grams per mile:							
HC	—	0.13	0.08	0.05	0.22	0.29	—/—/—
NMOG	—	0.36	0.20	0.10	—	—	
OMHCE	0.25	0.16	0.10	0.06	—	—	0.125/.075/.040
CO	0.2	0.82	1.67	0.80	2.69	4.34	3.4/3.4/1.7
NO_x	0.45	0.51	0.39	0.22	0.60	0.81	0.4/0.2/0.2
CH_3OH	—	0.33	0.18	0.07	—	—	—/—/—
Toxics, milligrams per mile:							
HCHO	5.0	27.2	7.5	5.7	1.5	2.4	15/15/8
CH_3CHO	—	ND	ND	ND	1.0	0.9	—/—/—
Benzene	—	ND	ND	1.0	9.3	12.3	—/2.0/—
1,3-Butadiene	—	ND	ND	ND	1.1	1.1	—/—/—

Notes:
[1] Reference 59.
[2] Reference 58.
[3] Reference 168: (20) Vehicles, (4) Gasolines.
[4] Reference 169: (7) Vehicles on Gasoline.
[5] Standards for vehicles < 3750 lbs loaded vehicle weight using alternate fuel.
ND= Measured but None Detected.

and spark timing. It had 16:1 compression ratio, swirl intake ports, a turbocharger, EGR and was outfitted for vehicle testing with a platinum oxidation catalyst with rapid warmup characteristics. FTP exhaust emissions of CO and OMHCE were below California TLEV standards but NO_x emissions slightly exceeded the TLEV limit of 0.4 GPM. Fuel economy on the FTP cycle was 15.1 miles per gallon MeOH.[59]

6.3.6.4 Evaporative emissions have not appeared to be a problem with neat MeOH and have been easily accommodated by carbon canisters that are commonly used on gasoline powered vehicles. Each of the three vehicles evaluated by AQIRP, including the Lumina on M85, emitted diurnal or hot soak evaporative losses below 0.3 grams per test of NMOG, OMCHE or MeOH.

6.3.7 Cold Starting with Neat Alcohol

6.3.7.1 The problem of cold starting and misfiring during warmup offsets the distinct thermodynamic benefits of neat alcohols.[60] In addition to unacceptable driveability, unsuccessful starting and misfiring during warmup of both spark-ignition and compression-ignition engines results in liberal washing of cylinder walls which increases cylinder bore wear and dilutes the engine lubricant.[61,62] Historically, U.S. manufacturers engineered passenger cars to successfully start at ambient temperatures as low as –20°F without requiring auxiliary starting aids, such as ethers or block heaters.[63] General Motors and Ford stated that customers want engines to start and run within 10 or 15 seconds, even at –20°F.[64,65] Seasonal increase of gasoline volatility by refiners has in the past been key to successful low temperature starting. The easy vaporization of light hydrocarbons from gasoline allowed empirical calibrations of carburetors that provided richer mixtures at lower temperatures and combustible vapor-air mixtures for satisfactory starting. With neat alcohols, however, mixture enrichment compensation for low temperature does not assure combustible vapor formation.

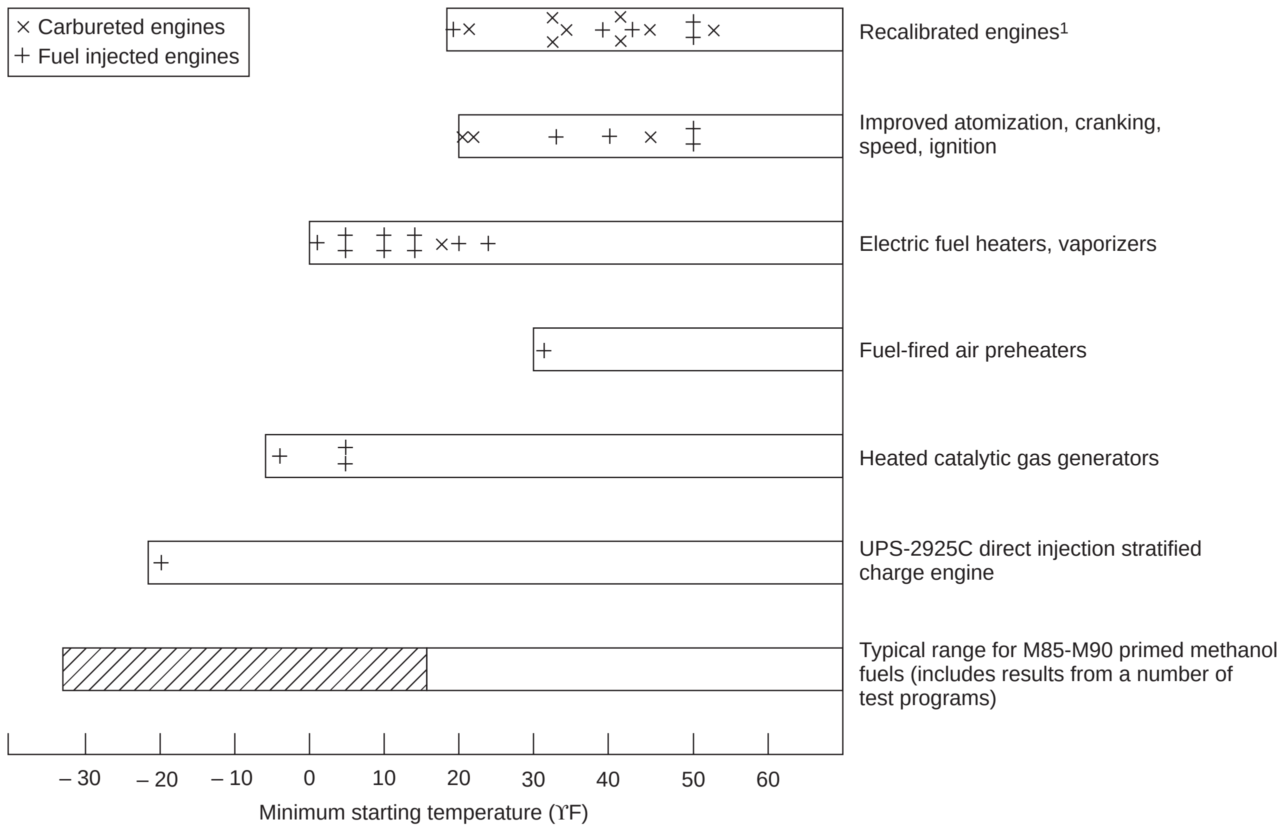
6.3.7.2 Neat alcohols are not sufficiently volatile to enable a cold engine to start, even at moderately low temperatures. In deference to gasoline, which has a range of low boiling point hydrocarbons, neat MeOH and EtOH have constant boiling points of 148 and 173°F, respectively. They require seven and four times as much heat, respectively, as gasoline to vaporize an amount of fuel required to produce equivalent combustion heat. In order to vaporize sufficient fuel to provide a lean limit combustible mixture, compared with gasoline, MeOH needs about six times as much heat. Using MeOH, carbureted engines have been started at ambient temperatures above 50°F without extra heating or starting aids.[66,67] Some carbureted engines using neat EtOH need temperatures above 100°F for unassisted starting.[68] Theoretically, the flammability/vapor pressure relationships indicate that a mixture of air and excess MeOH will be too lean to ignite below about 50°F.[69,70] Equilibrium temperatures for EtOH and higher molecular weight alcohols are even greater than that of MeOH.[71] If sufficient MeOH vaporization does not occur, starting is impossible at temperatures at which gasoline engines usually have no starting problems. At –4°F, theoretically only about 10 percent of the MeOH vapor necessary for lean limit combustion would be available.[72]

6.3.7.3 Some heat for vaporization is provided by the compression heat generated by engine cranking during starting attempts. Cylinder compression temperatures increase with ambient temperature, engine compression ratio and cranking speed. Peak compression air temperatures of 270°F to 340°F above ambient were observed in three different studies in engines with compression ratios between 12:1 and 13:1.[73,74,75] In other tests, a single cylinder engine with 9.5:1 compression ratio was observed to have an average temperature rise of about 130°F above ambient.[76] At very low cranking speeds, as might be encountered in frigid ambients, the net heat of compression may be negligible. Charge heating by electrical elements at individual cylinder intake ports was found able to vaporize sufficient MeOH for cold starting at temperatures almost as low as 10°F. However, the energy needed was as high as 60 watts per cylinder, about 8 times the rate of heat flux to vaporize sufficient MeOH for a lean limit flammable mixture.[35]

6.3.7.4 Figure 22, developed by Battista, et al.,[72] using data from several sources, summarizes results of MeOH startability tests of engine configurations with different levels of technical sophistication. The two upper bars show that starting could not be obtained below 20°F by means of engine recalibration, changes in ignition, cranking speed, or fuel atomization. The combination of high compression ratio and port fuel injection provided better low temperature starting characteristics with MeOH than theory would predict. Iwai, et al., found starting to be possible with MeOH at 20°F with a 12:1 compression ratio engine with port fuel injection after cranking for 60 seconds.[77] They tested another 12:1 compression ratio engine but with a carburetor and found it could not be started below 34°F. They were able to start a 10:1 compression ratio engine with port fuel injection and a cold start injector at 27°F. In these studies, fuel enrichment for starting was 12.5 to 20 times that necessary for stoichiometry. Throttling rich mixtures during cranking has been found to reduce cylinder pressure and enhance MeOH vaporization.[72,76]

6.3.7.5 Devices have been developed to assist MeOH vaporization using finer atomization.[35,60] Development work with ultrasonic nozzles demonstrated some success in achieving starting within 5 seconds at 41°F, a reduction of 75 seconds from the time required with a carburetor.[60] High pressure fuel injection at the intake port provides better atomization in the cylinder than carburetors or throttle body injection.[35,60,78] MeOH at higher temperatures atomizes more readily through either high or low pressure injectors. Studies have shown that MeOH vaporization increased within the engine cylinder under cranking conditions if fuel droplets in sizes below 50 microns diameter could be delivered. Reduced droplet size from 50 to 10 microns reportedly lowered starting temperature from 64°F to 5°F.[79] The size of MeOH droplets emerging from pintle type port fuel injectors was found to be a direct function of liquid viscosity. The mean diameter of MeOH particles at –18°F was more than three times that at 75°F.[80]

6.3.7.6 Vaporization and ignition of finely atomized MeOH droplets has been enhanced by long duration, high energy igniters, similar to the ignition technology employed in jet engine combustors. Successful starting and running on MeOH was obtained within 10 seconds at –20°F on a port fuel-injected Chevrolet Lumina with a modified 8.8:1 compression ratio engine that incorporated plasma jet engine igniters and early EGR.[81] The early EGR provided extra heat to the incoming cylinder charge by means of a modified camshaft that re-opened the exhaust valves and inducted exhaust gas back into the cylinders. The igniters required about 30 – 35 watts electrical power for cold starting, much less than glow plug heaters.[82]



[1]Recalibrations made for performance improvements (other than those specifically for low temperature starting) e.g., compression ratio, EFE heater, etc.

Source: Reference 72

Figure 22—Neat MeOH Startability of Engines at Low Temperatures

6.3.7.7 Other endothermic concepts of cold starting assistance examined the possibility of generating hydrogen by partial oxidation and dissociation of neat MeOH. Hydrogen has wide flammability limits and ignites readily. It is possible to dissociate MeOH into hydrogen and carbon monoxide by heating or by passing it over noble metal catalyst controlled to optimum temperature for maximum hydrogen production.[83]

6.3.7.8 Dissociated gases have been used with atomized MeOH to provide enough energy for starting and warmup. One experiment employed a precombustion chamber to partially oxidize MeOH and generate quantities of hydrogen that were fed to the engine's cylinder for starting. The main fuel source was provided by port fuel injection. Air was fed to the pre-chamber, and an ultrasonic injector supplied fine particles of MeOH around the electrodes of a spark plug.

The energy of the spark discharge was sufficient to vaporize and ignite the mixture. The combustor generated about 15 percent hydrogen. The engine started with a mixture of 7 percent hydrogen in air at –18°F within three seconds.[84] Another laboratory study, with simulated MeOH decomposition, found that at –18°F engine firing was possible within five seconds with a mixture of 5 percent hydrogen in air and sustained running obtained with 12 percent hydrogen.[85] Because dissociated MeOH is gaseous, it reduces engine volumetric efficiency and maximum engine power output compared with either vaporized or liquid MeOH. Thus, its most optimistic passenger car potential would be for starting and low load operation, in conjunction with liquid MeOH for high output.[60,80,86]

6.3.7.9 Direct injection of MeOH into the combustion chamber has been found to greatly improve cold starting, especially when the fuel charge is stratified so that combustible mixture surrounds the spark discharge. A direct injection stratified charge (DISC) engine with 13:1 compression ratio, demonstrated startability on MeOH at –20°F within four seconds.[73] In this engine, the injector directed highly atomized fuel toward the spark plug that produced a prolonged duration spark. The exceptional starting characteristics were attributed to the distribution and motion of the burning fuel mixture within the cylinder, and not the result of charge compression heating.[87] The DISC engine configuration, sans sparkplug, is comparable with that of open chamber diesel engines.

6.3.7.10 Domestic manufacturers reported that experimental alcohol-powered cars, once started and warmed-up, have the same or better driveability as gasoline cars.[2,36,78,88] Although some early experimental MeOH vehicles experienced poor driveability caused by port fuel injector fouling, injector design modifications addressed the problems.[34,91] Driveability experience with mass-produced alcohol-powered automobiles has been limited to Brazilian and German models that were not calibrated to meet U.S. standards for exhaust or evaporative emissions. Brazilian experience with "neat EtOH" dictated the need for an onboard auxiliary supply of volatile fuel, such as a gasoline-EtOH blend, that could be introduced into the engine for cold starting. The Volkswagens in the California MeOH program of 1981 – 1983 were equipped with a gasoline-assist starting system similar to that used in Brazil.

6.3.7.11 General Motors developed its first MeOH demonstration vehicle with an auxiliary onboard propane injection system to assist cold starting. This system provided reliable cold starts down to –4°F.[78] Figure 23 illustrates the GM starting system and other vehicle components that were modified to allow the use of neat MeOH. Currently, development of dual fuel systems for U.S. passenger cars to allow primary operation on neat MeOH has been abandoned. Although considerable scientific progress was made to measure and technically define the MeOH cold start problem, practical vehicle implementation of potential solutions remained an obstacle. In addition to vehicle complexities, the requirements for special handling and an infrastructure necessary for MeOH distribution were considerations that favored adoption of mixtures of MeOH and gasoline.

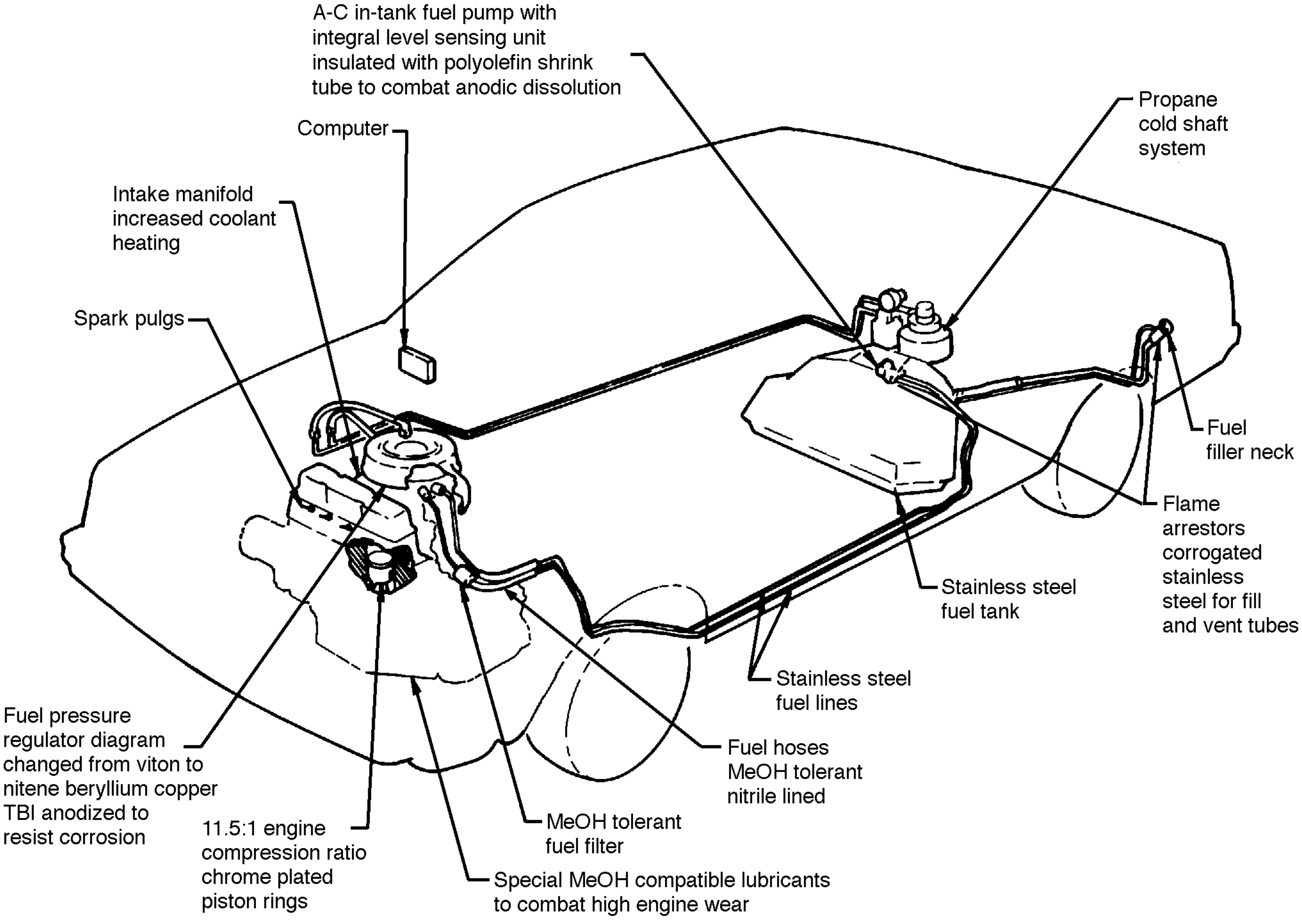
6.3.8 Cold Starting Spark-Ignition Engines with Near-Neat Alcohols

6.3.8.1 The addition of volatile hydrocarbons to MeOH or EtOH was found to be an acceptable practical answer to the cold engine starting dilemma. Figure 24 shows the effect of supplemental hydrocarbons and gasoline on simulated minimum cold starting temperatures from laboratory bench tests that allowed for evaporative cooling, but not for compression heating.[40,69] Addition of 15 percent gasoline to EtOH reduced the temperature necessary for a flammable mixture from 86°F to 45°F. The addition of 6 percent by volume pentane to MeOH provided about the same minimum flammable temperature as the addition of 15 percent gasoline. MeOH responded better to addition of 15 percent gasoline, and the flammable mixture temperature was reduced from 61°F to 9°F.

6.3.8.2 Iwai, et al., measured the effects of MeOH-hydrocarbon mixtures on the startability of three different engines. The engine tests confirmed that startability temperature was reduced as much by use of either a blend of 5 percent isopentane (IP) in MeOH or a blend of 15 percent average vapor pressure gasoline (MVP) in MeOH. Figure 25 also shows that a blend of 5 percent dimethyl ether (DME) was not nearly as effective as M85 although it had vapor pressure two psi greater than the isopentane blend. Low concentrations of dimethyl ether in MeOH reportedly do not have the disadvantages of phase separation experienced with some hydrocarbons such as isopentane.[77] Both M85 with high vapor pressure gasoline (HVP) and a five percent butane (BU) blend in MeOH provided startability at temperatures below –20°F for the fuel injected engines. Although five percent butane would help low temperature starting as much as 15 percent gasoline, it would increase vapor pressure excessively and in service would weather quickly from the blend.[90] Pentane addition to MeOH was successfully used during the first two years of the State of California field test program beginning in 1980.[91] Later, Ford demonstrated startability using M85 at –20°F in an experimental engine with computer-controlled starting.[19] General Motors reported that reliable starts of a "variable fuel" vehicle were obtained with M85 containing winter volatility gasoline at temperatures as low as –8.5°F.[92]

6.3.9 Combustion Luminosity, In-Tank Explosivity and Toxicity of MeOH

6.3.9.1 Additional incentives for blending gasoline into MeOH relate to safety considerations. MeOH presents a par-



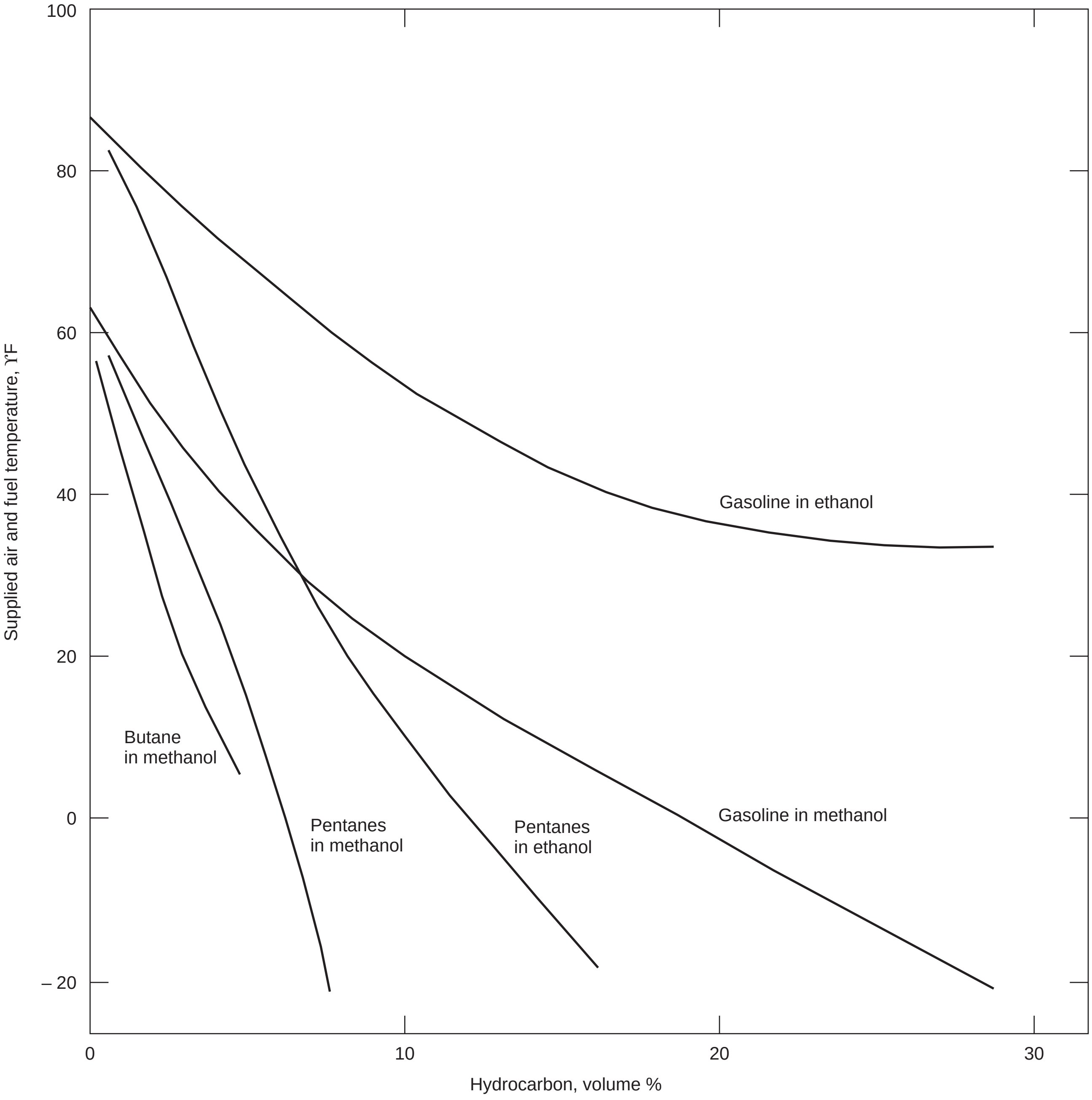
Source: Reference 78

Figure 23—General Motors Methanol Vehicle

ticular safety hazard because it burns with a flame that is invisible, particularly in daylight. For safer handling of MeOH, it was found desirable to add hydrocarbon for increased flame luminosity from carbon combustion.[90] Toluene, which contains 91 weight percent carbon, at concentrations as low as 2 volume percent, produces high flame luminosity. However, its flame luminosity fades, even at 5 percent concentration, leaving 30 to 50 percent of the MeOH unburned. Luminous flames can be produced by 5 percent by volume gasoline or reformate, but luminosity lasts for a shorter period and disappears, while 70 to 80 percent of the MeOH still remains. M85 blends containing gasoline with at least 40 percent aromatics content provides a luminous flame that will persist until all of the MeOH is consumed.[93]

6.3.9.2 Another concern of onboard vehicle safety is the potential explosivity of MeOH. Saturated vapor over neat MeOH in a fuel tank is flammable at temperatures between about 45 to 110°F. Ignition of MeOH vapor is possible from a spark source such as the exposed brushes of an electric fuel pump in a fuel tank that has run out of fuel. GM experimented with foam fillings in fuel tanks, that essentially eliminated the continuous vapor space required for explosion hazards with flammable mixtures.[94] Another effective solution offered was the addition of gasoline or pentanes to MeOH to enrich the vapor beyond the rich flammability limit. For example, MeOH with 15 percent gasoline produced vapors beyond the rich flammability limit above about 10°F.[93] Lower concentrations were less effective. (See Chapter 8 for a discussion of MeOH flammability and storage safety.)

6.3.9.3 ASTM has been developing a standardized test for combustion luminosity of near-neat MeOH blends. The approach is to compare the intensity of luminosity throughout a burn of near-neat MeOH with that of neat EtOH. ASTM has included details of the preliminary apparatus and results in ASTM D 5797-95, Specification for M70-M85.[95]



Source: References 40 and 69

Figure 24—Simulated Cold Starting Minimum Temperatures Based on Laboratory Bench Tests

6.3.9.4 A third safety concern relates to the toxicity of MeOH. MeOH is colorless and nearly tasteless and odorless and therefore may not be recognizable to many people who are familiar with hydrocarbon fuels. This increases the potential for misuse of neat MeOH. Adding hydrocarbons such as gasoline to MeOH gives the fuel an unpalatable taste and odor and thus reduces the possibility of accidental poisoning.

6.4 SPARK-IGNITION ENGINE OPERATION WITH NEAR-NEAT ALCOHOL

6.4.1 General

For spark-ignition engine applications of methanol, practical considerations relating to cold engine starting and safety issues about flame luminosity and explosivity supported the implementation of M85 and Ed85. Because gasoline is not a desirable fuel for diesel engines, there is no incentive to use M85 or Ed85 as fuels compression-ignition engines. Blends or mixtures of alcohols with hydrocarbons or other compounds are referred to as “near-neat” alcohols. Accepted engineering nomenclature identifies neat alcohols as M100 for neat MeOH, and Ed100 for neat EtOH. Ed100 is defined by ASTM as neat EtOH that has been made unfit for beverage use by the addition of denaturants.[96] A “near-neat” mixture of 85 percent MeOH and 15 percent hydrocarbon is conventionally designated as M85. Similarly, Ed85 is a near-neat mixture of nominally 85 percent EtOH and 15 percent hydrocarbon. ASTM has developed specifications for M70-M85 and Ed75-Ed85 that include requirements for seasonal vapor pressure for all 50 states to assure adequate cold starting, and minimum hot fuel handling problems and evaporative emissions.[95,97] In addition to limits for catalyst contaminants, namely lead, phosphorus and sulfur, the standards also include requirements for maximum contents of higher alcohols, acidity, gum, chlorides, and water. M70-M85 limitations of sulfur (for two of the three volatility classifications) and water content are more stringent than for Ed75-Ed85, primarily for protection against corrosion and water separation. Designation ASTM Ed75-Ed85 has composition limits for copper content based upon findings that the catalytic activity of as little as 12 ppm copper in commercial gasolines caused gum formation.

6.4.2 Vehicles for Dedicated Use of Near-Neat Alcohols

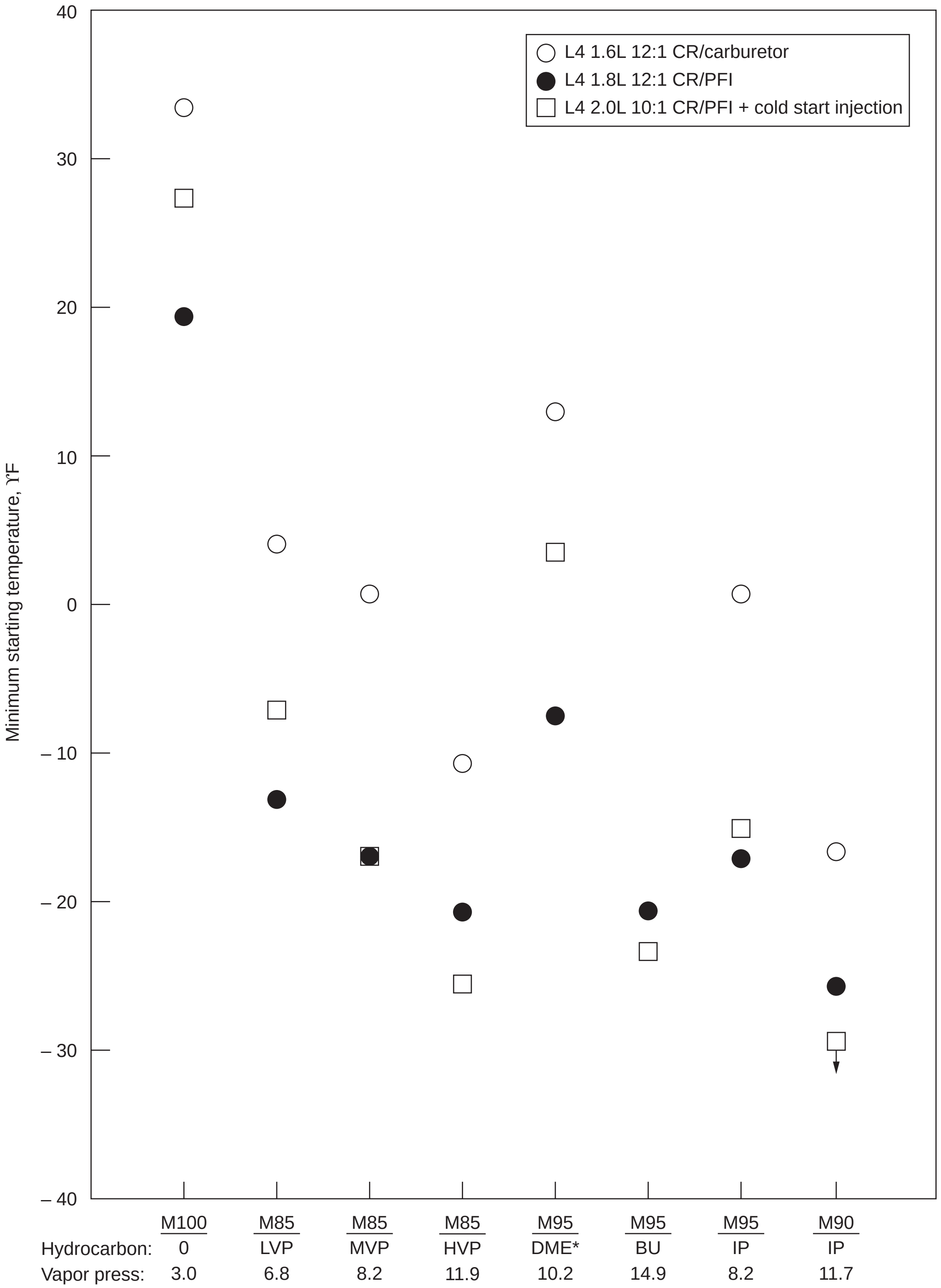
6.4.2.1 Engines that have been developed to operate exclusively on M85 or Ed85 generally have taken advantage of the superior octane performance and sought increased fuel economy through higher compression ratios. Thermal fuel economy resulting from increased compression ratio can be traded off for reductions in exhaust emissions of alcohol-fueled engines in much the same manner as accomplished with gasoline engines. In the near-neat MeOH test program by the State of California, Ford Escorts, designed with 11.5:1 compression ratio, demonstrated thermal fuel economy 16 percent better than gasoline-powered counterparts that were calibrated to the same exhaust emissions level of 1.0 grams per mile NO_X. When near-neat MeOH cars were calibrated to emit only 0.4 grams per mile NO_X, the thermal fuel economy advantage disappeared.[98]

6.4.2.2 Toyota’s second generation lean-burn MeOH vehicle with 11:1 compression ratio, described earlier, was developed to use M85 composed with premium gasoline. NO_X emissions of the Corolla were 0.39 grams per mile and FTP fuel economy was 19.7 mpg MeOH, 7 percent better than when operated at stoichiometric mixture. Exhaust emissions of CO and Organic Material Hydrocarbon Equivalent (OMHCE) were very low at 1.1 and 0.15 grams per mile respectively. Formaldehyde emissions initially were 10 mg/mile, but similar to NO_X emissions, greatly increased with subsequent mileage accumulation.[57]

6.4.2.3 AQIRP tested an experimental dedicated M85 Chevrolet Lumina for exhaust emissions using M85, a blend of 85 percent MeOH and 15 percent gasoline. The Lumina incorporated several technical features commonly associated with dedicated MeOH engines: 11:1 compression ratio, high turbulence combustion chamber, colder spark plugs and both a close-coupled catalytic converter and an underfloor converter. Although the Lumina had the poorest fuel economy of the three vehicles tested by AQIRP, it had the lowest emissions and met California LEV standards. Emissions of formaldehyde and benzene, a result of the gasoline in the fuel, were present in the exhaust but were below the limits of LEV standards.

6.4.3 Fuel Flexible Vehicles

6.4.3.1 The concept of operating fuel flexible vehicles on any combination of M85, or Ed85, and gasoline was met with mixed enthusiasm from branches of the government and the automobile and oil industries. Supporters of neat alcohol as motor fuel contended that engines and vehicle pollution controls should be optimized for neat alcohol, and not be compromised to accommodate gasoline, in order to achieve maximum potential environmental benefits and national energy self-sufficiency advantages offered by alcohol. Proponents of fuel flexible vehicles maintained that mass production of fuel flexible vehicles would promote consumer acceptance of alcohols as motor fuels and, particularly, the development of a MeOH distribution network. Also, they felt that consumer acceptance of fuel flexible vehicles would accelerate the availability of neat MeOH vehicles. Critics challenged the technical merits and questioned consumer acceptance. GM was not optimistic about customer acceptance of vehicles compromised to run on both MeOH and gasoline. GM stated that fuel flexible vehicles would have greater initial cost, increased complexity, shorter



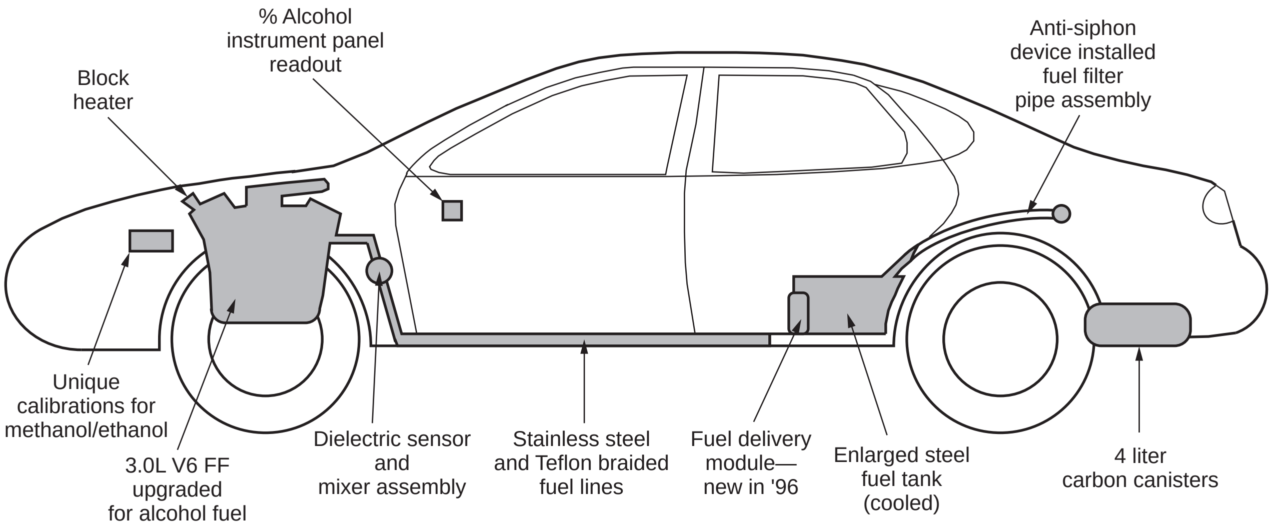
*Ether

Source: Reference 77

Figure 25—Minimum Starting Temperature With Various Methanol Blends

driving range, and poorer fuel economy than neat MeOH vehicles. In its analysis, GM viewed fuel flexible vehicles as transitional hybrid vehicles that would enjoy only temporary acceptance in the marketplace similar to that met by the diesel-powered passenger car in the United States.[37]

6.4.3.2 Near-neat alcohol presents the same menu of potential problems associated with gasoline-alcohol blends described in Chapter 5: vapor lock, increased hydrocarbon emissions, and incompatibility with fuel system materials. Also, near-neat MeOH does not provide all of the desirable emissions benefits attributed to neat MeOH. Engine efficiency benefits of higher compression ratio that would be possible with neat MeOH must be compromised in order to accommodate the lower octane quality of gasoline. In development programs, such as for Ford's fuel flexible vehicle, regular grade gasoline was used to establish engine compression ratio.[4] A design based on higher octane fuel would have allowed a greater compression ratio. Currently, premium grade gasoline has the highest octane generally available with a minimum 91 (R + M)/2 octane rating. Premium unleaded would have allowed a compression ratio increase between one and two units above the ratio for operation on regular grade unleaded, 87 (R + M)/2.[22] However, this increased compression ratio would have provided only about 30 to 40 percent of the gain in energy equivalent fuel economy that potentially could have been obtained with a compression ratio that utilized the high octane of MeOH.



Source: Reference 104

Figure 26—1996 FFV Taurus (Ethanol and Methanol)

6.4.3.3 Experimental fuel flexible vehicles began to emerge from automakers for demonstration projects in 1983.[99,100] Most worldwide automobile manufacturers activated research and development programs in this area. The concepts of fuel flexible vehicles, although similar among manufacturers, were named differently: Ford's Flexible Fuel Vehicle (FFV); GM's Variable Fuel Vehicle (VFV); Chrysler's Gasoline Tolerant MeOH Vehicle (GTMV); and Volkswagen's Changeable MeOH Concept (CMC) and Multi Fuel Concept.[4,36,38,92,109] By 1987, three California state agencies began evaluations of seven experimental FFV Ford Crown Victorias.[4,19] In 1988, the State of California Energy Commission, with participation of the automotive and oil industries, initiated a five year demonstration program of fuel flexible vehicles with the capability of operating on unleaded gasoline, methanol-gasoline blend M85, and any combination thereof.[101] The vehicles were targeted to meet California regulations for evaporative and exhaust emissions from gasoline vehicles plus an aldehyde limit. General Motors delivered its first demonstration VFV, a Chevrolet Corsica, to California in 1988, and followed up with 20 more in 1989. Ford placed 185 FFV Crown Victorias in service in 1989. By 1993, more than 6,000 fuel flexible vehicles from ten manufacturers were in service in California. [102]

6.4.3.4 A state of the art production fuel flexible vehicle, the 1996 Ford Taurus FFV, is shown in Figure 26. The vehicle has a single fuel tank which supplies the engine with fuel

Table 41—Composition of Exhaust and Evaporative Emissions from a Flexible-Fueled Vehicle (all results expressed in mg/mi for standard tests, except as noted)[a]

Component	M0 Exh.	M0 Evap.	M15 Exh.	M15 Evap.	M50 Exh.	M50 Evap.	M85 Exh.	M85 Evap.
Methanol	1.2	0.0	38.2	51.7	106.0	66.8	215.00	84.9
Formaldehyde	7.2	0.0	11.1	0.0	16.8	0.0	36.70	0.0
Acetaldehyde	2.2	0.0	2.1	0.0	1.6	0.0	0.46	0.0
Total Hydrocarbon	229.0	122.0	210.0	99.8	172.0	67.0	50.60	25.0
Individual HC as Carbon % of THC								
Methane	15.8	0.0	7.5	0.0	11.9	0.0	26.80	0.0
Ethane	3.4	0.0	1.2	0.0	1.2	0.0	0.00	0.0
Ethylene	6.1	0.0	7.0	0.0	7.0	0.0	10.00	0.0
Acetylene	1.3	0.0	3.5	0.0	2.3	0.0	5.80	0.0
Propylene	4.7	0.0	4.8	0.0	4.5	0.0	4.90	0.0
Propyne	0.4	0.0	0.0	0.0	0.1	0.0	3.00	0.0
Isobutylene	3.7	0.0	3.6	0.0	3.5	0.0	3.20	0.0
Isobutane	0.6	9.0	1.1	2.2	0.2	1.3	0.20	1.7
1,3-Butadiene	0.4	0.0	0.6	0.0	0.6	0.0	0.70	0.0
Butane	2.3	43.4	8.3	10.4	2.8	7.7	1.60	43.6
Isopentane	3.5	4.8	9.5	8.8	3.8	10.9	4.40	11.4
Pentane	2.9	2.6	3.2	4.4	2.6	5.0	2.40	4.5
Isohexane	1.5	1.0	1.1	1.9	1.3	2.1	1.40	2.3
Hexane	0.9	0.8	0.8	1.6	1.1	2.0	0.60	0.6
Benzene	4.2	0.9	4.0	1.8	4.6	2.0	4.00	1.7
2-Methylhexane	4.1	3.5	4.3	5.4	4.3	4.9	2.40	4.0
Isooctane	9.2	5.6	9.2	8.8	9.4	10.4	6.80	6.2
2, 3, 4-Trimethylpentane	1.5	1.4	1.5	2.3	1.8	3.0	1.10	1.8
Toluene	14.7	13.0	13.7	27.0	14.4	27.6	10.00	13.8
% of THC listed here	81.0	86.0	84.0	75.0	77.0	77.0	89.00	92.0

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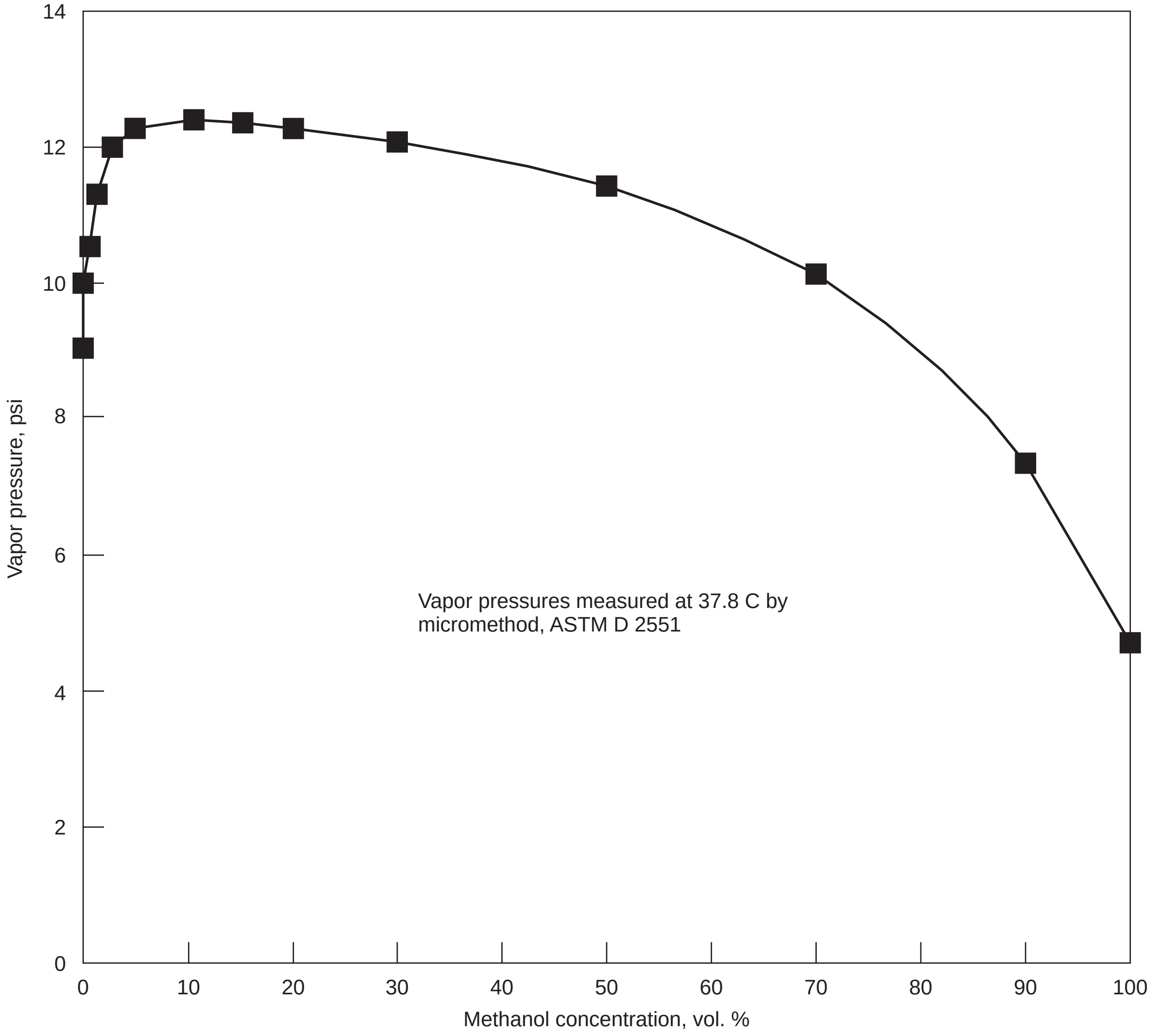
[a] $$\text{Evap. Emissions, } {}^{mg}/_{mi} = \frac{(3.05\ {}^{trips}/_{day} \times \text{hot soak emissions, } {}^{mg}/_{trip}) + \text{diurnal emissions, } {}^{mg}/_{day}}{31.1\ \text{mi/day}}$$

Source: Reference 106



Source: Reference 108

Figure 27—Vapor Pressure of Gasoline—Methanol Blends

ranging from gasoline to M85, or mixtures of the two. In this vehicle, a dielectric sensor in the fuel system detects the ratio of MeOH to gasoline so that the fuel rate and ignition timing can be electronically adjusted for optimum performance, fuel economy, or emissions. An oxygen sensor/feedback system controls air-fuel mixture at stoichiometric for most driving conditions. Exhaust particulate emissions from FFVs using M85, Ed85 or gasoline, even under rich mixture operating conditions, have not been found to be of concern.[103] An Ed85 version of the Taurus has considerably less complicated exhaust emissions control than that of the M85 version.[104] Manufacturing costs of a fuel flexible vehicle have been estimated to be $300 to $400 greater than comparable gasoline vehicles.[105]

6.4.4 Exhaust and Evaporative Emissions from Fuel Flexible M85 Vehicles

6.4.4.1 The hydrocarbon species of evaporative and exhaust emissions from vehicles operated on near-neat MeOH or near-neat EtOH have been found to be characteristic of the gasoline component of the blend. Reactive evaporative emissions from vehicles fueled with MeOH-hydrocarbon blends consist mainly of the hydrocarbon component. Table 41 identifies the components that contained elemental hydrogen and carbon in the evaporative and exhaust emissions from a fuel flexible vehicle. Comparison of the exhaust emissions using fuels ranging in MeOH concentrations from zero to 85 percent, shows that hydrocarbons decreased with increased MeOH while emissions of MeOH and formaldehyde

Table 42—1992/1993 FFV/VFV AQIRP Fleet Description

Vehicle	Manufacturer	Model	Engine Displacement	Fuel Metering	EGR	Catalyst Type	Catalyst Location	Market
C01	Chrysler '93	Acclaim	2.5L I-4	SFI	No	TWC	CC	FED
C02	Chrysler '93	Spirit	2.5L I-4	SFI	No	TWC	CC	FED
F01	Ford '93	Taurus	3.0L V-6	SFI	Yes	TWC	CC + UF	CA
F02	Ford '93	Taurus	3.0L V-6	SFI	Yes	TWC	CC + UF	CA
GO1	GM '92	Lumina	3.1L V-6	PFI	Yes	TWC	CC + UF	CA
GO2	GM'92	Lumina	3.1L V-6	PFI	Yes	TWC	CC + UF	CA

Key:
SFI—Sequential Fuel Injection
PFI—Port Fuel Injection
TWC—Three-way Catalyst
CC—Close-Coupled
CC + UF—Close-Coupled plus Under-Floor

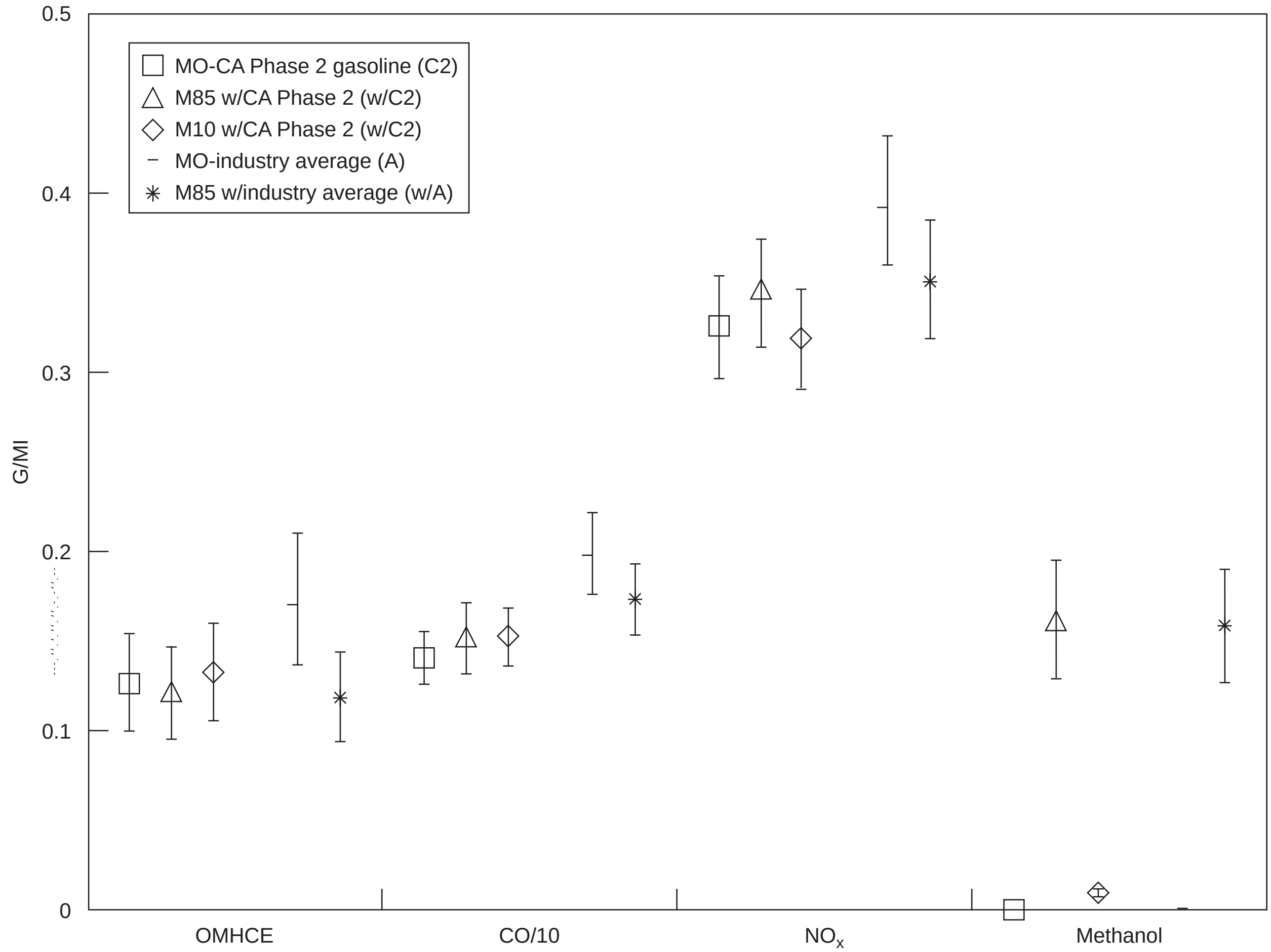
Reference: 110

increased. Total evaporative emissions were highest using M15, where the vapor pressure effect was greatest.[106] In other tests, Nissan observed hot engine restart problems using M10 and higher evaporative emissions using M25 in its prototype fuel flexible vehicles.[107] Small amounts of gasoline added to MeOH or EtOH elevate the vapor pressure of the blend beyond the vapor pressure of either the neat alcohol or the gasoline component, as described in Chapter 2. The same phenomenon occurs with M85 and gasoline mixtures as illustrated in Figure 27.[108] In a vehicle situation, for example, the addition of 18 gallons of 9 psi gasoline to a fuel tank with two gallons of 4.5 psi M85 results in a fuel blend with a vapor pressure over 12 psi. Ford found that mass evaporated emissions with M85 were about the same as neat MeOH in 1985 FFV Escorts and a 1986 FFV Crown Victoria. However, with M50 in the Escorts, emissions increased 140 percent over those with gasolines and 390 percent over neat MeOH.[19] Volkswagen sold about 80 fuel flexible MFV Jettas, calibrated to meet TLEV standards, to the California Energy Commission for evaluation beginning in early 1991. A unique alcohol composition sensor allowed the Jettas fuel flexibility for M85, Ed85, and/or gasoline. Regulated TLEV emissions were met easily using all fuels with the exception of tailpipe NMOG using Ed85. NMOG emissions with Ed85, adjusted by a 0.67 RAF, placed Ed85 exactly at the NMOG limit for TLEV standards. Volkswagen stated that high NMOG with resulted from poor cold starting due to low vapor pressure. Startability with Ed85 was limited to ambient temperatures above 23°F. For either M85 or Ed85, the majority of the NMOG emissions were unburned MeOH or EtOH. Excessive evaporative emissions with M35 were corrected through improved activated charcoal and reduced permeability of the fuel tank surface.[109]

6.4.4.2 Mass produced fuel flexible vehicles have demonstrated acceptable emissions levels. Six 1992-1993 model year production FFV and VFV vehicles, certified to meet California emissions standards, were tested for FTP exhaust and evaporative emissions by the AQIRP using M85 and combinations with gasolines. A description of the vehicles is shown in Table 42. The M85 fuel variations included gasoline components that represented both AQIRP U.S. industry average gasoline and 1996 California Phase 2 gasoline. Also the two gasolines were tested in the fuel flexible vehicles without the presence of MeOH. A fifth test fuel, M10, composed of 17.6 percent M85 and 82.4 percent California Phase 2 gasoline, simulated a potential vehicle-tank cross blend with maximum vapor pressure.

6.4.4.3 Average exhaust emissions of the fleet were below the standards for certification, and met those for California TLEV. The graph of Figure 28 shows that the emissions from the five fuels were remarkably similar with the exception of the low or non-existent MeOH emissions from the M10 fuel and the gasolines. There was no significant difference between emissions from the M85 fuels and the California Phase 2 gasoline. The industry average gasoline tended to produce higher emissions of OMCHE, CO and NO_X than M85 that was formulated with it, but the difference was not significant at the 95 percent confidence level. Exhaust emissions of toxics are plotted in Figure 29. Benzene levels were roughly consistent with those of the fuels. Although formaldehyde emissions were greatest for M85 fuels, the levels were below the 15 milligram per mile standard.

6.4.4.4 The combined hot-soak and diurnal evaporative emissions were significantly lower from the California Phase 2 gasoline and the M10 than they were from the other fuels. However, all fuels produced less than the 2 grams per test



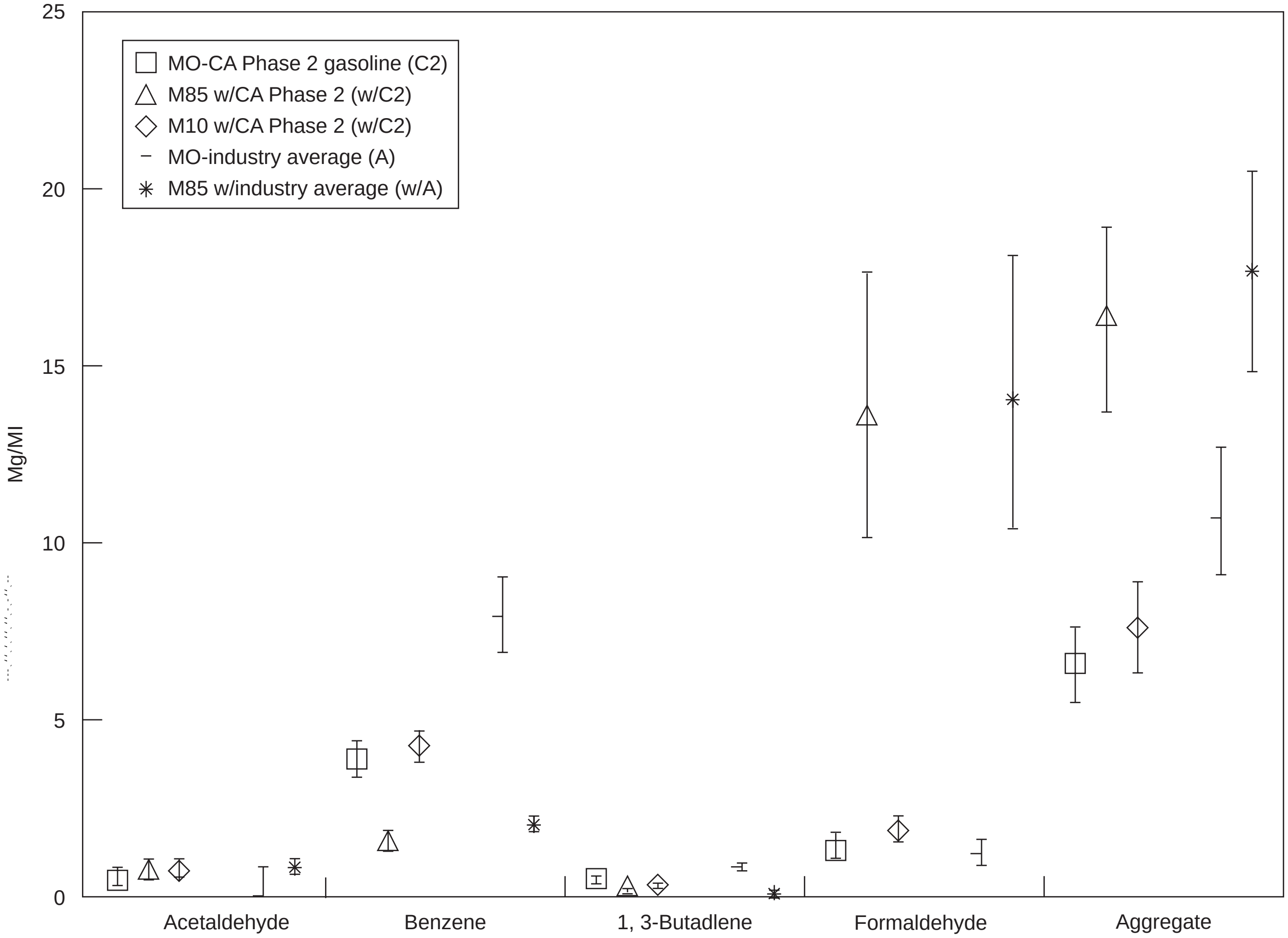
Note: Bars represent 95% confidence intervals for comparing methanol fuel and corresponding gasoline means.

Source: Reference 110

Figure 28—Auto/Oil AQIRP 1993 FFV/VFV Fleet—FTP Exhaust Emissions

standard.[110] For exhaust emissions control of its 1996 model M85 FFV Taurus, Ford employed both light-off catalysts and underfloor converters easily met more stringent California LEV emissions standards. To achieve satisfactory control of evaporative emissions, 1996 Ford Taurus FFVs are equipped with four liters of vapor storage capacity, twice that of comparable gasoline-powered vehicles.

6.4.4.5 As part of a large U. S. Department of Energy demonstration program[111] of alternative fuel vehicles, 97 fuel flexible M85 vehicles that had seen service in four metropolitan U. S. Federal fleets were tested for emissions. Seventy-one 1993 Dodge Spirits and sixteen 1993 Ford Econoline E150 heavy light-duty vans were measured for FTP exhaust and evaporative emissions using M85, M50, and California Phase 2 gasoline (RFG). The M85 and M50 blends were made with the RFG. Mileage on the vehicles ranged between 4,000 and 40,000 miles with unknown fuel usage and variability of operation. Both the average exhaust emissions of OMCHE and CO of the Spirits and of the Econolines were slightly less when using M85 than when using RFG. NO_x emissions were somewhat greater with M85 for both sets of vehicles. The levels of M50 emissions were between those of M85 and the gasoline. Average emissions of the Spirits for all three pollutants were well below EPA Tier 1 Emissions standards, in grams per mile of 0.25 OMHCE, 3.4 CO, and 0.4 NO_x. The Econolines also had average emissions that were well below the specified gram per mile standards for their classification, heavy light-duty trucks, of 0.4 OMHCE, 5.0 CO, and 1.1 NO_x. Average formaldehyde emissions were 12.3 and 8.1 milligrams per mile for the Spirits and Econolines, respectively, and met California LEV standard. Evaporative emissions were controlled, even with M50 fuel, to less than 50 percent of the emission standard of 2 grams per test.



Note: Bars represent 95% confidence intervals for comparing methanol fuel and corresponding gasoline means.

Source: Reference 110

Figure 29—Auto/Oil 1993 FFV/VFV Fleet—Average Exhaust Toxic Emissions

6.4.5 Exhaust and Evaporative Emissions from Fuel Flexible Ed85 Vehicles

6.4.5.1 Chrysler, Ford and General Motors have developed fuel flexible Ed85 vehicles primarily for fleets with accessible fuel. The AQIRP reported measurements of FTP tailpipe exhaust emissions of three Ed85 fuel flexible vehicles representative of 1992-1993 technology employing three way exhaust catalysts. The Chevrolet Lumina was certified for EPA Tier 1 emissions, 0.25 NMHC, 3.4 CO, 0.4 NO_x (grams per mile for all three). The Ford Taurus and Plymouth Acclaim were production prototypes. NO_x emissions were significantly lower, at the 95 percent confidence level, than reformulated gasoline by an average of 37 percent. However, OMHCE and CO emissions were higher, although not statistically significant, by an average of 25 percent and 56 percent, respectively. As expected, toxics emissions of benzene and 1,3-butadiene were significantly higher with gasoline than with Ed85. Toxics emissions of acetaldehyde and formaldehyde, derived from EtOH origin, were significantly higher with Ed85 than gasoline. Average acetaldehyde emissions were 0.6 milligrams per mile with RFG, and were 16.9 milligrams per mile with Ed85. EtOH emissions averaged 86 milligrams per mile.[112]

6.4.5.2 Ford compared engine and tailpipe exhaust emissions from a production Ed85 FFV 1996 model Taurus using Ed85 to the emissions using Indolene gasoline. Engine NO_x emissions were much lower with Ed85 than with gasoline. However, because of lower exhaust gas temperature with the use of Ed85, the exhaust catalyst was not as effective on hydrocarbon oxidation as it was with the use of gasoline. As a result, even though engine emissions of hydrocarbons were lower with Ed85, tailpipe emissions of hydrocarbons and CO were no better than those measured with gasoline. Emissions of acetaldehyde were 43 milligrams per mile. Although the cooler exhaust did not promote catalyst activity, it did increase engine power output by 4 percent over gasoline and improve vehicle acceleration ability. Cold starting with Ed85 was limited to about zero °F. Gasoline with 11 psi vapor pressure provided successful cold starting down to –11°F. Hot engine starting, essentially due to vapor lock, was a problem with Ed85 following a 20 to 60 minute hot soak at ambient temperatures above 104°F.[104]

6.5 ALCOHOL FUELS FOR COMPRESSION-IGNITION ENGINES

6.5.1 General

Alcohols by themselves are far from ideal fuels for compression-ignition engines, either from the physical or thermodynamic standpoint, but offer attractive reductions of emissions of particulates, sulfur compounds, and NO_x. Because alcohols resist compression ignition and have long ignition delay, they cannot be used effectively as neat fuels in conventional diesel engines without engine or fuel alterations that optimize autoignition. Typical engine autoignition enhancements have included elevated compression ratio, modified air control, and glow plugs or spark plugs. Other engine design modifications have been found necessary to compensate for wear, corrosion and materials compatibility problems associated with the use of alcohols, particularly MeOH. The use of alcohols has also dictated vehicle design revisions to incorporate larger fuel tank capacity, fire suppression systems and exhaust system catalysts. Fuel additives for MeOH and EtOH have been found to be another way to promote autoignition and obtain some emissions benefits in modestly modified or older heavy duty diesel engines.

6.5.2 Heavy Duty Diesel Vehicles Using MeOH

6.5.2.1 Heavy-duty trucks and urban buses are major contributors to air pollution by NO_x. In California, the release of NO_x emissions from diesel heavy-duty trucks and buses has been estimated to be almost 40 percent of the total from automotive sources, although they constitute only about one percent of the vehicle population.[9] More than 80 percent of the air borne exhaust particulate from all vehicles is produced by those with diesel engines. In California, although diesel engine particulate emissions have been lowered significantly by state regulation of diesel fuel aromatics and sulfur content, they comprise about 70 percent of the particulate from all vehicles.

6.5.2.2 Alcohols have been long recognized as supplemental fuel for diesel engines to reduce exhaust smoke. They burn without soot formation that is common from diesel fuel combustion at rich mixtures. They also reduce peak combustion temperature and NO_x as a result of their high heat of vaporization. Fumigation of alcohol into engine intake air allows increased power with low exhaust smoke. The basic concept is to supplement diesel fuel combustion with as rich an alcohol-air mixture as the process will tolerate without quenching. Engine combustion with fumigated MeOH has been found satisfactory with up to about 60 percent by volume MeOH, or about 26 percent of the total heat input. Devices to introduce alcohol into the airstream included heated vaporizers, carburetors, manifold injectors, and mist generators.[113,114,115,116,117] Other mechanical schemes employed separate injection systems for alcohol. Dual injection has allowed increased engine thermal efficiency, reduced exhaust emissions of NO_x and particulates, without producing excessive aldehyde emissions compared with unmodified diesel engines.[118,119,120,121,122] However, dual fuel injection control systems are complex and unnecessary for engines that utilize neat alcohol as the sole fuel.

6.5.2.3 A considerable number of state- and federal-sponsored research programs and field tests have been conducted to demonstrate the emissions effects of alcohol use in medium-duty and heavy-duty two- and four-stroke cycle diesel engines in truck, bus, and farm tractor service.[123] Many engine manufacturers have cooperated extensively in studies of alcohols as alternative fuels in heavy-duty engines. Since they have completed the majority of the objectives of heavy-duty automotive engine research programs on alcohols, several manufacturers have shifted their alternative fuel research activities toward CNG.[9]

6.5.2.4 Detroit Diesel Corporation (DDC), Maschinenfabrik Augsberg-Nurnberg (MAN), and Kloeckner-Humboldt-Deutz AG (KHD) developed the earliest versions of heavy-duty MeOH diesel engines to demonstrate operation in transit buses.[34,124,125] Most of KHD's experience was with air-cooled MeOH powered city buses in Europe. Cummins MeOH L10 engines were operated in revenue bus service for several years.[126] Caterpillar, Navistar, and Daimler-Benz AG also built experimental MeOH versions of their heavy-duty engines for evaluation in truck service.[127,128] Komatsu of Japan field tested its MeOH derivation of its prechamber design in tractors.[129]

6.5.2.5 Both DDC and MAN MeOH engines were extensively tested in transit bus service. DDC 6V-92TA has been the most widely used engine in transit buses in the U.S., and was the first heavy-duty engine to receive emissions certification by California and the U.S. EPA. DDC engines, designated as 6V-92TA and 6L-71TA, feature two-stroke cycle, scavenging-blower, turbocharger, direct cylinder unit fuel injectors and aftercooler. Both DDC engines were modified for autoignition enhancement by incorporation of 23:1 compression ratio, in-cylinder glow plugs, programmed scavenging air, and electronically-regulated heated intake air.[130] Vehicle installations of DDC engines included exhaust oxidation catalyst for control of HC, CO, unburned MeOH, and formaldehyde.[131]

6.5.2.6 Early versions of the MAN MeOH four-stroke cycle engine incorporated spark-plug ignition, had 18:1 compression ratio and were naturally aspirated. Studies of spark-assisted diesel engines found MeOH combustion to be mainly flame propagated, similar to that in a gasoline engine.[132] MAN observed improved thermal fuel economy for the MeOH-powered engine in laboratory tests and confirmed the finding in bus field tests that showed up to 5 percent improvement in thermal fuel economy.[133] Emissions of NO_x were up to 50 percent lower than the diesel-powered model, and exhaust particulates and smoke were essentially eliminated. In bus service, volumetric MeOH consumption was 2.3 times greater than that typical with diesel. On an energy consumption basis, fuel economy was about equal for both fuels. MAN developed a higher performance version that included a turbocharger, intercooler, 15:1 compression ratio and oxidation catalyst. Regulated exhaust emissions were below limits for 1991 U. S. EPA standards.[134]

6.5.2.7 Emissions of buses with MAN and DDC MeOH engines were measured on a chassis dynamometer by Eberhard, et al., using a simulated city transit driving cycle. Without exhaust catalysts, both makes emitted only 11 and 16 percent of the amount of particulate from diesel-fueled buses. NO_x emissions of the DDC MeOH bus were 63 percent lower than a comparable diesel-fueled bus. NO_x emissions of the MAN-powered buses were slightly lower than those of the diesel-fueled bus. It was demonstrated with the MAN MeOH bus that organic emissions were controllable by an oxidation catalyst.[135]

6.5.2.8 Table 43 contains measurements of exhaust emissions of three makes of heavy-duty MeOH engines using the transient cycle FTP expressed as grams pollutant per brake horsepower-hour (g/bhp-hr). Also listed are results of tests using M85 and, Ed95, Ed85 and a mixture of 80% EtOH and 20% distilled water.[9] Emissions of hydrocarbon, CO, particulate, and formaldehyde are substantially reduced by oxidation catalysts. The Caterpillar engine was not tested with an exhaust catalyst and had the largest emissions of the group. With M100 and M85, NO_x emissions were lower than the limit of 1998 federal standards. However with Ed95 or Ed85, NO_x emissions exceeded standards. With a blend containing 20 percent water, NO_x emissions were low but were accompanied by high levels of the other pollutants.

6.5.2.9 Combination of hydrocarbons or additives that reduce ignition delay with alcohols has been studied extensively. MeOH and EtOH have extremely low cetane number ratings, 0 to 5, compared with desirable values for diesel fuels in the range of 40 to 50 cetane.[136,137,138] Cetane quality of MeOH and EtOH can be upgraded by the addition of long chain hydrocarbons or ignition improver additives, usually nitrated compounds. Diesel fuel and MeOH are insoluble and must have separate fuel systems. Blends of diesel fuel with more than 30 percent EtOH have been found impractical because of serious water tolerance and phase separation problems (see Chapter 2).[139] Certain soluble nitrate additives have shown promise. For example, a mixture of about 15 to 16 percent volume cyclohexylnitrate with MeOH or EtOH improved cetane rating to 40, and resulted in slightly better engine specific fuel consumption than diesel fuel without measurable exhaust smoke. Other additives have been identified as MeOH ignition improvers: Dimethyl Ether (DME), 2-Ethylhexyl nitrate, Triethylene glycol dinitrate, and the ester nitrate in Avocet, a commercial additive package. Typically, functional concentrations of ignition improvers for MeOH range from 6 to 13 mass percent.[9,127,140,141,142]

6.5.2.10 Fumigation and dual fuel injection systems have been found to be effective methods to introduce ignition improvers into engines. Studies of DME fumigation into a MeOH Cummins diesel with 17:1 compression ratio varied the amount of DME input that was needed for stable combustion.[143] Over the engine operating range, the highest requirement for DME, as a fraction of total fuel consumption, was 59 mass percent at idle. Under high power output conditions, only 1 – 2% DME was needed. Exhaust emissions measurements using the (then current) Federal heavy-duty engine emissions test cycle met the 1990 model year standards for NO_x. Hydrocarbon emissions using optimum DME with MeOH were reduced 90 percent from those measured using neat MeOH and auxiliary glow plug heaters. In this program, fumigation of DME as the total fuel allowed successful engine starting at 1°F. DME was also tested by AVL List GmbH as a complete fuel for a passenger car diesel engine, and showed low very low emissions of NO_x and particulate.[52]

6.5.2.11 Ignition improvers have appeal for use in older vehicles without mechanical features for improved autoignition. Major engine modifications, such as cylinder heads with glow plugs and pistons for increased compression ratio, are necessary to make older engines suitable for MeOH operation. Exhaust emissions of a high mileage 1979 DDC 8V-71 transit bus engine operated on M100 and E95 containing Avocet were compared with those measured from operation on diesel fuel. The concentration of Avocet for acceptable running on both alcohols and for test purposes was established at 7.5 volume percent. Only modest changes were made to the engine in order for the alcohols with Avocet to match engine power output of the diesel fuel, namely, fuel injectors and injection timing. Compared with diesel fuel, transient FTP emissions of hydrocarbons (OMHCE) and NO_x were about the same with M100, while CO and particulate were lower by about 30 percent and 20 percent respectively. Emissions of OMHCE were 50 percent higher with E95 than with diesel fuel. Emissions of CO were the same but emis-

Table 43—Emissions of Heavy-Duty Diesel Engines Using Alcohol[1]

			Grams per brake horsepower-hour				
Engine	Fuel	Catalyst	OMCHE	CO	NO_x	Particulate	HCHO
DDC 6V-92TA 300 BHP	M100	No	2.2	3.2	2.9	0.11	0.12
DDC 6V-92TA 350 BHP	M100	No	2.0	3.8	2.6	0.2	0.14
DDC 6V-92TA 253 BHP	M100	Yes	0.1	2.0	1.7	0.03	0.07
DDC 6V-92TA 277 BHP	M100	Yes	0.3	1.3	2.0	0.03	0.06
DDC 6V-92TA 300 BHP	M100	Yes	0.2	0.3	2.6	—	0.06
Navistar DT466 210 BHP	M100	No	1.1	3.4	4.7	0.12	—
Navistar DT466 210 BHP	M100	Yes	0.1	0.1	3.5	0.05	—
DDC 6L-71TA 300 BHP	M100	No	1.8	3.5	3.3	0.12	0.16
DDC 6L-71TA 300 BHP	M100	Yes	0.1	0.5	2.7	0.02	0.05
Caterpillar 3406B 350 BHP	M100	No	4.5	12.4	3.1	0.15	0.49
DDC 6V-92TA 300 BHP	M85	No	2.2	6.7	3.4	0.09	0.12
DDC 6V-92TA 300 BHP	M85	Yes	0.6	1.1	3.4	—	0.07
DDC 6V-92TA 253 BHP	M85	Yes	0.2	1.6	4.1	0.03	0.08
DDC 6V-92TA 253 BHP	Ed95	Yes	0.7	1.7	4.2	0.04	0.02
DDC 6V-92TA 249 BHP	Ed85	Yes	2.4	8.7	4.5	0.41	0.12
DDC 6V-92TA 249 BHP	Ed160[2]	Yes	2.3	7.9	2.4	0.11	0.13
1998 Federal Emissions Standards:			1.3	15.5	4.0	0.1	—

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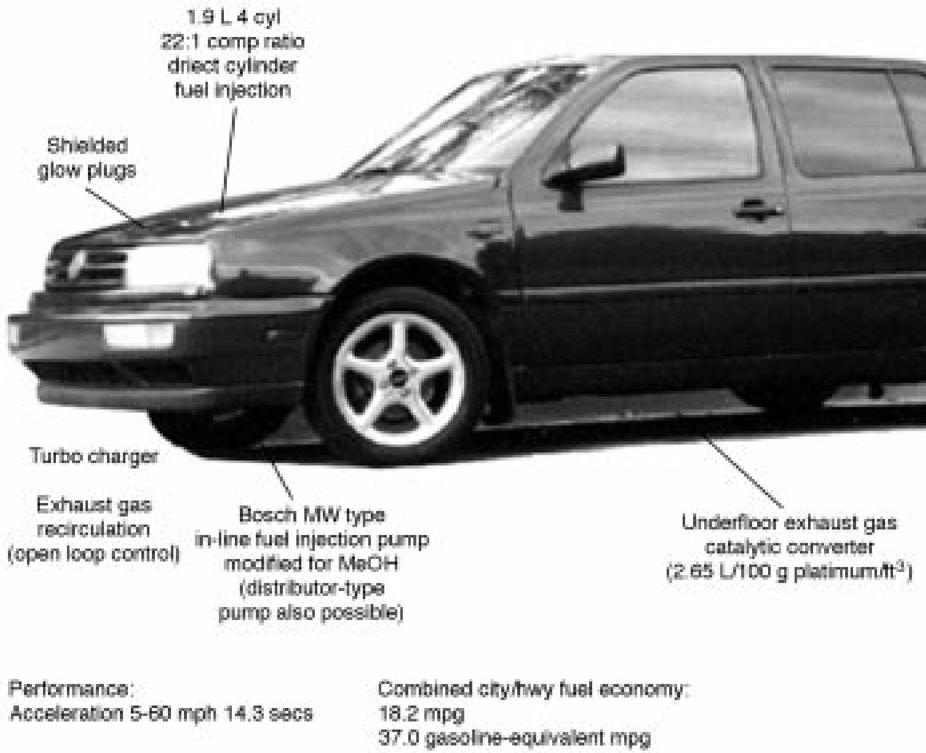
[1] Data from Table 25, Reference 9.

[2] Ed160 = 80% EtOH and 20% distilled water.



Source: Reference 145

Figure 30—Volkswagen Jetta Methanol Vehicle

sions of NO_x and particulate were reduced by 14 percent and 27 percent respectively.[141] In other tests of contemporary DDC engines operated on M100 without glow plugs, NO_x emissions doubled with M100 containing Avocet, but were below the limits of the 1998 emissions standards.[9]

6.5.2.12 Additive treatment does not offer economic incentive to convert engines to operate on M100. Older vehicles must have MeOH compatible components in addition to injection system modifications. Additive treatment costs are also a major consideration. Calculations of the cost effectiveness of additives for cetane improvement must include the heating value differences between alcohols and diesel fuel. On a volumetric basis, 2.3 times as much MeOH is needed for the same heating value as diesel fuel. EtOH requires 1.7 times as much volume. Compared on this basis (equal heating value) or power output, the amount of additive required for 13 percent additive treatment of MeOH is about 30 percent the volume of diesel fuel required for the same heating value.

6.5.3 Emissions of MeOH Light Duty Diesel Vehicles

6.5.3.1 In addition to the experience of the manufacture and sale of more than two million "neat EtOH" vehicles in Brazil, Volkswagen participated in test programs of dedicated MeOH vehicles around the world. Most of the early experience was with spark-ignition engines. A Volkswagen Jetta passenger car, shown in Figure 30, with a prototype compression ignition engine was tested for exhaust emissions and cold starting.[144,145] The engine, optimized for operation on neat MeOH,[146,147] incorporated a turbocharger, direct cylinder fuel injection, 22:1 compression ratio, shielded glow plugs in the combustion chambers, and open loop control exhaust gas recirculation. An underfloor oxidation catalyst complemented the vehicle installation.

6.5.3.2 Regulated emissions, including toxics, were comparable to those of the passenger cars with spark-ignition engines listed in Table 40 and were sufficiently low to meet California's standards for Transitional Low Emissions Vehicles. The exhaust catalyst played a key role in emissions control because, as engine emissions data showed, the vehicle would not have met any of the TLEV standards without it. The vehicle attained 16.1 miles per gallon MeOH on the FTP cycle, which was not as good as the Toyota or Corolla. For the combined EPA city-highway schedule, it attained 18.5 miles per gallon MeOH, or 37.1 miles per gallon on a gasoline energy equivalent basis. For comparison purposes, the gasoline-powered 1990 Volkswagen Jetta 1.8L was rated by EPA at 27.7 miles per gallon. Cold startability with MeOH was not difficult at room temperature FTP conditions, but was a problem at very low temperatures. At –20°F, combustion initiation was extremely difficult even with application of 40 seconds of glow plug heat and 10 seconds cranking. After repeated fuel injection manipulation, the engine began firing and, after some warmup, reportedly delivered good driveability.

6.6 MATERIALS COMPATIBILITY, CORROSION, AND ENGINE WEAR

6.6.1 As discussed in Chapter 5, MeOH is a highly polar material and chemically attacks elastomers and metals that perform satisfactorily with gasoline or diesel fuel. Potential problems are corrosion of metals and the swelling or deterioration of plastics and elastomers. Both neat MeOH and MeOH-gasoline blends have been reported to attack the lead-tin coated (terne plate) steel used to fabricate domestic vehicle gasoline tanks. In one case involving a fuel-injected car, MeOH effectively stripped the coating from the tank in two days. Severe corrosion developed on the exposed sheet steel, and the whitish, lead corrosion product partially plugged the fuel filter. A wide variety of corrosion inhibitors have been screened, including polyamide, polyamine, dithiocarbamate, thiophosphate ester, organic acid, sulfide, and selenide types, but as yet none have been found to be effective.[66,148] Coating metals with polyolefin films appears to offer a solution to anodic dissociation. Some manufacturers coated the inside of steel fuel tanks for use with gasoline-MeOH blends with an aluminum-rich epoxy. However, in service with neat MeOH, this coating blistered and flaked off after seven months.[42] Type 304 stainless steel has been found compatible with MeOH and has been the preferred premium material.[78,149] Nickel-plated steel also has been found resistant to corrosion.[36] High density polyethylene has been found suitable as a material for fuel tanks for neat or near-neat MeOH but deteriorates if not coated and becomes permeable with MeOH.[94]

6.6.2 Other investigators have found evidence of increased corrosion of copper, brass, bronze, magnesium, and die-cast zinc by MeOH compared with gasoline.[40,146,150,151] Metal corrosion is common in racing cars fueled with MeOH, particularly if dissimilar metals are present and galvanic action is established.[11] Anodic dissociation takes place where MeOH is exposed to electrical potentials as in fuel level sensor units and in-tank electric fuel pumps. Because MeOH is many times more electrically conductive than gasoline, a significant flow of current can take place, and metal is removed from the anode.[94] In addition, soluble fuel contaminants, such as chloride or peroxides, increase conductivity and have been found to significantly promote increased corrosion and wear in a MeOH engine.[152,158] Corrosion of anodized aluminum engine fuel rail connectors was identified as being caused by as little as 2 ppm chloride ion contaminants in M85.[153] Fuel filter plugging in vehicles using M85 have been attributed to aluminum hydroxide gels resulting from galvanic corrosion of service station aluminum dispenser nozzles. Electrolytic corrosion of electric fuel-pump armature-windings was also found caused by denatured EtOH with high conductivity and acidity. To preclude corrosion of these types, ASTM Specifications (ASTM D 5798-95 and D 5797-95) for fuel MeOH and fuel EtOH limit chloride content to 2 ppm and acidity to 50 mg/kg as acetic acid.[95,96]

6.6.3 Modifications to MeOH engine components, such as the use of chrome-plated piston rings, have been found to reduce wear in MeOH engines.[159,161,154] Chrome-plated rings have been used in production vehicles to improve durability.[155]

6.6.4 Physical properties of elastomers generally deteriorate more in mixtures of MeOH and gasoline than in either neat fuel. Carburetor and fuel gauge floats, both commonly made of plastics, have been noted to swell and gain weight in cars operated on MeOH-gasoline blends.[94] This reduces their buoyancy and, for fuel gauge floats, causes falsely low fuel level readings. In one case a fuel pump failed after 4000 miles because the plastic pump head shrank and cracked.[156] MeOH may also attack methyl methacrylate parts, soften fiber gaskets, and dry and crack cork gaskets.[66] Race cars use more expensive plastic parts to resist swelling or hardening of seals and diaphragms.[11] Fluorocarbons, such as Vitons, are among the favored elastomers for conventional fuel system applications. They have good sealing characteristics over a wide temperature range and excellent resistance to hydrocarbons.[157] However, MeOH attacks the Vitons and results in swelling and dimensional changes as high as 25 percent over a 24-week soaking period. There is not much change in hardness, however.[40] Increasing fluorine content has been found to improve the compatibility of fluoroelastomers with MeOH.[99] Table 44 lists physical properties of fuel resistant elastomers after three days immersion in M100 and M75. The gasoline component, Indolene HO-III, of the M75 blend contained 30 percent aromatics.[158] One exception is the fluorocarbon, in this case Viton A, that has high swelling characteristics in MeOH, and low swelling in other alcohols and gasoline.

6.6.5 Vehicle fuel filter plugging in vehicles using M85 was ascribed to leachate of plasticizers and corrosion products of zinc from service station M85 dispenser hoses and fittings.[159] MeOH dilution of the engine lubricant was identified in one test program as the cause of valve stem O-ring embrittlement and valve stem seal softening, which can result in increased oil consumption. Also, conventional cork gaskets used as seals for oil pans and rocker arm covers were found to crack and leak oil by capillary action.[99]

6.6.6 Alcohols have low viscosity and poor lubricity. As a result, they have caused wear problems in conventional diesel fuel injection systems that relied upon the fuel to provide

Table 44—Effects of MeOH on Fuel Resistant Elastomers

Material	Fuel	Properties After 72 Hour Immersion at Room Temperature					
		Tensile Strength, Mpa	Elongation, %	Modulus @ 100% Elongation, Mpa	Hardness, Durometer, Shore A, points	Volume Swell, Change, %	Extractables, %
Fluorocarbon	M100	4.3	87	—	57	100	0
Polyether F-70A	M100	6.5	128	4.4	73	11	7
Polyester Urethane	M100	15.8	396	2.6	51	18	2
Fluorosilicone	M100	4.5	246	1.8	—	8	3
Epichlorhydrin copolymer	M100	12.5	229	5.1	65	31	2
Polysulfide	M100	8.8	220	4.4	64	18	2
Butadiene-Acrylonitrile (Nitrile)	M100	11.0	190	5.5	65	14	2
Fluorocarbon	M75	4.8	96	—	57	95	0
Polyether F-70A	M75	4.6	114	4.0	68	19	7
Polyester Urethane	M75	13.4	356	2.4	55	27	2
Fluorosilicone	M75	4.6	196	1.9	--	15	4
Epichlorhydrin copolymer	M75	11.3	212	5.0	64	50	2
Polysulfide	M75	7.6	198	4.0	63	23	2
Butadiene-Acrylonitrile (Nitrile)	M75	9.0	135	6.7	58	34	3

Source: Reference 158

lubrication of high pressure pumps and unit fuel injectors. About 15 percent EtOH decreases the viscosity of a typical ASTM 2-D fuel from 2.4 centistokes to below the viscosity limit for ASTM 2-D (1.9 centistokes @ 40°C). About 62 percent EtOH in typical ASTM 2-D fuel yields a blend viscosity below the limit for ASTM 1-D fuel (1.3 centistokes @ 40°C).[160] Fuel injector system wear caused by MeOH was corrected by addition of less than 0.1 volume percent a proprietary fuel additive.[161]

6.6.7 Cylinder and piston ring wear are accelerated by the use of neat EtOH and MeOH.[162] MeOH has been found to be particularly aggressive on cylinder wall wear at the upper end of the top piston ring travel, generating as much as seven times the wear rate as observed with unleaded gasoline.[163] Startup wear is caused by metal to metal contact resulting from the washing away of the normal oil film by liquid alcohol during starting. Startup wear occurs when very long cranking times are required to start the engine.

6.6.8 Corrosive wear has been identified with the use of MeOH during warmed-up engine operation. The increased cylinder and ring wear was theorized to be a result of formic or performic acid formation during combustion and the direct attack of the acid on the iron.[164,165,166] New formulations of lubricating oil additives were developed to control corrosive wear of the upper cylinder. Service station engine oils that meet the requirements for conventional gasoline engines have been found inadequate for MeOH engines, and special formulations have been specified for field tests.[78,147] Even with special lubricants, however, most MeOH vehicle manufacturers recommend more frequent oil changes than for gasoline vehicles.[159,167]

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7 Gasoline Oxygenate Blends in Non-Automotive Fuel Uses

7.1 In recent years there has been a great deal of confusion about the use of oxygenated fuels in various non-automotive applications. Federal and state programs requiring the use of oxygenated fuels and reformulated gasoline have heightened interest in this topic.

7.2 There are several categories of non-automotive gasoline powered equipment. These categories include lawn and garden power equipment, motorcycles, marine craft, recreational products, aviation, and stationary power equipment. While many of these categories have similar considerations concerning fuel quality and characteristics, some categories also have considerations unique to their application. Much of this equipment is subject to seasonal use and therefore extended storage periods. Additionally, compared to an automobile, much of this type of equipment is relatively inexpensive and consumers do not exercise the same degree of care that they would with the family car.

7.3 Manufacturers are currently confronted with a growing amount of environmental regulations designed to lower emissions from their products. These regulations are in addition to an extensive array of laws pertaining to noise level and safety.

7.4 These manufacturers are also confronted with the need for extremely low production costs, specialized considerations for unique applications, and often limited research and development budgets. Yet they must produce equipment that is safe, reasonably quiet, durable, consumer friendly, capable of operating on today's fuels, and with increasingly lower exhaust emissions.

7.5 Initially, during the early 1980s, the predominant oxygenate used in gasoline was ethanol. During this time frame, gasoline-ethanol blends comprised only a small percentage of the gasoline marketplace and were viewed as somewhat of a novelty. Small engine/equipment manufacturers were slow to conduct tests on a fuel with limited market share and an uncertain future. Little technical data about the use of gasoline-ethanol blends were available and, of course, there was little field experience upon which to base decisions regarding its use in such applications. These factors initially led to the majority of manufacturers recommending that gasoline-ethanol blends not be used in their products.

7.6 By the mid 1980s manufacturers began to indicate that gasoline-ethanol blends could be used in their products provided certain storage precautions were followed. The degree of approval often varied with some simply stating gasoline-ethanol blends could be used while others stated such use was permitted but not recommended.

7.7 Today, most mainstream manufacturers approve of the use of gasoline-ethanol blends[1,2] although some still provide special instructions for its use. Additionally a number of manufacturers now mention MTBE in their owners manuals and indicate that it too is approved for use.[1,2]

7.8 The issues most often cited as areas of special consideration for non-automotive spark ignition engines operating on oxygenated gasoline include the following:

7.8.1 Materials Compatibility

The two predominant fuel oxygenates, ethanol and MTBE, have been extensively tested for their effects on various metals, plastics, and elastomers. Such tests have included both controlled laboratory testing as well as field demonstration projects. Some equipment manufacturers and others have also conducted tests on specific equipment.[4,5,6,7,8] In the early to mid 1980s, some manufacturers did find it necessary to upgrade a few of the materials used in their fuel systems. Whether or not this was necessitated by the use of alcohols and ethers or other factors is often a subject of some debate. In any event, manufacturers now use upgraded materials that are largely unaffected by properly formulated oxygenated fuels. This is evidenced by manufacturer recommendations that now include permission to use such fuels. Further, responsible aftermarket suppliers provide only replacement parts that are designed for use with oxygenated fuels. As an example, Walbro Engine Management Corp., a major supplier of carburetor rebuild kits and other parts, has indicated that Walbro parts are resistant to alcohol-related decomposition as long as the volume of alcohol is within legal limits.[3]

7.8.2 Lubricity

In the past some manufacturers (especially of two-stroke cycle engines/equipment) have expressed concern about whether or not gasoline-oxygenate blends provide lubricity comparable to that of conventional gasolines. To date, there has been very little published work on this issue. Some works have indicated that the lubricity of gasoline-oxygenate blends is at least comparable to conventional gasoline,[7,10] while others have indicated that their lubricity may be slightly lower.[7,11] While this issue warrants further examination, data to date do not demonstrate a significant lubricity difference between gasolines containing oxygenates and those that do not.

7.8.3 Enleanment

7.8.3.1 Oxygenates chemically enlean the air-fuel mixture. As an example, in engines set at an air-fuel ratio of 14.7:1 on all hydrocarbon fuel, the introduction of 2.7 wt.% oxygen in the fuel would enlean the air-fuel ratio to about 15.15:1. Computerized vehicles can compensate for this shift by sending a command to increase fuel flow. Most non-automotive equipment is not sophisticated enough to accomplish this. Enleanment has an impact on two areas about which some equipment manufacturers have expressed concern. First, the majority of non-automotive spark ignition engines are air-cooled. As such the air-fuel ratio is part of the design for engine cooling and leaner air-fuel charges result in increases in combustion temperatures. The maximum combustion temperature (and resulting engine temperature) occurs at an air-fuel ratio of 14.7:1. Going rich or lean from this point will result in lower temperatures. Therefore, equipment with richer initial air-fuel ratio settings such as 13 or 14 to 1 may experience increased operating temperatures when switched to oxygenated fuels. This increase is not significant and most manufacturers do not require any modifications. However, some have offered specific guidance to increase carburetor jet size, i.e., "jet-up" to increase fuel flow[1] or to make other minor adjustments. These recommendations are primarily for equipment that is designed for cold weather operation such as snowmobiles and snowblowers. This is because cold air is denser, containing more oxygen, and when combined with oxygenated fuels may result in leaner operating conditions.

7.8.3.2 The second issue with enleanment concerns octane requirement. Increases in combustion temperature raise the octane requirement of an engine.[12] Since enleanment can raise operating temperatures, it may increase octane requirement in some applications. For instance Polaris, who initially recommended "jetting-up" their snowmobiles, has since indicated no modifications are necessary to operate on 10v% ethanol blended gasoline provided "the oxygenated gasoline has an octane rating 2 points higher than the original Polaris recommendations."[13]

7.8.3.3 Recommendations for higher octane fuels or modifications in carburetor settings are limited to a handful of manufacturers, primarily for those applications with a lot of wide-open-throttle (WOT) operation, cold weather applications, or other circumstances that result in stressed use.

7.8.4 Storage Considerations

7.8.4.1 Phase separation concerns pertain primarily to alcohol based oxygenated fuels. Alcohols attract moisture. If excessive moisture is absorbed, the alcohol and water can phase separate (fall out of suspension) from the gasoline blend. This would result in a mixture of alcohol and water in the bottom of the fuel tank. Aside from the fact that the engine would not operate on this alcohol/water blend, it can also cause corrosion of various metals it comes in contact with. However, the potential for phase separation must be put in perspective. It would take about four teaspoons of water per gallon to phase separate a gasoline-ethanol blend. This would be a large amount of water to be accidentally introduced into the system. To absorb this much moisture from the atmosphere (at a relative humidity of 70%) would take hundreds of days even if the gasoline cap was left off.[12] Therefore, these concerns can be addressed simply by exercising caution that no water is introduced into the system, ensuring that the equipment has a gasoline tank cap that seals properly and filling the tank before extended storage periods (note that some manufacturers recommend draining of the fuel tank and system before storage).

7.8.4.2 All gasoline, whether conventional, oxygenated, or reformulated, deteriorates in storage. The gasoline "oxidizes" making it more prone to deposit formation. The peroxides that form not only contribute to formation of gums in the fuel but can also reduce its octane level. Because power equipment and recreational products are stored for extended periods, often six months or longer, manufacturers often make recommendations about storage.

7.8.4.3 A few recommend draining the fuel tank and fuel system. Many recommend treating the fuel with a fuel stabilizer which inhibits oxidation (i.e., antioxidant). Such products are available over the counter with manufacturers recommending various brands. Some companies, including Briggs & Stratton, Toro/Lawnboy, and Yamaha sell a fuel stabilizer under their own brand name.

7.8.4.4 It is important that each manufacturer's storage recommendations be followed since some gasoline may not be of suitable stability for storage periods in excess of 60 – 90 days from time of retail purchase.

7.8.5 Overblending

In the early years of ethanol use, there were some reports of overblending. Today however the oxygenate blending process is much more sophisticated. Ethers, such as MTBE, are usually blended at the refinery and therefore subject to the normal refinery quality control process. Ethanol continues to be blended at the terminal to avoid moisture contamination. Most terminals now use computer controlled in-line blending equipment or pre-set metering devices. These improvements have made overblends of oxygenates a rare occurrence.

7.9 In addition to the aforementioned issues, the following covers topics that pertain to each equipment category.

7.9.1 Power Equipment

7.9.1.1 The major power equipment manufacturers have indicated that gasolines containing MTBE or ethanol are acceptable for use in their products.[1,2] This category includes lawn mowers/tractors, lawn and garden equipment such as blowers/vacs, weed trimmers, edgers, pruners, and chain saws. Larger equipment is usually four-stroke cycle while smaller hand held equipment is nearly all two-stroke cycle. Equipment is typically air cooled.

7.9.1.2 The typical life cycle of most of this equipment falls in the five to ten year range. Consequently most equipment is relatively new and therefore compatible with oxygenated fuels. Older equipment, however, may have some parts that are not as compatible with oxygenates as newer equipment.

7.9.1.3 Another factor is the recent emissions regulations imposed on the power equipment industry. These regulations will result in leaner air-fuel ratios that cannot be adjusted once leaving the factory. While air-fuel ratios of pre-control equipment can be altered to compensate for fuel oxygen content, they cannot be adjusted on new equipment. Consequently, some of this equipment may be more sensitive to higher oxygen levels.

7.9.2 Motorcycles

The major motorcycle manufacturers indicate that MTBE and ethanol can be used in their products. Primary concerns usually relate to older model bikes. Unlike power equipment, there are numerous motorcycles on the road which are fifteen or more years old and data of their compatibility with oxygenates are often lacking. To date there has been one recall in which MTBE was alleged to have been a contributing factor. In October 1996, Harley Davidson issued a recall on certain models with a vacuum operated fuel valve. When the motorcycle was improperly started with the valve in the off position, failure of the part would result.[15] While Harley Davidson mentioned reformulated gasoline containing MTBE in their recall notice, they did not indicate they had done any testing to substantiate their claim. Despite this recall, Harley Davidson has stated that they stand in full support of the reformulated gasoline program.

7.9.3 Recreational Products

This category includes snowmobiles and all-terrain vehicles (ATVs). The manufacturers involved are also manufacturers of motorcycles and personal watercraft. No major concerns about the use of oxygenated fuels in ATVs have been voiced. As mentioned earlier, some snowmobile manufacturers have issued guidance for minor modifications[1] or increased octane fuels.[13] Manufacturers which approve of MTBE and ethanol 1 include ArcticCat, Honda, Kawasaki, Polaris, Ski-Doo, Suzuki, and Yamaha.

7.9.4 Marine Applications

7.9.4.1 This category includes boats and personal watercraft (e.g., jet skis). There are some unique issues concerning the use of oxygenated fuels for this category. The life cycle of this equipment often spans 20 to 30 or more years. Some of these older watercraft may have materials in their fuel systems that were not extensively tested on oxygenated fuels.

7.9.4.2 The U.S. Coast Guard (USCG) explored this issue in the 1980s and found no conclusive evidence of problems with ethanol[16]. The USCG consumer fact sheets on this issue are rather outdated. Of important note the USCG, in 1987, encouraged boat owners to retrofit their boats with a new fuel hose designated as SAE J1527. There are four types of J1527 hoses (USCG A1, A2, B1, and B2). Manufacturers may use the different grades depending on where in the system the fuel hose is used. For purposes of owner retrofit the use of hoses marked J1527 USCG Type A1 is recommended.[16,17]

7.9.4.3 Honda Marine, Kawasaki, Mercury Marine, OMC, Pleasurecraft, TigerShark (Arctco), Yamaha Marine, and others have issued guidance, primarily through the watercraft owners manual, indicating that gasoline containing MTBE or ethanol may be used.

7.9.4.4 Mercury Marine and OMC Marine Power Group have issued bulletins on the use of oxygenated fuels. While these bulletins permit the use of oxygenates, they do recommend more frequent inspection of fuel system components in older boats, i.e., 1985 or older in the case of OMC and 1979 or older in the case of Mercury marine. These bulletins are quite extensive and contain various caveats and instructions regarding the use of oxygenated fuels.

7.9.5 Aviation-Piston Engine Aircraft

7.9.5.1 This group contains two categories, small planes certified to operate on street gasoline and ultralight aircraft.

7.9.5.2 Manufacturers of aircraft and aircraft engines specify the use of Aviation gasoline meeting ASTM D 910—Standard Specification for Aviation Gasoline. However in an effort to reduce fuel and maintenance costs, some organizations have put certain aircraft/engine combinations through a testing and certification process which allows them to be operated on gasoline meeting ASTM D 4814 (formerly ASTM D 439). Aircraft/engine configurations receiving such certification receive a Supplemental Type Certificate (STC) from the Federal Aviation Administration (FAA) to operate on automotive gasoline.

7.9.5.3 Not all automotive gasoline is approved for aviation use. The gasoline must meet ASTM D 4814 and cannot contain any alcohol. Much of the original testing to obtain STCs utilized fuels that did not contain ethanol or methanol. Consequently there are unanswered questions about the effects alcohols may have on various fuel system parts and engine operation.

7.9.5.4 Gasolines containing MTBE are included in the STCs. In December 1992, the Small Aircraft Directorate issued guidance on MTBE use with automotive gasoline STCs.[21]

7.9.5.5 This guidance states, in part, that research testing conducted at the FAA Technical center, with autogas blended with MTBE have not shown any safety related problems. Materials compatibility and performance data supplied by the Experimental Aircraft Association and Petersen Aviation, the main holders of autogas STCs, also have not shown any safety related problems with autogas blended with MTBE. FAA service difficulty reports do not reveal any materials compatibility or safety issues. The majority of the future fuel blends being developed as part of the American Society for Testing and Materials (ASTM) task force programs have included MTBE as an additive. Accordingly, the FAA has determined that autogas blended with MTBE can be used safely in aircraft that are approved for the use of autogas by STCs.

7.9.5.6 The existing prohibition on the use of alcohol additives remains in effect. It is the operators responsibility to assure that the autogas conforms to ASTM Specification D 4814, or the predecessor Specification D 439.

7.9.5.7 Autogas blended with MTBE is approved for use in aircraft that are approved for the use of autogas by STCs. AC 23.1521-1A is being revised to remove the prohibition on MTBE additives.

7.9.5.8 Many oil companies and light aircraft airframe and engine manufacturers do not recommend the use of automotive gasoline in any light aircraft because the testing and quality protection measures applied to automotive gasoline are much less stringent than those for aviation gasoline. Further, federal regulations now require the use of deposit control additives in automotive gasoline and these additives have not been extensively tested in air-cooled aircraft engines nor have they been approved by aircraft engine manufacturers. Additional factors relating to potential adverse effects on engine/aircraft operation and flight safety when using automotive gasoline in aircraft are the broader boiling range, greater volatility, and shorter stability life of automotive gasoline.[25]

7.9.5.9 Alcohol can also be used as a "neat" aviation fuel. In fact, a few planes have received STCs to operate on ethanol and transoceanic flights have been made on ethanol.[22]

7.9.5.10 Ultralight aircraft are generally light weight, open cockpit aircraft designed to seat only the pilot. These aircraft are generally powered by two-stroke cycle engines with the most popular engine manufacturer being Rotax. The U.S. distributor for Rotax engines has issued various precautionary bulletins about the use of alcohols in the Rotax engine[23] but has generally indicated that MTBE is acceptable for use.[24]

7.9.6 Recent Test Data

7.9.6.1 As mentioned earlier, a variety of tests on non-automotive engines operating on oxygenated fuels have been carried out in recent years. Due to the extremely competitive nature of their business segments, manufacturers do not often publish any reports on their tests or otherwise make the information available. One can assume that the experience of most manufacturer's tests are, to some degree, reflected in their owners manual statements (see next section).

7.9.6.2 However some test results have been published.[4,5,6,7,8,9,10] The most recent and perhaps the most comprehensive tests of non-automotive gasoline powered equipment are the performance and compatibility tests completed by the California Air Resources Board (CARB) in March 1996[7] to assess the use of California Reformulated Gasoline (CaRFG) in a broad range of equipment.

7.9.6.3 This study included not only CARB's testing but was supplemented by a number of industry sponsored tests. A brief description of the programs in this study is as follows:

7.9.6.3.1 Harley Davidson: Harley Davidson selected eleven motorcycles representing a cross section of engine families, models, and mileage levels. This test included performance testing, driveability, and fuel economy. Driveability and Engine Durability were unaffected. Fuel economy was one to four miles per gallon lower (3 – 13%).

7.9.6.3.2 Off Road Fleet: Seven major categories including both two- and four-stroke cycle engines were included. The seven categories included:

a. Lawn, garden, and utility equipment.
b. Pleasure craft and small marine engines.
c. Offroad motorcycles and all terrain vehicles.
d. Personal watercraft.
e. Industrial and construction vehicles and equipment.
f. Snowmobiles.
g. Agricultural vehicles and equipment.

7.9.6.3.3 The above categories encompassed 233 units.

7.9.6.3.4 All of the above categories experienced satisfactory operating results operating on CaRFG when compared to the conventional gasoline control fuel.

7.9.6.3.5 Some manufacturers have ongoing test programs which continue to explore the effects of the use of oxygenated fuel in this equipment and further information may be expected in the future.

7.9.7 Manufacturers Fuel Recommendations

As mentioned earlier, several manufacturers have, in recent years, modified their equipment owners manuals to permit the use of gasolines containing ethanol and/or MTBE. Still others do not make mention of these ingredients at the present time. Table 45 provides an overview of the fuel recommendations of a number of manufacturers in each major category.[1,12]

7.9.8 Stationary Power Sources

7.9.8.1 Neat or near-neat alcohol fuels can be used advantageously in turbines and boilers because of their lower flame luminosity and combustion temperatures. The principal requirements in using alcohols are increased fuel storage and pump capacity and a modified nozzle size/spray pattern that compensates for the reduced energy content and lower viscosity of the fuel.

7.9.8.2 Methanol is an extremely clean burning fuel when compared with conventional industrial fuels other than natural gas. The combustion of neat methanol generally will result in the lowest NO_x, emissions and virtually no sulfur or particulate emissions. Sulfur emissions are non-existent since, unlike liquid petroleum-based fuels, methanol contains no sulfur. Particulate emissions are also low with methanol and are comparable to those with natural gas.[26]

7.9.8.3 In tests carried out in turbines and boilers without emissions controls, neat methanol fuel reduced NO_x emissions to levels significantly below those with middle distillate fuel or natural gas. They were also lower than the emissions in tests where water injection was used with middle distillate fuel or natural gas. NO_x emissions with methanol were lower because of cooler flame temperature.[27] In addition gas turbine testing with methanol fuel indicated a slight gain in power output over that obtained with middle distillate fuel.[28] Testing also indicated that a methanol fuel turbine would be internally cleaner than a turbine operated on middle distillate fuel for a similar period of time.

7.9.8.4 Although not serious obstacles, methanol has a low heating value and low lubricity compared with distillate fuel. Fuel systems would need to be designed to accommodate methanol's low flash point and wide flammability range. Extreme care would be required in the shipping and storage of methanol to prevent salt water (sodium) contamination. Sodium will cause corrosion of turbine nozzles and blades.

7.9.8.5 In 1987 experimental data was reported on the first use of methanol with oil or natural gas in the dual fuel combustion process.[29] Dual fuel combustion is a technique discovered by Jones and Mansour[30,31] to reduce the amount of NO_x emitted from power boiler burner combustion. The technique involves burning a fuel containing less nitrogen in the top row of burners over a fuel containing more nitrogen in the bottom row of burners. The technique works particularly well with methanol because a) methanol contains no fuel-bound nitrogen, b) methanol's theoretical flame temperature is lower than fuel oil or natural gas, and c) methanol allows fuel-lean combustion in the upper burner region, permitting fuel-rich (less NO_x) combustion in the lower burner region. The NO_x emission reductions reported using this technique in a utility boiler at a level of 35 megawatts are summarized in Figure 31. Preliminary data on this type of equipment indicates that for good flame stability, 30 percent methanol should be the minimum concentration of methanol used. Experiments in which one of the six methanol burners was shut down (a procedure known as "staging") showed the potential for even further NO_x reductions.

7.9.8.6 Power plants are under development in which methanol and electric power are coproduced using an integrated coal gasification combined-cycle plant. Synthesis gas from the coal gasification process is used to produce methanol in a "once through" process without recycle. The unconverted synthesis gas is utilized in combined-cycle equipment to produce electricity. The methanol, which is easily stored, is used to fuel gas turbines to provide additional power during peak demand periods.[27]

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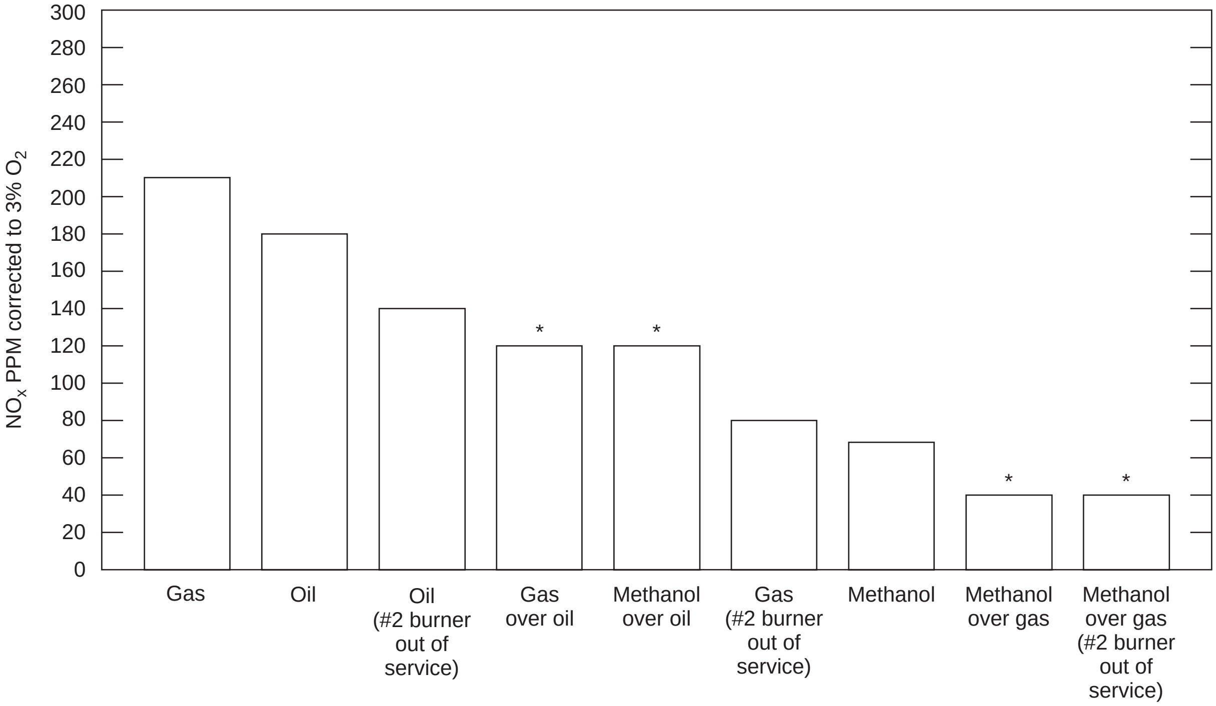
Table 45—Summary of Non-Automotive Gasoline Powered Equipment Manufacturers' Positions on Oxygenated Fuel Use

Manufacturer	Ethanol	MTBE
Power Equipment		
Am.Yard Prd/Roper/Rally	yes*	NM
Ariens	yes[1]	NM
Bolens/Troy-Built	yes*	yes
Briggs & Stratton	yes	yes
Coleman	yes*	NM
Cub Cadet	NM	NM
Dixon	yes	yes
Echo	yes	yes
Grasshopper	NM	NM
Homelite	yes	yes
Honda Power Eq.	yes	yes
John Deere (4 stroke)	yes	NM
Kawasaki	yes	yes
Kohler	yes	yes
Kubota	NM	NM
McColloch	yes*	yes*
MTD	yes	yes
Onan	yes*	yes*
Poulan/Weedeater	NM	NM
Ryobi	yes*	yes*
Sears	yes*	yes*
Shindaiwa	NM	NM
Simplicity	yes	NM
Snapper	NM	NM
Stihl Inc.	NM	NM
Tecumseh	yes*	yes*
Toro/Lawnboy	yes	yes
Motorcycle		
Harley Davidson	yes	yes
Honda	yes	yes
Kawasaki	yes	yes
Suzuki	yes*	yes
Yamaha	yes	NM
Recreational		
ArcticCat (Arctco)	yes*	yes*
Honda	yes	yes
Kawasaki	yes	yes
Polaris	yes*	yes*
SkiDoo/Bombardier	yes	NM
Suzuki	yes*	yes
Yamaha	yes	NM
Boats/Marine		
Honda	yes	yes
Kawasaki	yes	yes
Mercury	yes*	yes*
OMC (Johnson/Evinrude)	yes*	yes*
Pleasurecraft	yes*	yes
Tigershark (Arctco)	yes*	yes*
Tracker	yes*	NM
Yamaha	yes*	NM

Note: This summary is based on a review of each manufacturer's equipment owners manuals. Wording may vary slightly across a manufacturers product line but is generally similar if not identical. Position and wording for a manufacturers two-stroke cycle versus four-stroke cycle models may vary. Also some manufacturers use several engine suppliers (e.g., Briggs & Stratton, Tecumseh, and Kohler) and may utilize the applicable engine manufacturer's fuel recommendations for models with those engines. Finally it should be noted that these recommendations are for new or late model equipment and may or may not apply to earlier models.

[1] Engine manufacturer indicates approval but equipment manufacturer does not.

Legend
yes = permitted/approved.
yes* = indicates approved but may contain precautionary language or require modification.
NM = not mentioned in owners manual.



Note: Asterisk indicates dual-mode combustion.

Source: Reference 29

Figure 31—Comparison of Stationary Combustion NO_x Emissions

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8 Distribution and Storage of Alcohols, Gasoline-Alcohol Blends, and Gasoline-Ether Blends—Transportation, Marketing, Safety and Fire Protection, and Measurement

8.1 CURRENT GASOLINE DISTRIBUTION SYSTEM

8.1.1 The current gasoline storage and distribution system is illustrated in Figure 32 and consists of a) refineries, b) refinery terminals, c) products pipelines, d) product tankers and barges, e) rail, f) pipeline and marketing terminals, g) bulk plants, h) tank trucks, and i) service stations or retail outlets.[1] The majority of gasoline today (55 to 60 percent) is shipped from refineries by pipeline to pipeline and marketing terminals. About 35 percent of gasoline is shipped from refineries by barge and tanker, and the remaining 5 to 10 percent is shipped by truck.[2–5] Gasoline is currently not shipped by rail in any significant amount. However, rail is often the major mode of transporting oxygenates to blending locations. From pipeline and marketing terminals almost all gasoline is moved by truck to bulk plants, service stations, and major users such as farms and large commercial customers.

8.1.2 The affinity of gasoline-alcohol blends for water and its intrinsic characteristic to loosen or scour rust and scale from pipeline walls generally makes alcohol addition at any point other than truck loading at terminals more difficult (see Figure 32). Other points further upstream in the distribution system can be exposed to water, and therefore phase separation could occur if gasoline-alcohol blends were introduced at any other point in the system. However, gasoline-alcohol blends have been successfully shipped by pipeline as part of commercial marketing of finished gasoline.[6–10] This was done, however, with extraordinary concern for quality control and dryness of the system and involved capital investments. Water contamination of gasoline-alcohol blends presents a major and costly potential problem in the distribution of these fuels.

8.1.3 There are many complexities that tend to make pipeline shipment of gasoline-alcohol blends more difficult. For example, refineries may blend gasolines from components continuously and deliver directly to a pipeline, or they may batch-blend the gasoline into shipping tanks. Long pipelines may have intermediate “breakout” tanks that are necessary for efficient operation of the pipeline. Most have multiple terminals or delivery points along the line.[38] Refinery shipping tanks, pipeline breakout tanks, terminal, and bulk plant tanks are wet; that is, water is always present. For example, many gasoline tanks are equipped with uncovered floating roofs that limit evaporation but do not completely exclude water. In addition products may be saturated with water when they leave the refinery. This is no problem with gasoline because any water from rainfall or snowfall leaking into the tank or condensing out of the product separates readily from the gasoline. The “water bottoms” that collect are drained from the tank as part of the routine maintenance activities of the pipeline or marketing terminal. However, water that enters a tank holding gasoline-alcohol blends could exceed the capacity of the blend to dissolve water. If this occurred, the water could extract the alcohol from the gasoline-alcohol blend, and phase separation would result. The resulting alcohol-water mixture would require more extensive waste treatment than for water alone. In addition, the loss of gasoline octane and/or oxygen content may need to be addressed because the resulting alcohol-deficient gasoline may not meet the original specifications. Chapter 2 provides information on the water tolerance and sensitivity of various gasoline-alcohol blends.

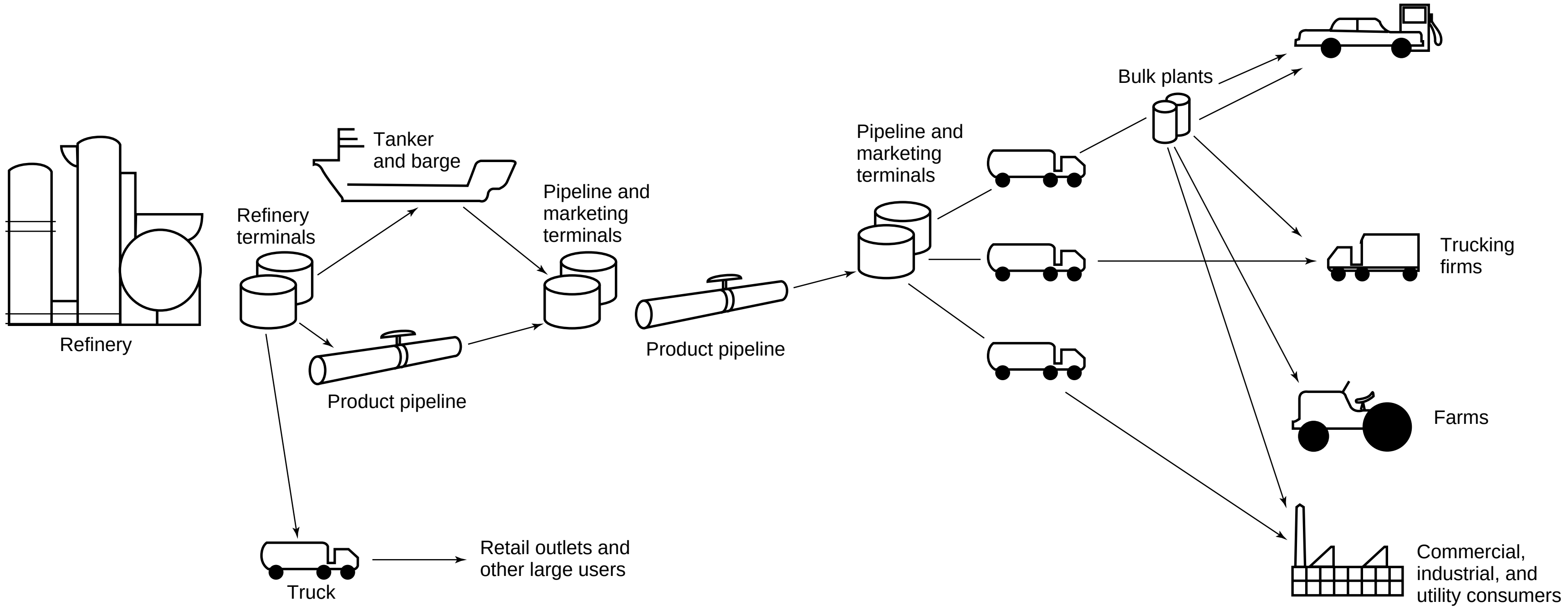
8.1.4 Because gasoline-MTBE blends are compatible with the current storage and distribution system and have a low affinity for water, MTBE is usually added at the refinery, and the blend is shipped by pipeline or any of the other modes of transportation as shown in Figure 32. MTBE can also be added at the marketing terminals. Although gasoline-MTBE blends are compatible with most elastomers found in automotive fuel systems and gasoline storage and distribution systems, it should be noted that fluorocarbon elastomers such as Viton A should not be used in contact with neat MTBE, as 100 percent MTBE has been found to degrade these materials.[11,12]

8.2 DISTRIBUTION AND STORAGE OF GASOLINE-ALCOHOL BLENDS—REFINERY, PIPELINES, TERMINALS, AND SERVICE STATIONS

8.2.1 Transportation Systems

8.2.1.1 If gasoline-alcohol blends currently approved under EPA rules and regulations were to be distributed starting at the refinery, which would be the case if the volume to be supplied required pipeline shipment, important changes or additions would have to be made to each mode of transportation—pipeline, tanker, barge, rail, and truck. Because there are differences between requirements for storing gasoline and requirements for storing gasoline-alcohol blends, changes to pipeline storage terminals would also be necessary.[13,14] More widespread use of gasoline-alcohol blends, moreover, could also require additional pipeline storage capacity.

8.2.1.2 Because of the affinity of alcohol for water, the largest change required for pipeline transportation of gasoline-alcohol blends could be installation of dehydrating equipment and filtration/coalescing equipment.[15] Complete pipeline dehydration would be required for large multiple shipper-multiple product systems because conventional hydrocarbon products and alcohol blends would be handled by the same pipeline. In such cases all petroleum products



Source: Reference 1

Figure 32—Typical Gasoline Distribution System

that are shipped by the pipeline would have to be dehydrated, and the pipelines might have to be cleaned much more frequently. Gasoline-alcohol blends can also interfere with the protection offered by commonly used corrosion inhibitors in pipeline systems. Moreover, pipelines may have to install additional tankage, install dome roofs on floating roof tanks, and install additional product testing instrumentation. Another concern is contamination of other products, especially aviation turbine fuel, with alcohol. Aviation turbine fuel contaminated with alcohol, besides being an illegal fuel, would carry increased amounts of dissolved water through the filter/coalescer units into the fuel tanks of aircraft. When the fuel cools down at high altitude, the water/alcohol will separate from the fuel and can cause stress to the fuel system components (corrosion of metals, leakage of sealants, and incompatibility with internal fuel bladders).

8.2.1.3 Shipping gasoline-alcohol blends by barge or ship would require replacement of tank coatings in some vessels, replacement of valve and pump seals with materials compatible with gasoline-alcohol blends, and other maintenance and product quality assurance operations. Replacing single-skin barges with double-bottom barges may also be required. These same concerns must be addressed with large shipments of neat alcohols and ethers.

8.2.1.4 Blending gasoline and alcohol at the refinery terminal or at pipeline terminals requires shipping the alcohol from the production site by rail, truck, or barge to the facilities. Additional tankage may also be needed for storing the alcohol for blending. Each refinery may need rail off-loading facilities, including tankage. Computerized in-line blending facilities are likely to be added to terminals where blending of gasoline and alcohol occurs.[16]

8.2.2 Marketing Terminals and Bulk Plants

8.2.2.1 Gasoline-alcohol blends currently approved under EPA rules and regulations can generally be stored at existing marketing terminals and bulk plants after some equipment modifications.[13,14] If the volume supplied necessitates, additional tankage would have to be installed.

8.2.2.2 Gasoline-alcohol blends should be stored in a tank with a fixed roof and an internal floating cover.[13,14] Facilities not so equipped should be modified. Extreme care must be taken to ensure that any tank lining is compatible with the gasoline-alcohol blend. If blending occurs at the terminal, additional tankage may also be needed for storing the alcohol for blending. For terminal blending of gasoline and alcohol, computer-controlled in-line or sequential blending is recommended.

8.2.2.3 The following list summarizes some of the factors that must be considered in order to convert an existing marketing terminal to handle gasoline-alcohol blends currently approved by EPA rules and regulations:[15]

a. Receiving facilities (valves/pump seals).
b. Storage tanks.
    1. Replace floating roof when required (that is, from aluminum to steel).
    2. Cover floating roof.
    3. Evacuate, clean, and inspect.
c. Loading facilities--pumps, valves.
d. Vapor recovery increased capacity.
e. Inline blending facilities.
f. Additional fire and safety facilities/alcohol-water bottoms drawoff.
g. Oily water/waste disposal (some form of environmentally acceptable waste water treatment).

8.2.3 Retail Facilities—Service Stations

8.2.3.1 Gasoline-alcohol blends currently approved under EPA rules and regulations can generally be handled at existing service station facilities after some maintenance and equipment modifications.[13,14,16] Service station tanks must be cleaned and dried before being used for gasoline-alcohol blends, and extra precautions must be taken to keep water from entering the tank after use begins. Water from rainfall or snowfall leaks can enter service station storage tanks through filler ports. Water can also enter as humid air is drawn into tanks during diurnal breathing cycles and when fuel is withdrawn from the tanks. This has not been a problem in the use of gasoline-alcohol blends because of their capacity to dissolve some water. Once dry, gasoline-alcohol systems have the potential to keep themselves dry with continuous use of the gasoline-alcohol blends. Care must be taken to ensure that any storage tank lining is compatible with gasoline-alcohol blends and alcohol/water tank bottoms. Filters must be installed in the final dispensing system to ensure the delivery of clean product, since gasoline-alcohol blends will loosen rust and dirt deposits throughout the system. Depending on the age and materials in the service station dispensing pump, the meters will require either replacement or recalibration when gasoline-alcohol blends are first introduced.

8.2.3.2 The following list summarizes some of the factors that must be considered in order to convert a retail service station to handle gasoline-alcohol blends currently approved by EPA rules and regulations:[15]

a. Storage tank compatibility.
b. Overfill protection.
c. Pumps and line leak detectors.
d. Pump meter replacement or recalibration.
e. Dispensers and filters.
f. Alcohol-resistant materials--hoses, seals, nozzles.
g. Storage tank cleaning and drying.

h. Protection from water contamination--dryers on vent lines and pressure vacuum vents, fill cap O-rings.

i. Application of special signs and decals.

8.2.4 Safety and Fire Protection

8.2.4.1 The safety and fire protection precautions for storing and handling EPA approved gasoline-alcohol blends are similar to those for gasoline. All applicable government and industry standards should be followed. Although there are similarities in extinguishing fires involving gasoline-alcohol blends, some important differences exist. API Recommended Practices 1626 and 1627 provide technical guidance on safety and fire protection procedures for gasoline-alcohol blends at service stations and distribution facilities.[13,14] API Publication 2300 treats differences in the selection and use of fire-fighting foams.[17]

8.2.4.2 Measurements of the upper and lower temperature and concentration limits of flammability for various gasoline-oxygenate blends containing ethanol and/or MTBE are provided in API Publication 4646.[26] The addition of either MTBE or ethanol or both to gasoline yields a moderate increase in upper flammability limits. Gasoline blends containing ethanol, including those commingled with MTBE, elevate the upper temperature limits of flammability to a greater extent than gasoline blends containing MTBE alone.[26]

8.2.4.3 In addition to safety and fire considerations for the gasoline-alcohol blends precautions and safety procedures for handling the alcohol at the point of blending must be followed, regardless of whether blending occurs at the refinery terminal, pipeline terminal, or marketing terminal. At those facilities handling alcohol for blending with gasoline, it is recommended that a polar-solvent (alcohol-resistant) foam be provided.[15] In case of a fire local authorities may not be certain what fuel is involved. The polar-solvent (alcohol-resistant) foam is suitable for all the situations that will likely be encountered and can eliminate uncertainty as to selection of the agent. This provides maximum protection. The water/alcohol bottoms drained from storage tanks may be flammable. Appropriate precautions should be taken during handling and disposal.

8.2.5 Measurement/Inventory Accounting System

8.2.5.1 Inventory accounting systems may be compromised, in some instances, by the presence of gasoline-alcohol blends in the distribution and storage system.

8.2.5.2 Product must be inventoried through a series of measurements during product distribution to ensure accurate custody transfer and compliance with loss prevention systems. The presence of alcohols in fuels compromises the accurate determination of volume adjusted for temperature because alcohols do not have the same density and coefficient of expansion relationship as hydrocarbons. A further compromise exists because of the volume growth that occurs when alcohol is added to gasoline (see Chapter 2). These measurement problems would be most important for bulk transfers involving pipeline measurements and associated storage. There is less concern for small transfers such as at truck transfers, small tanks, or bulk plants.

8.2.5.3 Currently, no generalized volume correction factors for gasoline-alcohol blends exist. Although no extensive assessment has been made to determine the loss of accuracy that occurs when using the gasoline volume correction factors for gasoline-alcohol blends, one study of a gasoline-ethanol blend did show that the increased error for correcting volume of that blend to 60°F was about 0.03 percentage points.[18]

8.2.5.4 Evaporation losses can be calculated for gasoline-alcohol blends stored in internal floating roof tanks using API Publication 2519[19] and prediction models.

8.3 DISTRIBUTION AND STORAGE OF NEAT OR NEAR-NEAT ALCOHOLS--REFINERY, PIPELINES, TERMINALS, AND SERVICE STATIONS

8.3.1 Transportation Systems

8.3.1.1 Transportation and storage capacity are primary considerations in the application of neat or near-neat alcohols as fuels. Methanol has about half the energy content of gasoline, and ethanol has about two-thirds the energy content of gasoline. As discussed in Chapters 2 and 6, it will most likely require about 1.8 gallons of neat methanol fuel to provide the same driving range as 1 gallon of gasoline. The greater quantities of alcohol needed to provide the same vehicle driving range could not be distributed and stored without the addition of facilities for each mode of transportation (pipeline, marine, truck, and rail) within the current distribution system.

8.3.1.2 In addition to substantially increased distribution and storage capacity, replacing gasoline with neat or near-neat alcohols requires the same changes to the transportation system as those discussed in the previous section for gasoline-alcohol blends. The following list summarizes some of the factors that must be considered in order to transport neat or near-neat alcohol fuels:[15]

a. Pipelines.

1. Capacity and throughput.
2. Dehydration equipment.
3. Materials compatibility.
4. Terminal tankage, tank roofs, product testing, inline blending, and truck loading facilities.
5. Maintenance.

6. Contamination of other petroleum products by alcohols.

b. b. Trucks.

1. Truck capacity for transport from refinery and terminal.
2. Capacity loss due to heavier payload.

c. Rail: capacity for transport to refinery or terminal.

d. Marine (ship transportation).

1. Capacity.
2. Materials compatibility (seals/valve packing, maintenance).
3. Product quality (coatings, new or renew).
4. Segregated ballast retrofit (hazardous substance).

e. Marine (barge transportation).

1. Material compatibility.
2. Double bottoms.

8.3.2 Marketing Terminals

8.3.2.1 As previously noted, the distribution and storage of neat or near-neat alcohols from marketing terminals would require substantial increases in storage capacity to supply the equivalent vehicle driving range requirements of gasoline. Storage facilities for neat or near-neat alcohols, like those for blends, must be equipped to prevent water from entering. This requires fixed roofs with internal floating covers.[13]

8.3.2.2 For the supply of near-neat alcohol the alcohol can be transported to the terminal and then blended, or the near-neat alcohol can be shipped to the terminal by pipeline from the refinery already blended. Either case requires additional storage tankage. The capacity of vapor recovery systems would need to be increased. Truck loading rack facilities would also be required. Inline blending facilities would be required for terminal blending of near-neat alcohols.

8.3.2.3 Care must be taken that all storage facility materials are alcohol compatible. Environmentally acceptable treatment systems for waste waters are also a concern. Water-contaminated alcohol fuels present a major and potentially costly problem in the distribution of these fuels. Such off-specification material is unmarketable and must be either disposed of or reprocessed in some way to remove the water.

8.3.2.4 The following list summarizes some of the factors that must be considered to convert an existing marketing terminal to handle neat or near-neat alcohol fuels:[13,15,20]

a. Receiving facilities (valves/pump seals).

b. Storage tanks.

1. Replacement of floating roof when required (that is, from aluminum to steel).
2. Evacuation, cleaning, inspecting, and refilling.
3. Valve seals.
4. Floating roof seals.
5. Floating roof cover.

c. Loading facilities--pumps, valves.

d. Vapor recovery capacity and material compatibility.

e. Inline blending facilities.

f. Additional fire and safety facilities.

g. Oily water/waste disposal--some form of environmentally acceptable waste water treatment.

8.3.3 Retail Facilities—Service Stations

8.3.3.1 At retail facilities neat or near-neat alcohol fuels would most likely be handled through the addition of a separate storage, pumping, and dispensing system. In addition to all the earlier described considerations for storing neat or near-neat alcohols the service station underground storage tank and lines would require some form of secondary containment under the proposed EPA underground storage tank regulations.

8.3.3.2 The following list summarizes some of the factors that must be considered when installing a new facility for neat or near-neat alcohols or for retrofitting or converting an existing system to be alcohol compatible:[15,20]

a. Storage tanks and underground lines with secondary containment system.

b. Piping (vents, fills, product lines).

c. Overfill protection.

d. Fillpipe spill containment.

e. Stage I vapor recovery.

f. Pumps and line leak detectors.

g. Dispensers.

h. Alcohol resistant materials—tank hoses, seals, nozzles.

8.3.4 Safety and Fire Protection

8.3.4.1 Fires involving neat or near-neat alcohol fuels present special fire fighting problems.[15] These fires require the use of alcohol-resistant foam concentrates or dry chemicals. Trends in local codes suggest that service stations dispensing neat or near-neat alcohol fuels may require maximum protection. References 13 and 17 provide technical guidance on the safety and fire protection considerations for alcohol fuels. Alcohols are generally stored in tanks with internal floating covers. However, the flammable and combustible liquids code, NFPA-30,[21] does not prohibit the use of cone roof tanks for this application.

8.3.4.2 The relative fire hazards associated with alcohols and gasoline can be compared by means of the properties listed in Table 46.[22] Figure 33 compares the vapor space flammability limits for methanol and methanol blended with various liquid fuels.[23] The vapor space over methanol will normally be in the flammable range at bulk liquid temperatures between about 45°F to 110°F. When blended with hydrocarbon fuels, the vapor space flammability limits of

Table 46—Comparison of Properties Relating to Fire Hazards for Alcohols and Gasoline

Property	Methanol	Ethanol	Gasoline
Flash point, °F	52	55	–45
Autoignition temperature, °F	867	793	495
Flammability limits, vol%	7.3 – 36	4.3 – 19	1.4 – 7.6
Vapor pressure at 70°F, psi	1.9	0.8	4.8
Vapor pressure at 100°F, psi	4.6	2.3	8 – 15
Concentration in saturated air at 68°F, vol%	13	5.4	25 – 50

Notes:

a. Ethanol and methanol tanks should be located within separate dikes, or if located within a common dike, intermediate dikes or proper drainage should be provided.

b. Special foam chambers and modified foam application techniques are required for protecting neat or near-neat alcohol tanks. Higher foam application rates may be required for extinguishing tank and dike fires. Subsurface foam injection is not effective in most polar fuels and is not recommended for extinguishing either ethanol or methanol storage tank fires.

methanol approach those of gasoline. As discussed in Chapter 6, methanol presents a special safety hazard because it burns without much visibility. Hydrocarbons blended with methanol have been found to effectively increase flame luminosity.[24]

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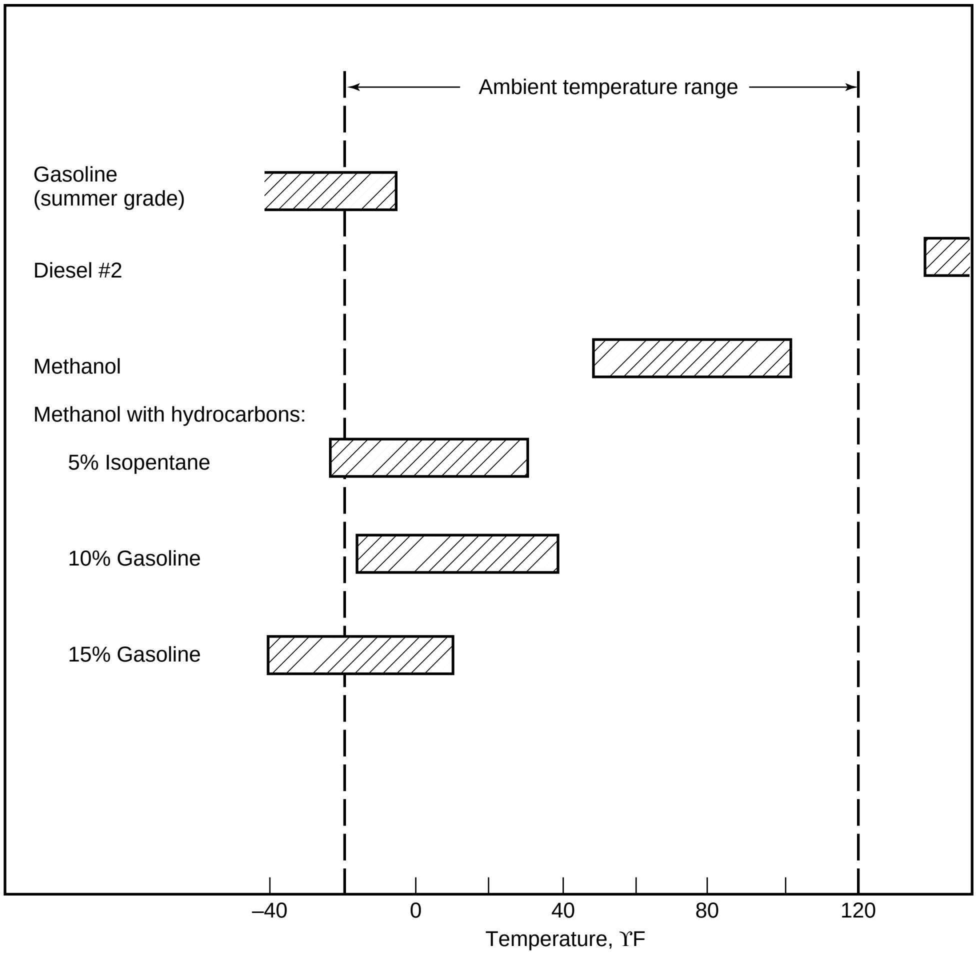

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9 Oxygenates in Ground Water: Occurrence, Behavior, and Remediation

9.1 GENERAL

The impacts of oxygenated gasolines when released to soil or groundwater has been the topic of considerable interest in the last several years. Several recent comprehensive federal and state studies provide excellent detailed summaries of the occurrence, behavior and remediation of alkyl ethers and alcohols in the subsurface.[8–12,16,17,22,23,24] A 1997 conference also reviewed the current state of knowledge regarding oxygenates in the environment.[1]

9.2 ENVIRONMENTAL BEHAVIOR AND FATE

9.2.1 Since only a few papers describe the environmental fate of oxygenates other than MTBE, the following summary focuses on MTBE. However, by referring to Table 2, it can be seen that the other alkyl ethers have relatively similar properties to MTBE, and so their subsurface fate and transport can be expected to be generally similar to what is known about MTBE. Alcohols will behave somewhat differently, primarily because of their complete solubility. The subsurface behavior of these oxygenates is best described by comparison to the aromatic compounds benzene, toluene, ethylbenzene and the xylenes (BTEX), the usual chemicals of concern at gasoline release sites.

9.2.2 MTBE has a relatively high water solubility, 4.3 wt. %, or about 43,000 ppm. Benzene is the most soluble BTEX compound, at about 0.18 wt. %, or 1,800 ppm. The other alkyl ethers are slightly less soluble, although roughly comparable to MTBE (see Table 2). Alcohols (e.g., TBA and ethanol) are 100% soluble—when in contact with water, they will completely dissolve. Water equilibrated with an oxygenated gasoline can contain relatively high concentrations of the oxygenate. For a gasoline with 10% vol. MTBE, laboratory water equilibrium concentrations were observed to be over 3600 ppm MTBE, while total BTEX was 114 ppm (API, 1991b). The same study reported equilibrium concentrations of 6700 ppm for a 10% ethanol gasoline, and 8000 ppm for a 10% methanol gasoline. Dissolved BTEX concentrations for these alcohol fuels were both about 120 ppm. A conventional gasoline (no oxygenates) tested in this study also had about 120 ppm dissolved BTEX.

9.2.3 These laboratory concentrations for MTBE are much higher than those observed in actual field situations. There are no reported literature values for field concentrations of ethanol from fuel spills. Concentrations of over 500 ppm MTBE have been measured in monitoring wells near point source releases, and concentrations over several thousand ppm have been reported for storage tank water bottoms in contact with oxygenated gasolines. These values are at least 10 – 50 times higher than the dissolved concentration for any single BTEX compound found in similar scenarios. While concern has been raised that oxygenates may increase the solubility of BTEX compounds when released to groundwater, several studies have shown the threshold for this effect occurs only when oxygenate:gasoline ratios are much higher than those likely to be found in oxygenated or reformulated fuels (e.g., much greater than the current upper limit of 15% vol. MTBE permitted in gasoline).

9.2.4 Once it is dissolved in groundwater, MTBE and other alkyl ethers will not be adsorbed to soil particles as readily as BTEX, and so are likely to travel at approximately the same velocity as the flowing groundwater. While recent studies of hundreds of gasoline release sites have demonstrated that intrinsic bioremediation of soluble BTEX plumes will typically keep the length of such plumes to less than 300 feet, those studies did not include MTBE data. It is expected that MTBE plumes would travel farther from the source than BTEX plumes, since 1) the initial dissolved concentration of MTBE at the source would be as great or greater than BTEX; and 2) MTBE does not appear to be as biodegradable as BTEX in groundwater.

9.2.5 Limited documentation of the real extent of MTBE plumes from point source releases (e.g., underground storage tanks) indicates that some MTBE plumes may grow to be 1.5 – 3 times larger than typical BTEX plumes.[9] Happel et al have recently characterized MTBE data of over 40 California UST release sites, concluding that MTBE does not appear to be attenuating as quickly as benzene, which would result in longer MTBE plumes.[25] Actual plume lengths will be dependent on the release scenario and other site specific factors. Weaver et al have identified some very long MTBE plumes on Long Island, New York, where groundwater velocities are quite fast. While earlier studies suggested that MTBE was not biodegradable in groundwater, more recent laboratory and field research has shown that it can be biodegraded under both aerobic and anaerobic conditions.[6,7,13,20,27] However, the biodegradation rates appear to be slower than for BTEX. While very few studies have been conducted on the biodegradability of other alkyl ethers and TBA, they are expected to show generally similar persistence in groundwater.

9.2.6 MTBE has not been shown to inhibit biological activity or decrease natural biodegradation rates for BTEX. Alcohols like methanol or ethanol are very biodegradable, but since they will completely dissolve in groundwater, they may be present in very high concentrations. Such a large amount of dissolved mass may take a relatively long time to biodegrade. It may also contribute to decreased BTEX biodegradation rates, since the alcohol could serve as a preferred energy source for groundwater bacteria. BTEX biodegradation may be slowed until most of the alcohol is consumed, allowing those compounds to migrate further than if no alcohol had been present, as shown in a controlled release of dissolved methanol/BTEX conducted in Canada.[5] A recent California study provides considerable details on this and other related aspects of the fate of ethanol in groundwater.[28]

9.2.7 Because it is less biodegradable and less likely to be sorbed to aquifer soils, dissolved MTBE is more mobile in groundwater than the BTEX compounds. Since MTBE travels at about the same rate as groundwater, it will usually be the first compound detected by chemical analysis in monitoring wells downgradient from a gasoline release, and can serve as an early indicator of a gasoline release. The leaching behavior of MTBE has recently been characterized in a series of laboratory and field studies. Its high solubility and mobility will facilitate relatively rapid leaching of MTBE in soils, with subsequent transport to groundwater.

9.2.8 Volatile emissions of MTBE in areas of high use may result in broad ambient atmospheric concentrations of about 2 ppbv, and higher local values of 20 – 30 ppbv. This vapor phase MTBE can partition to snow or rainfall, and become a potential source for subsequent transport to ground water. This atmospheric washout of MTBE may have a detectable influence on water quality. Modeling studies have shown that over time (at least 5 – 15 years or more) an equilibrium may be established between atmospheric MTBE concentrations and those in surface and shallow ground water.[15] At 20°C and ambient air concentration of 2 ppbv, rainfall may contain about 0.4 ppb wt. % MTBE (0.4 ug/L). Colder temperatures appear to enhance MTBE washout. For the same ambient air concentration, precipitation occurring during cooler atmospheric temperatures may have higher concentrations of MTBE than during warmer temperatures [e.g., at 0°C and 2 ppbv air concentration, MTBE in precipitation would be almost 3 ppb (ug/L)]. Studies to measure MTBE in precipitation are in progress. Stormwater also may contain low concentrations of MTBE (e.g., 0.5 – 4 ppb), along with other fuel hydrocarbons and a variety of other VOCs.[10] Infiltration of stormwater can also contribute to low level impacts on groundwater quality.

9.3 REMEDIATION

9.3.1 Site remediation is usually a combination of 1) the initial removal of MTBE from the subsurface in either an air or aqueous phase, and 2) subsequent treatment of these effluents to remove MTBE before final discharge. Limited case studies are available that characterize soil or aquifer restoration after being impacted by MTBE. Most of the technologies commonly used today for fuel release remediation in soils and groundwater should also be effective for removing MTBE and the alkyl ethers from dissolved plumes or in the residual gasoline near the source of the release.[9] These technologies include “pump and treat” (i.e., pumping impacted groundwater to the surface for treatment), air sparging, soil vapor extraction (SVE), and dual phase extraction. The use of natural attenuation as a remediation option may be limited when MTBE is present in a dissolved plume.

9.3.2 The relatively high vapor pressure of MTBE suggests that soil vapor extraction (SVE) should be effective for removing this compound from residual or free phase gasoline residing in soil or at the water table. Limited data is available on the effectiveness of air sparging for removing MTBE from groundwater. Because of its low Henry’s Law Constant, MTBE is not likely to be as amenable to this in situ air stripping process as BTEX. MTBE in water or air effluents generated during remediation processes may be treated by conventional technologies like air stripping and carbon adsorption. Much larger air to water ratios are required for air stripping, and effluent heating may be a cost effective enhancement in some applications. The higher concentration of MTBE in some effluent streams and the lower carbon adsorption capacity for MTBE will likely require larger capacity and/or more frequent carbon replacement. These design factors are likely to increase treatment costs by 1 – 2 times or more, depending on the regulatory discharge levels allowed.

9.4 REGULATORY GUIDELINES

There are no federal standards for MTBE or alkyl ethers in surface or ground water, and there are no federal requirements for monitoring MTBE or alkyl ethers in surface or ground water. At least nineteen states have specific cleanup criteria, mostly directed toward MTBE in groundwater. Limits range from 0.005 mg/L to 50 mg/L for groundwater, and 3 mg/kg to 2600 mg/kg for soil.[30] In 1992 the EPA Office of Drinking Water and Ground Water issued a Draft Drinking Water Health Advisory, which provided a lifetime acceptable exposure range of 20 – 200 ppb. EPA extensively revised this report and officially released it in late 1997 as a “Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on MTBE”[19]. In this revision the EPA indicates that the taste and odor threshold of MTBE is in the range of 20 – 40 ug/L. No companion health-based guidance concentration is provided. EPA does indicate that a level in drinking water that could cause potential health effects would be much higher than 20 – 40 ppb, and that the taste and odor of MTBE at those lower levels should preclude chronic exposure to water with higher levels. The advisory is considered EPA guidance only, and does not assume any formal legal standing for regulatory enforcement or compliance.

9.5 SUMMARY

Regarding possible ground water impacts from gasoline containing oxygenates, the solubility and biodegradability of MTBE and other alkyl ethers are the properties of greatest importance. Their dissolved concentrations in groundwater may be relatively high, especially if reformulated or oxygenated fuels are spilled. Since their apparent biodegradability is much less than BTEX, these dissolved plumes have the potential to migrate further from the site than BTEX. When dissolved in water, MTBE is considerably more difficult to remove than BTEX compounds with conventional technologies. The taste and odor thresholds for MTBE and other alkyl ethers in water are low (20 – 40 ppb), and are far below the concentrations that may cause health effects with chronic exposure.

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10 Toxicity of Alcohols and Ethers

The health effects of ethers and alcohols used as fuel oxygenates have been extensively reviewed[17,23,24] The discussion in this section will briefly summarize the health effects for methanol, ethanol, TBA and MTBE and describe recent findings. Information on ETBE, TAME and DIPE are provided in greater detail.

10.1 ALCOHOLS

10.1.1 Methanol

10.1.1.1 Methanol, like ethanol, can cause central nervous system depression, but its important toxic effects in man are blindness and acidosis, which can be fatal. These effects are due to metabolism of methanol to formic acid and formate. Formic acid excess leads to acidosis, and formate has been shown to cause partial or complete blindness in monkeys.[39] Chronic exposure to high levels can also lead to blindness in humans. These effects have been manifested after ingestion, inhalation, or dermal exposure.[40] Evidence of developmental toxicity is unclear with reported effects occurring only at very high levels.[41] A series of acute and chronic exposures have recently been conducted by the New Energy Development Organization of Japan.[42] In these experiments continuous inhalation exposure of monkeys to 3000 parts per million of methanol for 3 weeks led to slight partial atrophy of the optic nerve. Continuous exposure to 1000 parts per million for 2.5 years did not have this effect, however. Carcinogenesis studies carried out using near-continuous inhalation exposure to 1000 parts per million in rats and mice showed no increase in tumors.

10.1.2 Ethanol

10.1.2.1 Chronic ethanol abuse induces liver and central nervous system toxicity.[43] Excessive consumption during pregnancy results in developmental toxicity in offspring.[44] Studies examining developmental toxicity by inhalation exposure were without effect at concentrations as high as 20,000 ppm ethanol[25]. Heavy ethanol drinkers show excessive mortality from cancers of the mouth, pharynx, larynx, esophagus, liver, and lung.[45] The acute toxicity of ethanol is low, with symptoms and death caused by narcosis.[46] Examination of blood ethanol levels in rats and mice following inhalation exposure revealed that anticipated exposures during refueling result in minimal blood ethanol levels and are unlikely to result in toxicity.[27]

10.1.3 TBA

10.1.3.1 Tertiary butyl alcohol (TBA) is five times more potent than ethanol in inducing narcosis with a much longer duration. This probably is a reflection of the fact that TBA is metabolized much more slowly.[47] Irritation of the eye, nose, and throat; headache; fatigue; and dizziness are noted as symptoms of excessive exposure.[48] TBA was not mutagenic in one test system.[49] Long term oral exposure to TBA produced kidney tumors in male rats and thyroid tumors in female mice.[14] The relevance of these tumors to human health has not been determined.

10.2 ETHERS

10.2.1 MTBE

10.2.1.1 The odor detection and recognition thresholds for MTBE in air range from 45 to 137 ppb.[24] Odor and taste thresholds in water range from 45 to 95 ppb.[24] Addition of 3, 11, or 15 vol% MTBE reduces the odor threshold of gasoline from 576 ppb to 500, 275, and 113 ppb, respectively.[2]

10.2.1.2 The health effects of MTBE have been extensively studied and reviewed.[17,23,24] Humans exposed to MTBE either at concentrations observed during refueling,[22,28] or to levels as high as 50 ppm, did not report any adverse health effects. MTBE produces transient reversible sedative effects in rodents at high exposure concentrations.[16]

Developmental toxicity has been examined in rats, mice and rabbits resulting in cleft palate and skeletal malformations in mice pups exposed to maternally toxic levels of 4000 and 8000 ppm MTBE.[8] MTBE exposure did not induce reproductive toxicity in two generation toxicity test in rats.[9] Body weight gains were reduced in the first and second generation pups at 3000 and 8000 ppm MTBE exposure.

10.2.1.3 MTBE is non mutagenic in several assays, Ames mutagenicity assay, unscheduled DNA synthesis, micronucleus, and chromosomal aberrations[21] with the exception of the mouse lymphoma assay with microsomal activation.[7] The positive response appears to be related to formation of formaldehyde in this *in vitro* test system. Subsequent research has demonstrated that exposure to 8000 ppm MTBE does not produce sufficient formaldehyde concentrations *in vivo* to produce mutations.[13]

MTBE produces tumors in rodents. Inhalation exposure to MTBE produced male rat kidney and testicular tumors, and liver tumors in female mice[10]. Kidney tumors appear to be linked to the a-2m globulin mechanism specific to male rats.[29] The EPA has found that tumors produced by this mechanism are not relevant in assessing human risk.[31] The interaction between MTBE and a-2m globulin appears to be weaker than that for d-limonene, and trimethylpentane. Testicular tumors (interstitial cell tumors) were elevated over concurrent control in the high dose group (8000 ppm), but were within the historical control range for this tumor type. Lifetime oral gavage exposure to MTBE resulted in testicular tumors in male rats and lymphohematopoietic tumors in female rats.[48] The testicular tumors (interstitial cell tumors) were observed in the high dose group which had a longer survival time than controls. An increase in lympho-hematopoietic tumors was observed after combining total number of leukemias and lymphomas (a practice not endorsed by the National Toxicology Program). The EPA has not finalized a cancer classification or conducted a quantitative risk assessment for MTBE.

10.2.2 ETBE

10.2.2.1 The odor detection and recognition thresholds for ETBE in air are 13 and 24 ppb, respectively. Addition of 15 vol% ETBE to gasoline reduces gasoline odor detection threshold from 578 ppb to 64 ppb.[2]

10.2.2.2 The absorption, disposition, metabolism and excretion of ETBE have been examined in humans and rodents. Humans volunteers were exposed to 5, 25, 50 ppm of ETBE for 2 hours.[20] Data indicate that approximately 25% of the inhaled ETBE was absorbed into the blood. A linear increase of ETBE concentrations in the blood was observed with increasing exposure levels. Approximately 30% of the absorbed dose was exhaled unchanged. Metabolism of ETBE was slow with only 1% of the absorbed dose appearing in urine as TBA. Rats and mice were exposed to 500, 1750 and 5000 ppm of ETBE.[11] After a single six hour exposure, urinary excretion predominated at lower exposure levels (500 ppm) while excretion was comparable between urine and exhalation at the highest exposure level (5000 ppm). Following two weeks of 6 hour exposures to 5000 ppm ETBE, the major route of elimination had shifted to urine suggesting an increase in ETBE metabolism.

10.2.2.3 The acute toxicity of ETBE has been examined in human volunteers exposed to 5, 25 and 50 ppm ETBE for 2 hours.[26] Reporting of symptoms such as headache, dizziness, or respiratory discomfort was not increased. Some minor changes in lung function were noted; however, these changes were judged not to be exposure related.

10.2.2.4 ETBE is not mutagenic potential in bacteria, Chinese hamster ovary cells,[38] or mouse bone marrow,[33,34] and does not produce chromosomal aberrations.[32].

10.2.2.5 Neurotoxicity was evaluated in rats exposed by inhalation for four weeks to 500, 2000 and 4000 ppm ETBE.[36] Sedation was noted in the high dose group. Effects on neurobehavioral parameters were observed in rats exposed at the highest concentration of ETBE. This effect was most likely due to sedative effect of the ether as these tests were conducted shortly after exposures ended. An increased liver weight was observed in high dose animals.

10.2.2.6 Rats and mice were exposed to 500, 1750 and 5000 ppm ETBE by inhalation for ninety days.[22] Neurotoxicology evaluations revealed only subtle, transient changes with no indication of neuropathology. Liver weights were increased in both rats and mice with increasing exposure concentrations. Degenerative changes were observed in the testicles of rats at 1750 and 5000 ppm. Kidney and adrenal weights were increased in rats with regenerative changes observed in male rat kidneys.

10.2.3 TAME

10.2.3.1 The odor detection and recognition thresholds for TAME in air are 27 and 47 ppb, respectively. Odor and taste thresholds in water are 194 and 128 ppb, respectively.[1] Addition of 15 vol% TAME to gasoline reduces gasoline odor detection threshold from 578 ppb to 114 ppb.[2]

10.2.3.2 The absorption distribution metabolism and elimination of TAME has been examined in humans, rats and mice. Human volunteers were exposed to 15 or 50 ppm TAME for four hours.[19] Respiratory uptake was approximately 48% of the inhaled TAME with 34% of the absorbed amount exhaled unchanged. Urinary excretion of unchanged ether was every low. TAME was metabolized to tertiary amyl alcohol; however, the urinary excretion accounted for approximately 0.3 - 1.2% of the absorbed dose.

10.2.3.3 Male and female rats were exposed by inhalation to 500, 2000, or 4000 ppm TAME for four weeks.[36] Mortality (3 males, 4 females) and reduced body weight gain were observed in the high dose group. Neurotoxicology evaluations revealed sedative effects at the highest dose. The effects were judged to be transient as all animals recovered on the next day. Liver weights were increased; however, no treatment related pathology was noted at any exposure level.

10.2.3.4 Developmental toxicity was examined in pregnant rats and mice exposed by inhalation to 250, 1500 and 3500 ppm TAME.[35] The no adverse effect level for maternal toxicity was 250 ppm for both rats and mice with reduced weight gain in rats and mice at 1500 and 3500 ppm and mortality at 3500 ppm in mice. The no adverse effect levels for fetal toxicity in rats and mice were 1500 ppm and 250 ppm, respectively. In rats, fetal toxicity was limited to body weight reductions, most likely due to reduced maternal body weight. In mice, fetal toxicity was pronounced at the high dose, late fetal deaths, enlarged cerebral ventricles and cleft palate. Cleft palate was also observed at 1500 ppm. This finding may be related to the stress in mice due to the marked anesthesia induced by high level TAME exposure.

Aquatic toxicity of TAME has been examined in daphnids, *Daphnia magna*,[4] mysid shrimp, *Mysidopsis bahia*,[5] rainbow trout, *Oncorhynchus mykiss*,[6] and freshwater alga, *Selenatrum capricornutum*.[3] The no observable effect concentrations in theses organism were 83 ppm, < 5.0 ppm, 310 ppm, and 17 ppb, respectively.

10.2.4 DIPE

10.2.4.1 Subchronic and developmental toxicity of DIPE have been examined.[15] For examination of subchronic toxicity, male and female rats were exposed by inhalation to 480, 3300 or 7100 ppm DIPE for 90 days. Liver and kidney weights were increased at the mid and high dose in male rats and at the highest dose tested in female rats. Hyaline droplets were observed in male rat kidneys at the highest dose tested. No other morphological changes in kidney and liver were noted at 3300 ppm exposure. No effects were observed at the lowest level of exposure (480 ppm). To examine effects of DIPE on developing animals, pregnant female rats were exposed by inhalation to 430, 3095, or 6745 ppm DIPE on days 6-15 of gestation. A slight reduction in body weight and reduction in food consumption were observed in the maternal animals exposed to the highest concentration. In the offspring, the only effect was an increase in rudimentary (short) 14th ribs at the mid and high dose. The significance of this effect is unknown.

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APPENDIX A—GLOSSARY

AAMA: American Automobile Manufacturers Association

alcohol-gasoline blend: blend of alcohol and hydrocarbons or gasoline, where the primary component is alcohol

AMC: American Motors Corporation

Antiknock Index: See (R + M)/2 Octane

API: American Petroleum Institute

ARCO: Atlantic Richfield Company

ASTM: American Society for Testing and Materials

blending value: fuel property blending value of component = {(property of mixture) – [(1 – component volume fraction) x (property of fuel before component addition)]} ÷ (component volume fraction)

Btu: British thermal unit

Bu: bushel

CBD: central business district

CMC: changeable methanol concept

CO: carbon monoxide

CO_2: carbon dioxide

complex model: a set of equations developed by EPA that predict volatile organic compounds, oxides of nitrogen, and toxic air pollutant reductions from 1990 technology vehicles based on the following gasoline parameters: aromatics, benzene, olefins, sulfur, oxygenate type and content, percent evaporated at 200°F, percent evaporated at 300°F, and vapor pressure

conventional gasoline: gasoline which does not meet the requirements of reformulated gasoline

CRC: Coordinating Research Council

°: degree

°C: degrees Celsius

°F: degrees Fahrenheit

DDC: Detroit Diesel Corporation, formerly Detroit Diesel Allison Division of General Motors

DDGS: distillers dried grain and solubles

DIPE: diisopropyl ether

DOE: Department of Energy

DuPont: E. I. DuPont de Nemours and Company

EI: Evaporative Index

EPA: U. S. Environmental Protection Agency

ETBE: ethyl tertiary-butyl ether

FAA: Federal Aviation Administration

FFV: flexible-fuel vehicle

FID: flame ionization detector

FTP: Federal Test Procedure

g: gram

gal: gallon, U.S.

gasohol: a mixture of one part ethanol and nine parts by volume gasoline

gasoline-oxygenate blend: a blend consisting primarily of gasoline and a substantial amount (more than 0.35 mass % oxygen, or more than 0.15 mass % oxygen if methanol is the only oxygenate) of one or more oxygenates

GM, GMR: General Motors Corporation, General Motors Research Laboratory

gpm: grams per mile; usually refers to the FTP driving cycle

GTBA: gasoline grade tertiary-butyl alcohol

GTMV: gasoline tolerant methanol vehicle

HC: hydrocarbons

H_2O: water

Indolene: special gasoline formulation supplied for motor vehicle emissions certification testing

IPA: isopropyl alcohol

ITC: Interagency Testing Commission

kg: kilogram

km: kilometer

lb: pound

LPG: liquefied petroleum gas

M.A.N.: diesel engine manufacturer, formerly Maschinenfabrik Augsburg-Nuernberg Aktiengesellschaft

MBSD: thousand barrels per stream day, there are 330 stream days per calendar year

MBTU: thousand Btu

MIR or MOR: maximum incremental reactivity or maximum ozone reactivity. Weighting factors of individual compound species in emissions which indicate the atmospheric reactivity tendency. The values were developed for the CARB by the University of California at Riverside for atmospheric modeling purposes. For atmospheres with low ratios of VOC to NO_x, the MIR factors have been used. For areas with moderate ratios of VOC to NO_x, the total ozone formation is at maximum, the MOR factors have been used. Revisions of the factors may take place because of uncertainties of the effects on atmospheric chemistry of organic compounds emitted by vehicles. Units: grams O_3 /grams NMOG.

MM: million

MON, M: Motor octane number; see ASTM Method D 2700

MTBE: methyl tertiary-butyl ether

MVMA: Motor Vehicle Manufacturers Association (now AAMA)

M100: 100 percent methanol

M90: 90 percent by volume methanol in gasoline

M85: 85 percent by volume methanol in gasoline

NBR: acrylonitrile-butadiene rubber

n_D: refractive index using the sodium D line as light source; see ASTM Method D 1218

NIPER: National Institute for Petroleum and Energy Research

NMHC: non-methane hydrocarbons. Total hydrocarbon emissions reduced by methane as determined by gas chromatography (because of the low reactivity of methane). Conventional units: grams per mile

NMOC: non-methane organic compounds. Same as California Air Resources Board ROG definition.

NMOG: non-methane organic gases. Total unadjusted weight of all measurable organic species, excepting CH_4, including non-oxygenated hydrocarbons containing 12 or fewer carbon atoms, and all oxygenated hydrocarbons containing 5 or fewer carbon atoms of: alcohols (C_nH_m –OH), ethers (C_nH_m –O), and aldehydes (C_nH_m –CHO). Units: grams per mile

NO_x: oxides of nitrogen

N_2: nitrogen

OFA: Oxygenated Fuels Association

OFA: ozone forming potential. Application of MIR or MOR factors to speciated compounds of vehicle emissions. Units: grams ozone per mile

OH: hydroxyl group

OFP: ozone forming potential. Application of MIR or MOR factors to speciated compounds of vehicle emissions. Units: gram ozone per mile

OMHCE: organic material hydrocarbon equivalent. Intended to equalize reactivity comparisons of emissions from gasoline and methanol vehicles. Includes methane and all hydrocarbons and hydrocarbon-like components of methanol and formaldehyde (HCHO) in the emissions. Excludes the oxygen portion of the methanol and formaldehyde emissions by using multiplication factors to correct the measured values of methanol and formaldehyde for the weights of their oxygen contents. Requires measurements of methane, methanol, and formaldehyde in addition to hydrocarbons. Units: grams per mile

opt-in: a provision of the Clean Air Act Amendments of 1990 allowing ozone nonattainment areas other than those mandated to request EPA to require the use of reformulated gasoline

oxygenate: an oxygen-containing, ashless, organic compound, such as an alcohol or ether, that may be used as a fuel or fuel supplement

O_2: oxygen

percent evaporated: ASTM Method D 86

PFI: port fuel injection

PM or PM_{10}: particulate matter. The mass of emissions of solid or liquid particles 10 microns or smaller collected from combustion exhaust or windblown dust. Units (mobile source emissions): grams per mile

ppm: parts per million

psi: pounds per square inch

psig: pounds per square inch gauge

(R + M)/2 Octane: average of Research and Motor octane numbers, Antiknock Index

reformulated gasoline (RFG): a gasoline-oxygenate blend certified to meet the specifications and emissions reduction requirements established by the Clean Air Act Amendments of 1990, required for use in automotive vehicles in extreme and severe ozone nonattainment areas and those areas which opt to require reformulated gasoline

Road Octane: octane number of fuel determined using a car on the road by CRC F-28 procedure

ROG: reactive organic gases. Gross hydrocarbon mass excepting methane. Units: grams per mile

ROI: return on investment

RON, R: Research octane number; see ASTM Method D 2699

rpm: revolutions per minute

RVP or DVPE: Reid vapor pressure or dry vapor pressure equivalent; see ASTM Method D 4953, D 5190, and D 5191

SAE: Society of Automotive Engineers

simple model: a set of specifications and equations developed by EPA that predict volatile organic compound and toxic air pollutant reductions from reformulated gasoline for 1990 technology vehicles based on the following parameters: aromatics, benzene and oxygen contents, and vapor pressure

SR: specific reactivity. Ratio of OFP to NMOG. Units: grams per mile

TAC or TAP: toxic air contaminant or toxic air pollutants. Compounds that may pose a present or potential hazard to human health. Vehicle emissions of four compounds have been regulated: formaldehyde (HCHO), acetaldehyde, benzene, and 1,3-butadiene. Oxygenated hydrocarbons are not regarded as producers of benzene or 1,3-butadiene. Conventional units: milligrams per mile

TAME: tertiary-amyl methyl ether

TBA: tertiary-butyl alcohol

TBI: throttle body fuel injection

TOG: total organic gases. NMOG plus methane emissions. TOG emissions are used in air quality modeling studies rather than NMOG or OMHCE emissions so that both the impact and methane emission changes and total chemical transformations are considered. Units: grams per mile

TSCA: Toxic Substances Control Act

TVA: Tennessee Valley Authority

$T_{V/L=20}$: temperature at which the *V/L* is equal to 20

UBHC or Total HC: unburned hydrocarbons. Gross hydrocarbon mass component measured by the flame ionization detector. It underestimates organic emissions of methanol. Conventional units: grams per mile.

VFV: variable fuel vehicle

V/L: vapor-liquid ratio; see ASTM Method D 2533 modified for glycerin soluble fuel components or D 5188

volatile organic compounds (VOC): consists of non-methane, non-ethane hydrocarbons and oxygenated hydrocarbons emitted by automotive vehicles

WOT: wide open throttle

APPENDIX B—PROPERTIES OF OXYGENATES, GASOLINE, AND NO. 2 DIESEL FUEL

Table B-1—Properties of Oxygenates, Gasoline, and No. 2 Diesel Fuel

Property	Methanol	Ethanol	IPA	TBA	MTBE	TAME	Gasoline	No. 2 Diesel Fuel
Formula	CH_3OH	C_2H_5OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$	$(CH_3)_3COCH_3$	$(CH_3)_2(C_2H_5)COCH_3$	C_4 to C_{12}	C_8 to C_{25}
Molecular weight	32.04	46.07	60.09	74.12	88.15	102.18	100–105[a]	200 (approx.)
Composition, weight %								
Carbon	37.5	52.2	60.0	64.8	68.1	70.5	85–88[a]	84–87
Hydrogen	12.6	13.1	13.4	13.6	13.7	13.8	12–15[a]	13–16
Oxygen	49.9	34.7	26.6	21.6	18.2	15.7	0	0
Specific gravity, 60°F/60°F	0.796[b]	0.794[b]	0.789[b]	0.791[b]	0.744[n]	0.77[o]	0.72–0.78[a]	0.81–0.89[c]
Density, lb/gal @60°F	6.63[a]	6.61[a]	6.57[a]	6.59[a]	6.19[n]	6.41[o]	6.0–6.5[a]	6.7–7.4[c]
Boiling temperature, °F	149[b]	172[b]	180[b]	181[b]	131[b]	187[o]	80–437[a]	370–650[c]
Reid vapor pressure, psi	4.6[p]	2.3[p]	1.8[p]	1.8[p]	7.8[d]	1.5[o]	8–15[l]	<0.2
Octane no. (see note 1)								
Research octane no.	—	—	—	—	—	—	88–98[l]	—
Motor octane no.	—	—	—	—	—	—	80–88[l]	—
Cetane no. (see note 1)	—	—	—	—	—	—	—	40–55
Water solubility, @ 70°F								
Fuel in water, volume %	100[b]	100[b]	100[b]	100[b]	4.3[d]	—	Negligible	Negligible
Water in fuel, volume %	100[b]	100[b]	100[b]	100[b]	0.6[o]		Negligible	Negligible
Freezing point, °F	–143.5[b]	–173.2[b]	–127.3[b]	78.0[b]	–164[b]	—	–40[f]	–40–30[j]
Refractive index, n_D @ 68°F	1.3286[b]	1.3614[b]	1.3772[b]	1.3838[b]	1.3689[b]	—	1.4–1.5[g]	1.4–1.5[g]
Viscosity								
Centipoise @ 68°F	0.59[k]	1.19[k]	2.38[k]	4.2 @ 78°F[k]	0.35[k]	—	0.37–0.44[i,q]	2.6–4.1
Centipoise @ –4°F	1.15[k]	2.84[k]	9.41[k]	Solid[k]	0.60[k]	—	0.60–0.77[i,q]	9.7–17.6
Coefficient of expansion, @ 60°F, 1 atmosphere, per °F	0.00067[f,i]	0.00062[f,i]	—	—	0.00078[d]	—	0.00067[i]	9.7–17.6
Electrical conductivity, mhos/cm	4.4×10^{-7} [h]	1.35×10^{-9} [h]	—	—	—	—	1×10^{-14} [h]	1×10^{-12}
Flash point, closed cup, °F	52[p]	55[p]	53[p]	52[p]	–14[d]	—	–45[a]	165[c]
Autoignition temperature, °F	867[a]	793[a]	750[a]	892[a]	815[d]	—	495[a]	600 (approx.)
Flammability limits, volume %								
Lower	7.3[p]	4.3[p]	2.0[p]	2.4[p]	1.6[d,f]	—	1.4[a]	1.0
Higher	36.0[p]	19.0[p]	12.0[p]	8.0[p]	8.4[d,f]	—	7.6[a]	6.0
Latent heat of vaporization								
Btu/gal @ 60°F	3340[a]	2378[a]	2100[b]	1700[b]	863[f]	—	900 (approx.)[a]	710 (approx.)
Btu/lb @ 60°F	506[a]	396[a]	320[b]	258[b]	138[f]	—	150 (approx.)	100 (approx.)

Table B-1—Properties of Oxygenates, Gasoline, and No. 2 Diesel Fuel (Continued)

Property	Methanol	Ethanol	IPA	TBA	MTBE	TAME	Gasoline	No. 2 Diesel Fuel
Btu/lb air for stoichiometric mixture @ 60°F	78.4[a]	44.0[a]	31.1[b]	23.2[b]	11.8	—	10 (approx.)	8 (approx.)
Heating value (see note 2)								
Higher (liquid fuel-liquid water) Btu/lb	9750[a]	12,800[a]	14,500[g]	15,500[g]	18,290[g]	—	18,800–20,400	19,200–20,000
Lower (liquid fuel-water vapor) Btu/lb	8570[a]	11,500[a]	13,300[g]	14,280[g]	15,100[g]	15,690[o]	18,000–19,000	18,000–19,000
Lower (liquid fuel-water vapor) Btu/gal @ 60@F	56,800[i]	76,000[i]	87,400[i]	94,100[i]	93,500[i]	100,600[i]	109,000–119,000	126,000–130,800
Gaseous fuel-water vapor Btu/lb @ 60°F	9080[a]	11,900[a]	—	—	—	—	19,000–19,300	—
Heating value, stoichiometric mixture								
Mixture in vapor state, Btu/cubic foot @ 68°F	92.5[a]	92.9[a]	—	—	—	—	95.2[a]	96.9[r,s]
Fuel in liquid state, Btu/lb of air	1330[a]	1280[a]	—	—	—	—	1290[a]	—
Specific heat, Btu/lb –°F	0.60[k]	0.57[k]	0.61[k]	0.72[k]	0.50[k]	—	0.48[f]	0.43
Stoichiometric air/fuel, weight	6.45[i]	9.00[i]	10.3[i]	11.1[i]	11.7[i]	12.1[i]	14.7[i]	14.7
Volume % fuel in vaporized stoichiometric mixture	12.3[a]	6.5[a]	—	—	2.7[f]	—	2.0[a]	—
Ratio moles product/moles charge	1.06[i]	1.07[i]	1.07[i]	1.07[i]	1.07[i]	1.07[i]	1.05[i,m]	1.06[i,r]
Ratio moles product/moles $O_2 + N_2$	1.21[i]	1.12[i]	1.10[i]	1.10[i]	1.10[i]	1.09[i]	1.08[i,m]	1.07[i,r]

Notes:
1. Laboratory engine Research and Motor octane rating procedures are not suitable for use with neat oxygenates. Octane values obtained by these methods are not useful in determining knock-limited compression ratios for vehicles operating on neat oxygenates and do not represent octane performance of oxygenates when blended with hydrocarbons. Similar problems exist for cetane rating procedures.
2. The higher heating value is cited for completeness only. Since no vehicles in use, or currently being developed for future use, have powerplants capable of condensing the moisture of combustion, the lower heating value should be used for practical comparisons between fuels.

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[c] "Diesel Fuel Oils, 1987," *Petroleum Product Surveys*, National Institute for Petroleum and Energy Research, October 1987.
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[p] API Technical Data Book—*Petroleum Refining*, Volume I, Chapter 1, Revised Chapter 1 to First, Second, Third, and Fourth Editions, 1988.
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