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Fuel Specifications: What They Are, Why We Have Them, and How They Are Used

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Foreword

THIS PUBLICATION, *Fuels Specifications: What They Are, Why We Have Them, and How They Are Used*, was sponsored by ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants. The co-editors are Salvatore J. Rand, consultant, North Fort Myers, Florida, and Allen W. Verstuyft, Al Verstuyft Consulting, LLC, Napa, California.

Acknowledgments

The publication of this manual was accomplished through the combined efforts of many individuals. First and foremost, we would like to convey our sincerest appreciation to all of them— particularly the thirteen authors, who are all experts in their particular fields and who bring a broad spectrum of interests, experience, and knowledge of fuels specifications to this manual. They have devoted considerable time, energy, and resources to support this endeavor. We also appreciate the assistance of the ASTM publication staff—particularly Kathy Dernoga, Monica Siperko, Sara Welliver, and Rebecca Edwards—who have given us much behind-the-scenes guidance and assistance from the outset of this venture. In addition, we are grateful to the 20 experts who have reviewed the various chapters and who, through their perusal of the chapters, made suggestions that permitted good manuscripts to be made better. Finally, we would like to extend our utmost appreciation to the industrial and governmental employers of all those involved in this publication. They, ultimately, make it possible for us to produce manuals such as this for the benefit of those who use petroleum standards worldwide.

To Agnes and Judy

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Chapter 1 | Introduction

Salvatore J. Rand¹ and Allen W. Verstuyft²

ASTM International Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants is responsible for standards for petroleum specifications and test methods [1]. The D02 committee and its various subcommittees have authored more than 800 standards and have developed specifications that provide for fuels with improved performance and environmental quality. A large number of parties and groups are interested in or affected by the specifications. These parties include regulators, producers, and users including:

- Federal and state regulators
- Producers, such as individual refiners
- Trade associations, such as the American Petroleum Institute, the American Fuels and Petroleum Manufacturers, and the Western States Petroleum Association
- Petroleum marketing organizations
- Additive suppliers
- Pipeline companies
- Vehicle and engine manufacturers using gasoline, diesel, aviation, and marine fuels
- · General interest groups, consumer groups, and consultants

The focus of this manual is ASTM fuel specifications—the intent of the specification and the effect of fuel properties on performance and use. Many other countries have similar organizations that develop specifications—such as the Canadian General Standards Board (CGSB) with CGSB 3.5-2011 for gasoline, and CGSB 3.511-2011 and CGSB 3.512-2013 for ethanol blends, including subsequent amendments; and the European Committee for Standardization (CEN), the specifications of which are translated by country, including British Adopted European Standard BS EN 228 (UK, NF EN 228 [French equivalent of BS EN 228]) and others. These non-ASTM standards and similar international standards for gasoline, diesel, aviation fuel, and other petroleum products will not be discussed in this publication, except to make note of the intent.

Each product has a history of development for its intended use. Liquid hydrocarbons offer the best combination of energy content, availability, and price. The internal combustion engine of Nicolaus Otto that was built in 1876 used a fuel that predates the primary distillation product of crude oil, which was kerosine or coal oil for lamps. Electricity diminished the need for lamp oil, but Ford's Model T automobile dramatically increased the demand for gasoline. Early aircraft engines were similar to those of automobiles and used the same fuels. By the early 1940s, turbine engines provided more power and required special aviation turbine fuels.

The expected performance of a fuel is achieved when the characteristics of the fuel match the fuel requirements for engines. Producers and engine manufacturers are mutually dependent partners. This relationship drove the fuels specifications until the later part of the twentieth century, when environmental requirements became a consideration in fuel characteristics for gasoline and diesel fuels and their respective engine designs. Producers and users of a product identify and control the properties necessary for satisfactory and reliable performance, particularly in aviation fuels. Diesel engines are used worldwide for transportation, manufacturing, power generation, construction, and farming. These engines vary in size and use. New environmental regulations have impacted the fuel, its distribution, and the respective engines in which the fuel is used.

Specifications represent the needs of the producer, user, and regulator for performance characteristics and environmentally friendly fuels. Specifications are constantly being updated to improve performance and to reflect changing environmental regulations. Committee D02 may have as many as 100 new standards registered as work items under development and additional standards registered for updates or revision. The information in this manual may be superseded by new regulations or advances in fuels or engine technology as new developments are introduced.

References

 Earls, A., "Taking Fossil Fuels to the Next Level," ASTM Standardization News, September/October 2014, pp. 30–34.

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Chapter 2 | Specifications—What They Are, Why We Have Them, and How They Are Used

Randy F. Jennings,¹ N. David Smith,² Ronald G. Hayes,³ and Stephen D. Benjamin²

2.1 Introduction

Manufacturers, in any industry, have a desire for specifications—in part, to produce a consistent product. Other considerations may include safety, controlling costs, and the efficiency of the manufacturing process. Some of their customers, especially other businesses, may require certain specifications be met for the products they are purchasing. But what about specifications at the consumer level? How can a consumer, purchasing fuel for his/her vehicle for example, be confident they are getting a "good" product? This is where the role of the regulator comes in, serving as the bridge between the manufacturer and the consumer with the purpose of helping to ensure the "quality" of the product being sold (Fig. 2.1). In order to accomplish this task, the regulators must not only use the same specifications as the manufacturers but must adopt them in some manner to make them a legal requirement that they can enforce.

Any document reviewing how specifications are used in trade must first establish the technical definition for the term "specification" as well as for allied terms. The *Regulations Governing ASTM Technical Committees* (also known as "the Green Book") defines specification, standard, guide, practice, and test method as follows and provides discussion points [1].

- *Specification*—An explicit set of requirements to be satisfied by a material, product, system, or service.
- *Discussion*—Examples of specifications include, but are not limited to requirements for: physical, mechanical, or chemical properties, and safety, quality, or performance criteria. A specification identifies the test methods for determining whether each of the requirements is satisfied.
- *Standard*—As used in ASTM, a document that has been developed and established within the consensus principles of the Society and that meets the approval requirements of ASTM procedures and regulations.
- Discussion—The term "standard" serves in ASTM as an adjective in the title of documents, such as test methods or specifications, to connote specified consensus and approval. The various types of standard documents are based on the needs and usages as prescribed by the technical committees of the Society.

- Guide—An organized collection of information or series of options that does not recommend a specific course of action.
- *Discussion*—A guide increases the awareness of information and approaches in a given subject area.
- *Practice*—A set of instructions for performing one or more specific operations that does not produce a test result.
- Discussion—Examples of practices include, but are not limited to: application, assessment, cleaning, collection, decontamination, inspection, installation, preparation, sampling, screening, and training (Fig. 2.2).
- *Test method*—A definitive procedure that produces a test result.
- Discussion—Examples of test methods include, but are not limited to: identification, measurement, and evaluation of one or more qualities, characteristics, or properties.

Therefore, it can be extrapolated from the definitions for "specification" and "standard" that a "standard specification" is a document that contains an explicit set of requirements to satisfy a material, product, system, or service that has been developed and established within the consensus principles of ASTM. Defining and understanding the significance of both terms is important because neither can stand alone and produce the end product that is needed by all stakeholders in the system.

Subsequent chapters in this document will more fully address individual product "specifications." The purpose of this chapter is to provide information on how regulatory officials use specifications and how they become legal requirements.

A broad range of stakeholders rely upon standard specifications developed by ASTM International, each with the common desire to have a fit-for-purpose material in the marketplace that will ultimately be conveyed to the end user (**Fig. 2.3**). Producers need a fairly developed specification that provides a level playing field and uniformity in the final product. Users, such as engine manufacturers, also rely heavily on a specification that will enable them to build equipment that can be satisfied by the products being produced. Finally, the general interest/consumer sector has to balance the viewpoints of both the producers and the users, ideally grounding positions based upon the most current data available relevant to the issues being considered.

ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants appropriately classifies government

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regulatory officials as general interest members. Most state agencies charged with enforcing fuel quality laws and rules directly adopt ASTM standard specifications by reference. The state agencies may adopt a standard specification either in full or in part, as long as the requirements are clearly written and understood by the regulated community. Federal agencies may also reference ASTM standard specifications in much the same manner as states doeither in full or in part. Both federal and state agencies can also adopt requirements that exceed or are more stringent than the ASTM standard specification if they can demonstrate the need. A rigorous process is required for government agencies to adopt an ASTM standard specification in law or rule form. In the United States, laws must be passed by both legislative houses (at the federal or state level, as applicable) and must withstand a potential veto by either the president or governor. Rules are also created by government agencies via a formal process that typically requires an initial filing of the proposed rules, adequate notice to the affected stakeholders, accepting public comment, responding to each comment, and finally providing notice of the final rule and effective date.

Although most states have some uniqueness in how their rules are written, the National Conference on Weights and Measures (NCWM) has developed a Uniform Engine Fuels and Automotive Lubricants Regulation that is published in the National Institute of Standards and Technology (NIST) Handbook 130. At the time of this writing, there are seven states that annually adopt the most recent version of the NCWM Uniform Engine Fuels and Automotive Lubricants Regulation. Many more states base their rules upon either the most recent version of the regulation or on an earlier one. The Uniform Engine Fuels and Automotive Lubricants Regulation references the most recent edition of ASTM standard specifications as the requirements for the various products covered. (The NIST Handbook 130 can be viewed at http://www.nist. gov/pml/wmd/pubs/handbooks.cfm.) Regardless of how a state or federal agency references an ASTM standard specification, the desire is to always reference the most recent edition. That can get complicated depending on individual state laws and regulatory procedures that may require state and federal agencies to reference a particular version or year whenever a document is adopted by reference.

The benefits of having standard specifications for regulatory agencies to adopt as rule are commonsensical. It simply is not feasible from a budgetary standpoint for an individual state agency to develop specifications that cover the entire spectrum of products that are to be regulated, nor would it be prudent for the marketplace to have standard specifications that vary vastly from one state to another. Additionally, developing specifications without input from manufacturers or users may result in products that are more costly, less effective, or both. As evidence of the value that standard specifications have to government agencies, in 1996, the U.S. Congress passed the National Technology Transfer and Advancement Act. This law requires federal agencies to increase their reliance upon-and participation in-the voluntary consensus standards systems, recognizing those specifications developed following the American National Standards Institute (ANSI) consensus standards process (to which ASTM International

FIG. 2.2 Inspector collecting a running sample per ASTM Standard Practice D4057.



FIG. 2.3 Retail facilities are a pivotal point of sample collection for many regulatory agencies.



adheres). This process results in specifications that are efficiently developed that, at the same time, meet the needs of the various stakeholders [2]. For fuel products, having standard specifications is particularly important because the U.S. distribution system is primarily based upon fungible products. Any refiner can produce a base fuel that can be commingled with another producer and distributed along a pipeline or other common carrier system. This allows branded products to be made unique at the point of loading transport tankers by the addition of proprietary additive packages.

Regulatory officials virtually will always reference a standard specification, such as ASTM **D4814**, *Standard Specification for Automotive Spark-Ignition Engine Fuel*, when addressing a product requirement. In the course of conducting their operations they rely on "guides," "practices," and "test methods" to ensure they are following the most correct and up-to-date methods for carrying out their duties. Where regulatory officials apply the requirements of a "specification" is critical and can vary depending on the circumstances. It is typical for regulatory officials to apply the requirements at the place of delivery to the end user. That may be at the fuel dispenser, bulk fuel tank, or at the domestic propane tank. Of course, the requirements of a specification may be applied anywhere along the supply chain, depending on the circumstances.

As noted earlier, most states do adopt ASTM standard specifications to ensure quality products are conveyed for consumption within their borders. However, the scope of the products regulated and routine tests performed may vary from state to state. Even though program budgets and priorities may not be the same in each state, there are certain core products and tests that almost every state will routinely regulate. The products and the properties that are most routinely monitored are as follows:

Gasoline is defined by ASTM D4814, Standard Specification for • Automotive Spark-Ignition Engine Fuel. One of the most important property categories of gasoline is fuel volatility. Fuel volatility is controlled by distillation, vapor pressure, and vapor lock protection by a vapor-liquid ratio of 20 (T V/L = 20). Oxygenate content is also routinely verified. One of the most widely tested gasoline quality parameters that, as of this writing, is not directly required under ASTM D4814 is the antiknock index (AKI, or octane rating). In the United States, the Federal Trade Commission requires that the automotive fuel rating for gasoline be certified throughout the distribution system. The automotive fuel rating for gasoline is the octane rating. Because every vehicle has a minimum octane need for optimum performance and fuel is marketed by various grades based primarily upon the octane rating, verifying that octane numbers are posted accurately is a core test for most states (Fig. 2.4). Finally, a basic requirement of gasoline and gasolineoxygenate blends is that the finished fuel must be clear and bright and free of undissolved water, sediment, and suspended matter, as stipulated in the workmanship section of the specification (Fig. 2.5). Gasoline that does not contain ethanol has very little tolerance to hold dissolved water-about 150 ppm at 70°F [3]. Gasoline-ethanol blends have a water tolerance that correlates to the temperature of the fuel and the amount of water that can be dissolved at fuel temperature, as represented in the chart shown in Fig. 2.6 [4].

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- Diesel fuel is defined by ASTM D975, Standard Specification for Diesel Fuel Oils. From the aspect of safety, flash point is of primary concern to the regulatory community. Although conductivity requirements in ASTM D975 have provided an additional safe handling characteristic to diesel fuel, flash point remains perhaps the most commonly regulated property of diesel fuel. Another basic parameter that is monitored is water and sediment—a property that can decline after the fuel leaves the refinery or terminal unless good housekeeping practices are
- FIG. 2.4 Chemist determining one of two engine tests required to verify compliance with octane posting antiknock index (AKI) requirement for gasoline.



FIG. 2.5 Gasoline sample contaminated with water.



FIG. 2.6 Water volume versus fuel temperature graph, E10 gasoline.

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utilized by downstream fuel handlers. Distillation is also a routine test that, as with other products, provides a very good visual representation of the boiling range of the compounds in a particular batch of diesel. The Cetane Index is generally verified because it only requires a calculation utilizing the distillation values determined. Although the Cetane Index is not a direct surrogate of cetane number, an index well above the 40 cetane minimum usually provides the regulatory official with some degree of confidence that the cetane number will meet the limit. Cetane number is tested in a number of regulatory labs, but it is not as routine as the Cetane Index. Sulfur is also monitored by various governmental agencies. Other properties that are often verified are biodiesel content, lubricity, and cold flow properties (cloud point, low temperature filtration test).

- Kerosine is defined by ASTM **D3699**, *Standard Specification for Kerosine*. Due to the critical nature of kerosine's use as a heating fuel—often for indoor, unvented, portable kerosine heaters—kerosine is generally regulated by the authorities having jurisdiction. Flash point is undisputedly the most commonly tested property verified on kerosine samples, followed closely by sulfur determinations. Because kerosine is susceptible to long-term storage degradation, Saybolt color is also closely monitored for compliance with the specification limits.
- Fuel oil is defined by ASTM **D396**, *Standard Specification for Fuel Oils*. Jurisdictions regulating fuel oils generally perform a scope of tests that are consistent with those performed on diesel fuel and kerosine: flash point, water and sediment, distillation, and sulfur.
- Denatured fuel ethanol is defined by ASTM D4806, Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel. Denatured fuel ethanol, as a blending component for gasoline, has flourished in the United States since implementation of the Energy Independence and Security Act of 2007. Hence, many regulatory jurisdictions are paying closer attention to the specification for ethanol and are performing tests to ensure that the

FIG. 2.7 Samples prepared for shipping to laboratory.



fuel meets those minimum requirements. Verification of ethanol and methanol content, solvent-washed gum, water, inorganic chlorides, and sulfates are routinely monitored by those testing denatured fuel ethanol.

- Ethanol fuel blends are defined by ASTM **D5798**, *Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines*. One of the most important specification limits for ethanol fuel blends is vapor pressure. The regional and seasonal requirements for vapor pressure have been established not only for capping a maximum vapor pressure but also for providing for a minimum vapor pressure to ensure cold start performance. Other common tests parallel those performed on denatured fuel ethanol: ethanol, methanol, water, acidity, and inorganic chloride content.
- Liquefied petroleum gas is defined by ASTM D1835, *Standard Specification for Liquefied Petroleum (LP) Gases.* Although most state laws and rules require LP to meet the standard, the volume of testing conducted is typically much less than for the liquid fuels. Collecting samples in pressurized vessels and shipping the containers requires extra attention to details. This, coupled with the fact that the LP compliance rate at retail is much higher than with most other liquid transportation fuels, leads most regulatory agencies to place less emphasis on LP testing. Nonetheless, when a regulatory agency samples LP, it is likely to confirm quality by performing a compositional analysis (ASTM D2163) of vapor pressure, sulfur, and moisture as a routine analysis.

In the event regulatory officials encounter a product that does not comply with their requirements, there are certain actions that may be taken. The following is the typical list of regulatory actions. Individual jurisdictions may be authorized to exercise actions not covered by this list.

• Stop sale order—Just as the name implies, a stop sale order instructs the seller to cease sales until the regulatory agency rescinds the stop sale order. Typically, this is the first regulatory action taken by a jurisdiction. The order may be directed at a single dispenser, or it may cover all products being sold at a particular location. Once the stop sale order has been issued, a number of other regulatory actions may be taken that are defined as follows.

- Civil penalty—A civil penalty is a financial penalty imposed by a jurisdiction as restitution for violation of its laws or regulations. The amount of the civil penalty is normally based upon the specific law that authorizes the agency to issue civil penalties. Penalties are usually issued anywhere between \$100 and \$10,000 per violation.
- Criminal citation—The ability to issue a criminal citation for a violation will be provided in a jurisdiction's enabling statutes. In some cases, the jurisdiction may need to apply to the local district attorney to issue the criminal citation because it will be the district attorney's job to prosecute the violation. The issuance of a criminal citation usually is rare and is reserved for unusual circumstances.
- Cease and desist order—Unlike stop sale orders, which tend to address an immediate problem that may be of short duration, a cease and desist order usually is directed to persistent, ongoing problems that are not being resolved. A jurisdiction will likely apply to a judge to issue the cease and desist order.

Once a stop sale order or other regulatory action is taken, the regulatory official often will supervise the disposition of the condemned product. The affected location may have several corrective action options, with the understanding that the product must meet specifications before the stop sale order is removed. The options a regulator can provide are dependent on the product and nature of the condemnation but, in general, will include one of the following:

- Product downgrade—This action may be taken when a product meets all specifications but the one that distinguishes it from a lesser grade. The best example is a premium engine fuel that fails to meet the "premium" octane designation. In some cases, the regulatory agency may allow the product to be sold as a "regular" grade. Usually, this means pumping the product into the lower grade tank and then having new fuel delivered to the previously condemned tank. However, there may be situations where the fuel dispenser is simply relabeled to reflect the downgraded product being sold. A downgrade designation may not eliminate further regulatory action.
- Remediation of product by blending with additional higher quality product may be allowed contingent on the final mixture

conforming to specifications. It is possible this cannot be accomplished entirely at the location because the tank may not have the capacity to handle the volume necessary to blend the product back into specification. In those cases, a portion of the product may have to be taken to other locations for blending at those sites. 7

- In disposition of substandard fuel, the regulatory agency will likely require confirmation of the transfer of the product to ensure fuel is properly disposed of and is not sold to the ultimate consumer in its substandard state.
- Some violations may be a result of missing labels or misplacement of labels at retail. Transfer documents may also be missing the product identity, grade, or added component. Once the missing information is provided, the violation is usually resolved.

In summary, the availability of high-quality consensusderived standards for use by all stakeholders—producers, sellers, purchasers, consumers, and regulatory agencies—is indispensably important to a fair marketplace. Referencing consensus standards in laws and regulations preserves a fair marketplace while permitting production and distribution goals to be met as efficiently as possible. ASTM International, the world's leader in producing high-quality consensus standards, provides an accessible platform to all that choose to participate in the development of these standards—a process that ensures that every comment received on a standards ballot is reviewed and addressed by the committee having jurisdiction. This type of transparency is ideally suited for every sector of business, particularly the regulatory community.

References

- ASTM International Regulations Governing ASTM Technical Committees, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- "The National Technology Transfer and Advancement Act," Government Printing Office, Washington, DC, 1996, www.gpo. gov/fdsys/pkg/PLAW-104publ113/pdf/PLAW-104publ113.pdf
- [3] Chevron, "Motor Gasolines Technical Review," Chevron Products Co., San Ramon, CA 2009, www.chevron.com/documents/pdf/ MotorGasTechReview.pdf
- [4] David Korotney to Susan Willis, May 26, 1995, memorandum,
 "Water Phase Separation in Oxygenated Gasoline," http://epa.gov/OMS/regs/fuels/rfg/waterphs.pdf

Chapter 3 | Discussion on Uses of the Specification for Liquefied Petroleum Gas (ASTM **D1835**)

Fred Van Orsdol¹

3.1 Introduction

Liquefied petroleum gases (LPGs) and natural gas liquids (NGLs) are typically derived either by extracting most of the hydrocarbon molecules heavier than methane from a natural gas or condensate stream or by separating or distilling (or both) light ends out of a barrel of crude oil. The most common LPG and NGL products include unfractionated raw mix natural gas liquids (typically ethane and heavier or propane and heavier major componentssometimes called Y-grade product), purity ethane, various mixes of ethane and propane, various grades of propane, various propane/butane mixes (with butane concentrations tending to be higher in warmer climates if the product is to be used for heating fuel), iso- and normal butane, iso- and normal pentane, and natural gasoline. Propane products may include HD-5 motor fuel/ special-duty grade propane, commercial propane, refrigerant grade (high purity) propane, propellant grade (high purity) propane, and other variations. In some locations, due to local or regional conditions, propylene may be a significant component in some propane products (greater than the 5 liquid volume percent maximum generally allowed by specifications). Propylene is not a naturally occurring component in natural gas or crude oil and is typically found only in LPG streams from refinery processes. It is important to understand that high propylene contents in propane fuel (greater than 5 liquid volume percent) may produce deposits in the fuel vaporization systems of an engine burning the fuel or result in soot production (or both) if the fuel is burned in industrial or residential heating systems.

One significant difference in LPG products derived from natural gas relative to LPG products derived from crude oil is the amount of ethane available for ethane and propane products. LPG derived from crude oil typically does not have sufficient ethane in it for refineries to produce ethane or ethane/propane mix products from the distillation process. The ethane level is usually so low in these refinery-derived products that the fractionated propane product will have only very low concentrations of ethane, and the vapor pressure of the propane product will tend to be significantly lower than propane from a natural gas processing facility that is often capable of extracting most of the ethane in a natural gas stream.

Natural gas streams suitable for extraction processes generally have significant concentrations of ethane, and many natural gas processing facilities (especially in North America) are designed to recover most of the ethane and essentially 100 % of the propane and heavier hydrocarbons in the gas stream. When HD-5 and commercial propane products are fractionated, the fractionation process is generally configured to leave as much ethane in the product as possible, without exceeding the vapor pressure limit typically specified for propane, which is 1434 kilopascals (208 PSIG) at 37.8°C (100°F). By leaving the maximum amount of ethane in the propane product, the facility essentially can sell ethane at propane prices. In order to not exceed the vapor pressure limits, maximum ethane levels will be less than 7 liquid volume percent. Because the Btu content of ethane is considerably lower than an equal volume of propane, the energy content of propane product derived from natural gas processing facilities tends to be lower than the energy content of propane product from refineries.

Note that during those times when liquid ethane product prices drop to the point that ethane is worth more in a gas plant's residue gas than it is in a liquid phase product stream, gas processing facilities may enter an "ethane rejection" operating mode and intentionally stop recovering ethane in the liquid phase. During ethane rejection, the ethane content in any propane product produced will tend to be lower than during periods of deep ethane extraction.

Each of the fractionated products should have well-defined specifications to ensure the product is suitable for its intended use—be it a motor fuel, heating fuel, or feedstock. Two documents establish a foundation for LPG and NGL product specifications. ASTM **D1835**, *Standard Specification for Liquefied Petroleum (LP) Gases* [1], lists some of the common specifications for these products. The Gas Processors Association also publishes GPA Standard 2140, *Liquefied Petroleum Gas Specifications and Test Methods* [2]. The standards are very similar and reflect many years of coordinated effort.

Some of the tests referred to in ASTM and GPA standards are intended to determine whether or not the composition of a product is within specification. Other test methods determine the level of contamination in a product and determine whether the product purity is sufficient. Some of the methods produce a simple "pass" or

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"fail" result. Others produce a test value or result, generally with an associated range of uncertainty that may be compared to the product specification relating to that method, to determine whether a product meets specification requirements.

Many of the test methods and specification limits shown for LPGs are also used as a basis for NGL products. For example, a raw mix natural gas liquid stream may have to meet many of the specifications for LPG products, using the same or similar test methods shown in the ASTM and GPA standards for LPGs. The user of these test methods must carefully review each method and specification limit to ensure it is appropriate for the product being considered.

Common contaminants in LPG and NGL streams include:

- Hydrogen sulfide (H₂S) may be naturally occurring in gas or liquid hydrocarbon streams being processed or may result from process contamination. In the presence of free water, it is very corrosive to soft metals and carbon steel. For this reason, H₂S in LPG products must be limited to very low levels, typically not to exceed 1-4 parts per million on a weight basis. It may also contribute to stress-corrosion cracking or hydrogen embrittlement, particularly when in contact with high-tensile-strength steels. H₂S is a very toxic material, and exposures as low as 300 to 500 parts per million in air may be lethal. If exposure to H₂S is anticipated, adequate training, proper safety systems and equipment, and a full understanding of the chemical and physical properties of H₂S are essential. Careful review of an appropriate material safety data sheet is recommended. (Note: Combustion byproducts for any fuel containing any sulfur species will tend to be corrosive when combined with atmospheric air and need to be limited to acceptable concentrations.)
- Carbonyl sulfide (COS) usually is introduced into LPG products via molecular sieve dehydration systems on the inlet of cryogenic gas processing plants or similar facilities. When the molecular sieve beds are regenerated, a portion or all of any H₂S not removed by upstream treating systems may be trapped by the molecular sieve beds during the drying cycle. During the hightemperature regeneration cycle for the beds, which is intended to drive trapped water off the beds, the H₂S may be converted into COS and driven out of the beds in the regeneration gas stream. Due to the volatility of COS, it tends to end up in the propane product once fractionation is complete. Note that COS is not corrosive but typically will convert back to H₂S, which is corrosive, over time. This is why it is critical for designers to carefully consider the stream composition when determining how to handle regeneration gas streams, and it may explain why a product that tested as noncorrosive at the source facility may prove to be corrosive in downstream pipelines and distribution systems.
- Other sulfur-containing species that may be naturally occurring or intentionally injected in the stream include elemental sulfur, disulfides, and mercaptans (including ethyl mercaptan, tertiary butyl mercaptan, thiophane, and other odorants).
- Excess methane in raw mix, purity ethane, ethane-propane mix or propane products is usually present due to poor product fractionation and will tend to cause product vapor pressures to be too high.

- Excess ethane in LPG products (propanes, butanes, propenes/ propylenes, and mixtures of these products) will cause the products to have vapor pressures exceeding typical specification limits.
- Carbon dioxide (CO₂) typically is naturally occurring in gas and liquid hydrocarbon streams and, when free water is present, it will be very corrosive to soft metals and carbon steel.
- Ammonia contamination often is due to cross-contamination when transports, railcars, storage vessels, and other equipment are used to handle ammonia or propane, depending on the season and demand.
- Methanol is often intentionally added to natural gas and natural gas liquid streams to prevent freeze-ups when free water is present, but it can be detrimental during product testing (by interfering with the freeze valve test, for example) and product use. It can also poison catalyst beds in some downstream processes. When excess levels of methanol are present in a product, it may extract plasticizers from rubber hoses in the distribution system and produce operating problems in equipment using the fuel.
- Plasticizers in concentrations sufficient to cause operating problems in propane fuel systems typically result from using excessive levels of methanol in the propane. The methanol can extract plasticizers from rubber hoses in the distribution system, which then fouls vaporizers, throttle bodies, carburetors, and other fuel inlet systems on engines using the propane fuel.
- Lubricants/greases can be from many sources but most often result from over-lubricated valves, compressor lube oil carry-over, or pump lubricant carryover.
- Chemical inhibitors usually result from upstream treating processes and may include many different types of chemicals.
- Glycol contamination is usually carryover from upstream glycol dehydration systems.
- Amine contamination is usually carryover from upstream amine treating systems.
- Molecular sieve particles and dust usually are carryover from molecular sieve dehydration systems as the molecular sieve beads are fractured or pulverized over time by the stresses induced from severe pressure or temperature changes (or both) inherent to the dehydration/regeneration process.
- Pipeline rouge, rust, and scale consist of fine solid particles that may foul downstream regulators and other equipment.
- Fluoride contamination in LPG is usually in the form of hydrofluoric (HF) acid contamination from refinery HF alkylation processes. It is a very dangerous material and must be prevented from entering any LPG distribution system.
- Mercury is not a common contaminant in most LPG distribution systems, but it may be naturally occurring in some natural gas and crude oil streams. It is a hazardous material, even in low concentrations.
- Other solids, regardless of the source, must not be present in sufficient quantities to interfere with the processes and equipment where the product is eventually utilized.

• Other deleterious substances/contaminants include anything else that may cause a product to not meet quality requirements.

3.2 ASTM Standards for LPG Products

ASTM **D1835**, *Standard Specification for Liquefied Petroleum (LP) Gases* [1], is a basic document for defining LPG products and the test methods for determining whether or not the products meet their specification requirements.

The scope of ASTM **D1835** [1] covers those products commonly referred to as liquefied petroleum gases, consisting of propane, propene (propylene), butane, and mixtures of these materials (commercial propane, commercial butane, commercial propane-butane mixes, and special-duty propane).

ASTM **D1835** [1] lists other ASTM standard test methods that determine whether or not each of the products defined by ASTM **D1835** [1] is within the specification limits set in ASTM **D1835** [1]. These include the following test methods.

3.2.1 ASTM D1265, PRACTICE FOR SAMPLING LIQUEFIED PETROLEUM (LP) GASES, MANUAL METHOD

This practice [**3**] offers guidelines for collecting a representative liquid phase sample of the LPG product in a single cavity sample container and then properly taking a 20 % outage from the liquid filled container to ensure the cylinder will not be overpressured by a temperature increase during subsequent handling or transportation.

Providing a 20 % outage after the liquid sample is collected means providing a vapor space in the container equal to 20 % of the internal volume of the container. A 20 % outage is usually sufficient to protect a system from the effects of thermal expansion should the temperature of the product increase during transportation or handling, but consideration should always be given to evaluating the anticipated extremes of ambient, process, or test conditions to determine whether a 20 % outage is sufficient to prevent the cylinder or container from becoming liquid filled again after the outage has been taken. If the temperature increase and resulting thermal expansion of the product is sufficient, it may cause the remaining liquid phase product to expand and liquid fill the container even after a 20 % outage has been taken. If the cylinder becomes liquid filled and the temperature continues to increase, an overpressure condition will occur and an unsafe condition will result if an uncontrolled release of product occurs.

If the sample is not representative of the stream or quantity of product being evaluated, the physical properties and component quantities of the product will be incorrect.

3.2.2 ASTM D1267, TEST METHOD FOR GAGE VAPOR PRESSURE OF LIQUEFIED PETROLEUM (LP) GASES (LP-GAS METHOD)

This test [4] describes the equipment and procedure necessary to determine the vapor pressure of an LPG product at 37.8°C (100°F).

The final vapor pressure reading is in kilopascals or in pounds per square inch gauge (PSIG)—meaning pressure above atmospheric pressure.

It is critical that the test procedure be followed exactly and that repetitive pressure readings be taken after heating and shaking cycles until two readings within the specified tolerance have been achieved.

If the test indicates a vapor pressure above that allowed by the product specification, it could lead to unsafe overpressure conditions in handling and transportation systems for the product. For example, the maximum vapor pressure for most propane products is 208 PSIG at 37.8°C (100°F). If a propane product with a vapor pressure higher than that is introduced into the existing transportation infrastructure (pipeline, rail, transport, barge, ship, etc.), it could result in overpressure conditions and unplanned releases.

It is also important to verify that the vapor pressure/volatility of the LPG product is not too low. For example, in very cold weather, propane used as heating fuel must be able to vaporize rapidly enough to provide adequate fuel flow to heating systems. If the concentration of heavy components exceeds specification limits and the resulting vapor pressure is too low, the flame may be unstable, too lean, or unable to support combustion.

In general, the LPG component vapor pressures and densities are related to the size of the LPG fraction molecule. For example, ethane molecules are very small relative to propane molecules. The density of ethane vapors will be less than the density of propane vapors at the same temperature and pressure conditions. Ethane is more volatile (higher vapor pressure) than propane at the same temperature, and it takes much higher pressure at the same temperature, or much lower temperature at the same pressure, to keep ethane in the liquid phase. Smaller molecules tend to have lower molecular weights, lower density, and higher vapor pressures. See GPA Standard 2145 [5] for direct comparisons of the various physical properties for the components typically found in LPGs and NGLs (at standard conditions of temperature and pressure). It should be evident that as molecular weights increase, vapor pressure will tend to decrease, and that as Btu content per gallon or per cubic foot increases, component densities will tend to increase.

Note that LPG vapor pressures may also be calculated using the method described in ASTM **D2598**, *Standard Practice for Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis* [6].

3.2.3 ASTM D1657, TEST METHOD FOR DENSITY OR RELATIVE DENSITY OF LIGHT HYDROCARBONS BY PRESSURE HYDROMETER

This test [7] requires a representative sample of product be collected in a container under pressure due to the product's vapor pressure at the indicated temperature of the product in the container. A hydrometer is placed in the container before the liquid product sample is introduced. The sample container must contain enough product to allow the hydrometer to float. The hydrometer will 11

indicate the relative density or the density of the product at the indicated pressure and temperature of the product. Temperature corrections may be applied to adjust the indicated density or relative density of the product to the density or relative density of the product at a standard temperature of 15°C or 60°F, or at another agreed-upon temperature.

3.2.4 ASTM D1837, TEST METHOD FOR VOLATILITY OF LIQUEFIED PETROLEUM (LP) GASES

This test [8] determines whether or not the product is as volatile as it should be by determining the temperature of the remaining product after 95 % of the product volume has been vaporized at test conditions. For example, when 95 % of a propane product has been vaporized, the temperature of the remaining product at test conditions should be -38.3° C (-37° F) or lower.

If the product does not meet the specification for this test, it contains material that has low volatility and will not vaporize as it should—especially during cold ambient conditions. This type of product will also tend to cause materials with low volatility to build up over time in storage tanks feeding from the vapor phase, such as domestic propane storage tanks.

Note that ASTM **D2598** [6] provides a means for calculating the vapor pressure of LPG products.

3.2.5 ASTM D1838, TEST METHOD FOR COPPER STRIP CORROSION BY LIQUEFIED PETROLEUM (LP) GASES

This test [9] is useful for determining whether or not a product is corrosive. Hydrogen sulfide (H_2S) and elemental sulfur are the most common contaminants causing a failure. LPG products may fail the test at concentrations as low as 1 ppm or less under test conditions.

If a freshly polished copper strip is discolored by the product under test conditions, it is likely to produce corrosion in transportation or handling equipment (or in both) in the distribution system for the product—especially those containing copper or copper alloys such as brass, which is common in LPG systems. Increasing concentrations of the corrosive materials will produce higher levels of corrosion in the presence of any free water and oxygen (or air).

When performing this test, follow the procedure exactly. Ensure the product sample container is clean and moistened using the steps outlined in the test method. Adding a trace of water to the cylinder as prescribed in the test method is a critical step toward ensuring that the sensitivity of the test is sufficient. The copper strip must be highly polished and suspended properly in the sample cylinder when a representative sample is introduced. Take the 20 % liquid volume outage to make sure the sample container is not overpressured as the product temperature increases to the water bath temperature of 37.8°C (100°F). After the test period is complete, safely depressurize the sample container and compare the copper strip to the comparator strip described in the test method to determine the number classification of the sample strip. Results worse than 1a or 1b cause the product to fail the test.

3.2.6 ASTM D2158, TEST METHOD FOR RESIDUES IN LIQUEFIED PETROLEUM (LP) GASES

In this test method [10], 100 ml of product is slowly weathered under controlled conditions until the product temperature has reached 38°C (100°F). The amount of any nonvolatile material remaining in the tube must be recorded (water, methanol, lubricants, inhibitors, etc.). A solvent is then added to the tube to capture any nonvolatile material in the solvent until the level in the tube is 10 ml. The oil stain portion of the test method is then performed to see if any oil stain remains after a measured quantity of the solvent-residue mixture is allowed to disperse on clean, white filter paper. Typically, the test results in a "pass" if no oil stain is present after 0.3 ml of the solvent-residue material has been deposited on the filter paper and two minutes have elapsed.

If an oil stain is present during the test, when the product is used as a motor fuel, residues will be left in the vaporizer/ regulator portion of the fuel system. Deposits may also be found in the carburetor or fuel injection system. Note that smaller engines tend to develop operating problems faster than larger engines when the same level of contamination is being fed to both under similar operating conditions (for example, forklift engines may be more sensitive to contamination than automobile or truck engines).

In vaporized product burner applications, failing the oil stain test may indicate the potential for soot buildups, unstable flames, and fouled burners.

3.2.7 ASTM D2163, TEST METHOD FOR ANALYSIS OF LIQUEFIED PETROLEUM (LP) GASES AND PROPENE CONCENTRATE BY GAS CHROMATOGRAPHY

This test method [11] is used for analyzing a representative sample of LPG to determine its C1 through C5 composition using a gas chromatograph. It is not to be used for C6 or heavier component analysis. The apparatus will separate the components and then will determine the quantity of each. Either gas phase or liquid phase samples may be used, but liquid injections are recommended. A flame ionization detector is preferred for measuring the system response (peak retention times and peak areas) for streams being analyzed using this method. This response is then related to the system response for multicomponent or pure component calibration standards to determine the true composition of the sample. Other types of detectors are allowed if they meet the requirements for response, linearity, and sensitivity for the components of interest. Although a specific column technology is referenced, other column types and configurations are acceptable if they provide adequate peak separation. The method also includes a recommended calibration procedure.

This method is typically used to determine whether or not an LPG product is within specification limits and to ensure it is suitable for whatever purpose it is intended. For example, if an ethane/ propane blend is to be used to produce ethylene, the test will determine whether or not the product is suitable feedstock for the process system where it will be utilized.

3.2.8 ASTM D2420, TEST METHOD FOR HYDROGEN SULFIDE IN LIQUEFIED PETROLEUM (LP) GASES (LEAD ACETATE METHOD)

Moist lead acetate paper exposed to a vaporized LPG stream has a very specific reaction with hydrogen sulfide (H_2S) in the stream. As the lead acetate converts to lead sulfide, the reaction will cause the paper to yellow or darken as a result of contact with even very low parts per million levels of H_2S . This method [12] can typically identify concentrations of H_2S at or below 1 part per million, similar to the detection threshold for ASTM D1838 [9], the copper strip test (discussed earlier). As concentrations increase, the strip will tend to get darker on subsequent tests, but the test is only generally quantitative and should be considered a "pass" or "fail" procedure. If the strip is darkened due to H_2S , the stream will be unacceptably corrosive as long as any free water and oxygen (air) are present.

Note that methyl mercaptan, which is a contaminant sometimes present in LPG, will also cause the lead acetate paper to turn yellow; but if the color change is due to methyl mercaptan only, the yellow color will fade in less than 5 min.

3.2.9 ASTM D2598, PRACTICE FOR CALCULATION OF CERTAIN PHYSICAL PROPERTIES OF LIQUEFIED PETROLEUM (LP) GASES FROM COMPOSITIONAL ANALYSIS

This practice [6] demonstrates how a compositional analysis of commercial and special-duty propane products meeting the recommended specification limits in ASTM D1835 [1] may be used to calculate the vapor pressure, relative density, and motor octane number (MON) of the product. For MON calculations, the propene composition must be 20 liquid volume percent or less, and the components in the product are limited to methane, ethane, propane, propene, iso-butane, and normal butane.

If the composition is not provided in liquid volume percent, ASTM Practice **D2421** [13] or other suitable methods (GPA, International Organization for Standards [ISO], etc.) may be used to determine liquid volume percent from mole percent or weight percent compositions.

3.2.10 ASTM D2713, TEST METHOD FOR DRYNESS OF PROPANE (VALVE FREEZE METHOD)

Carefully following this test method [14] will determine the amount of time it takes propane product flashing through a very small port to freeze-up and stop flowing. Typically, the product should spew into the ambient air for at least one minute to verify that the product is dry enough that sufficient ice will not be available to block the port and stop the product from escaping to the atmosphere. If methanol is in the product, the test results may not be representative of the actual stream as it moves through the distribution system, and operating problems may occur in the system even though the freeze valve was unable to predict the problems due to the interference from methanol. The primary problem associated with excess water in the product is the potential for freeze-ups in pressure regulators providing fuel to heating or fuel systems. Although the test is "pass" or "fail" (depending on whether or not flow is sustained for 60 seconds), it is not a truly quantitative method for determining water concentrations in parts per million. However, experience has shown that under typical operating conditions, a water content of approximately 16 parts per million on a weight basis or greater is present when failures occur.

3.2.11 ASTM D2784, TEST METHOD FOR SULFUR IN LIQUEFIED PETROLEUM GASES (OXY-HYDROGEN BURNER OR LAMP)

This test method [15] burns a sample of product in an oxy-hydrogen burner, or in a lamp or closed system in a carbon dioxide-oxygen atmosphere. The oxides of sulfur are absorbed and oxidized to sulfuric acid in a hydrogen peroxide solution. The sulfate ions are then determined using either a barium perchlorate titration process or by turbidimetric means (where the sulfate is precipitated as barium sulfate and the turbidity of a suspension of the precipitate is measured with a photometer). ASTM D2784 [15] is not recommended for determining trace levels of sulfur in LPG.

It is important to determine sulfur levels in LPGs for several reasons. Sulfur can poison catalysts, contribute to corrosion, and, when present during a combustion process, it produces SO_2 and other sulfur-containing compounds that may be additional sources of corrosion, smog, acid rain, and haze.

3.2.12 ASTM D3700, PRACTICE FOR OBTAINING LPG SAMPLES USING A FLOATING PISTON CYLINDER

Floating piston cylinders are usually the preferred method for collecting representative spot or composite samples of an LPG product [16]. Prior to being placed in service, the cylinders must be carefully inspected and free of any product or contaminants from previous samples that were in the cylinder.

When properly used, the product side of the piston will contain varying amounts of all liquid-phase product once sample injection into the cylinder begins. An indicator system is provided to show the user how much product is in the cylinder.

The backpressure side of the piston in the cylinder is typically precharged with an inert gas (typically helium) to a pressure above the maximum expected vapor pressure of the product at the worst expected operating conditions (lightest composition and highest temperature) to ensure that the product remains a single-phase liquid product on the product side of the piston.

Users of this method must ensure sufficient outage (vapor space) is available on the backpressure side of the piston to prevent the possibility of overpressuring a cylinder that has been liquid filled and then experiences a temperature increase. (See also the latest revision of GPA Standard 2174, *Obtaining Liquid Hydrocarbon Samples for Analysis by Gas Chromatography* [17].)

3.2.13 ASTM D6667, TEST METHOD FOR DETERMINATION OF TOTAL VOLATILE SULFUR IN GASEOUS HYDROCARBONS AND LIQUEFIED PETROLEUM GASES BY ULTRAVIOLET FLUORESCENCE

This test method [18] is for determining *volatile* sulfur levels at very low concentrations from 1 mg/kg to 196 mg/kg (1 to 196 parts per million on a weight basis). The method will not determine sulfur content for sulfur species that will not vaporize at test conditions (such as elemental sulfur, for example).

The method should not be used with products having a halogen content equal to or greater than 0.35 % on a mass basis (such as fluorine, chlorine, bromine, etc.). Note that such high levels of halogens in LPG products are both rare and undesirable (see respective material safety data sheets for any species identified).

Note that the presence of sulfur species not only may indicate the potential for corrosion (particularly with H_2S), the concentration of odorants (ethyl mercaptan, tertiary butyl mercaptan, and others), and decomposition products of odorants (dimethyldisulfide and disulfide oils, for example), but it is also an indicator for how much sulfur will be available from the volatile sulfur species to produce air contamination when the product is burned as a fuel (SO, emissions primarily).

3.2.14 ASTM D6897, TEST METHOD FOR VAPOR PRESSURE OF LIQUEFIED PETROLEUM GASES (LPG) (EXPANSION METHOD)

This method [19] is intended to determine product vapor pressure that will correlate well with the results achieved when using ASTM D1267 [4] under similar test conditions but without having to handle the large volumes of pressurized product required by ASTM D1267 [4]. It is intended for use with automated vapor pressure determination systems; ASTM D1267 [4] is a manual method. Although the scope of the method allows a range of vapor to liquid ratios and temperatures, it is most commonly used at 37.8°C (100°F) and with a vapor to liquid ratio of 0.5:1. As with ASTM D1267 [4], the test is intended to verify whether or not the vapor pressure/volatility of a product is suitable for its intended use.

References

- ASTM D1835-13, Standard Specification for Liquefied Petroleum (LP) Gases, ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [2] GPA Standard 2140, *Liquefied Petroleum Gas Specifications and Test Methods*, Gas Processors Association, Tulsa, OK, 1997.
- [3] ASTM D1265-11, Standard Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method, ASTM International, West Conshohocken, PA, 2011, www.astm.org
- [4] ASTM D1267-12, Standard Test Method for Gage Vapor Pressure of Liquefied Petroleum (LP) Gases (LP-Gas Method), ASTM International, West Conshohocken, PA, 2012, www.astm.org

- [5] GPA Standard 2145, Table of Physical Properties for Hydrocarbons and Other Compounds of Interest to the Natural Gas Industry, Gas Processors Association, Tulsa, OK, 2009
- [6] ASTM D2598-12, Standard Practice for Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [7] ASTM D1657-12e1, Standard Test Method for Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [8] ASTM D1837-11, Standard Test Method for Volatility of Liquefied Petroleum (LP) Gases, ASTM International, West Conshohocken, PA, 2011, www.astm.org
- [9] ASTM D1838-14, Standard Test Method for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases, ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [10] ASTM D2158-11, Standard Test Method for Residues in Liquefied Petroleum (LP) Gases, ASTM International, West Conshohocken, PA, 2011, www.astm.org
- [11] ASTM D2163-14e1, Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/ Propene Mixtures by Gas Chromatography, ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [12] ASTM D2420-13, Standard Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method), ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [13] ASTM D2421-13, Standard Practice for Interconversion of Analysis of C5 and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Mass Basis, ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [14] ASTM D2713-13, Standard Test Method for Dryness of Propane (Valve Freeze Method), ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [15] ASTM D2784-11, Standard Test Method for Sulfur in Liquefied Petroleum Gases (Oxy-Hydrogen Burner or Lamp), ASTM International, West Conshohocken, PA, 2011, www.astm.org
- [16] ASTM D3700-14, Standard Practice for Obtaining LPG Samples Using a Floating Piston Cylinder, ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [17] GPA Standard 2174, Obtaining Liquid Hydrocarbon Samples for Analysis by Gas Chromatography, Gas Processors Association, Tulsa, OK, 2014.
- [18] ASTM D6667-14, Standard Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence, ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [19] ASTM D6897-09, Standard Test Method for Vapor Pressure of Liquefied Petroleum Gases (LPG) (Expansion Method), ASTM International, West Conshohocken, PA, 2009, www.astm.org

Chapter 4 | Discussion on Uses of the Specification for Gasoline (ASTM **D4814**)

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4.1 The Importance of Gasoline Specifications

To say that gasoline is an important commodity for the public would be an understatement. What other single product exists that has its price, brand, and availability posted right on the street in front of every store that sells it? The consumption of gasoline in the world is immense in proportion to other commodities, with about 30 million barrels (1.3 billion gal) consumed every day in 2013 [1]. Consumers like you and me depend upon the quality of this product to deliver a satisfactory driving experience every time we start and drive our vehicles. We most often never give it a second thought as we consume this product that enables our personal mobility and powers our recreational and lawn and garden equipment. Upon the rare occasion that the gasoline product delivers poor performance, we are surprised and disappointed. The fact that all of us most often have a good experience is the result of gasoline being made to specifications.

To produce that expected performance under all different climatic and weather conditions requires that the manufacturers, shippers, distributors, and retailers deliver a product made to certain critical specifications. It is critically important that the fuel is made to these specifications and that the stakeholders involved in setting these specifications all agree on the types and limits of the values in the specifications. Without specifications, engine designers would have no parameters with which to design an engine, and regulators would not have enforcement targets, nor would they be able to reduce emissions from the fuel. The trading of gasoline among suppliers would be very difficult because there would be no common standard on which to base commerce. Owners of pipelines would not have a way of ensuring that shippers supplied uniform products into the pipeline. Finally, the consumer would be impacted by poor quality gasoline that could cause inadequate vehicle performance and malfunctions. Specifications are critical.

4.2 Test Methods and Definitions

As important as the specifications are for gasoline, it is equally important that those involved in determining conformance to these specification limits all agree on the test methods that will be used to demonstrate the conformance. These test methods, like the specifications, also need to be standardized and agreed upon by the stakeholders involved in testing the fuel. Similarly, it is also important that the stakeholders involved in using specifications and test methods agree upon the terminology used to set the specifications and test methods. For example, if one refers to the minimum "octane" number of gasoline, it is important to know *which* "octane number" is to be referenced. There is the research octane number (RON), the motor octane number (MON), the antiknock index (AKI = [RON+MON]/2), or the actual vehicle road octane. Terminology may seem mundane, but it is also critically important to the specification process.

4.3 Gasoline Specifications— Where Do They Come From?

Specifications for gasoline are the minimum requirements set by members of a consensus-based standards development organization (SDO, e.g., ASTM International is an SDO) that deliver adequate performance in the equipment (e.g., vehicle) for which its use was intended. These types of specifications are set by a consensus process involving all the stakeholders that have an interest in developing such specifications. They are most often performancebased and the limits are set by review and agreement of results from test data from the types of gasoline that span the range of values of interest. The test data are often developed by experts in the field under controlled conditions with experiments designed to provide statistically valid results. It is important to have such an organization that develops these consensus-based specifications because having each and every government authority set their own specifications for fuel would be a severe impediment for trade and commerce among jurisdictions governed by these different authorities.

Because vehicles and equipment burning gasoline contribute significantly to the emission of undesired pollutants and greenhouse gases, regulatory authorities have for many years also set specifications for gasoline that limit their environmental impacts. These specifications are not set by a consensus process but, depending upon the regulatory authority, they may involve commentary from stakeholders and they (the regulators) may consider test

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results from emission testing programs. Of course, the specifications set by a regulatory authority supersede those values for the same property that may have been set by an SDO. Because gasoline and vehicles affect emissions, gasoline and gasoline-ethanol blends are highly regulated in most countries where pollution regulations are prominent.

4.4 The Stakeholders Involved in Specifications

There are many stakeholders involved in gasoline specifications development. Beginning with the manufacture of the petroleumbased crude refined into gasoline, refiners are involved to make sure that the fuel they produce delivers acceptable performance to the customer for a reasonable value. Marketers of gasoline that do not have a refining capability are involved to make sure the fuel they purchase delivers the same performance, again for a reasonable value. Pipeline and shipping companies are involved to make sure that the specifications set are adequate for them to operate a fungible shipping system where gasoline of the same type may be commingled for efficient and cost-effective shipping and distribution. Federal, state, and local regulators are involved to make sure that the specifications deliver adequate performance to their constituents, protect the public, and that they meet environmental objectives. Companies that make chemicals for addition to gasoline are involved because specifications are sometimes achieved only with the addition of these performanceenhancing chemicals. Manufacturers of renewable fuel components are involved because the presence of these renewable components affects the performance of the gasoline, and specifications may limit the amount of renewables used. Makers of vehicles and engines that use gasoline are involved because they need to design adequately performing vehicles and engines based on the gasoline specifications.

As you may imagine, this group of stakeholders is rather large and has diverse views on how specifications should be set. That is exactly why the SDOs exist—to provide a consensus-based forum for these stakeholders to come together and decide on the specifications for gasoline that deliver all these diverse objectives.

4.5 How Are Specifications Used?

Consensus-based specifications such as ASTM D4814, *Specification* for Spark-Ignition Engine Fuel [2], are used for many purposes. ASTM D4814 is updated frequently and published electronically by ASTM International and in an annual volume, ASTM Committee D02, Standards for the Petroleum Products, Liquid Fuels, and Lubricants. Many regulatory authorities (e.g., U.S. Environmental Protection Agency [EPA], U.S. states, and other countries) adopt this specification in whole or in part as their legal requirement for gasoline and gasoline-ethanol blends. Pipeline and shipping companies either adopt this specification or use the values in it to set their shipping requirements. Marketers and suppliers of gasoline use this specification to base their trade of gasoline in contracts. Vehicle and engine designers use this specification to design engines for their customers.

4.6 How Are They Enforced?

It is a subtle but important distinction that the SDO *does not* develop legal requirements for gasoline and gasoline-ethanol blends. It is only when a regulatory authority having jurisdiction to do so adopts the specification in whole or in part that this then becomes a legally binding requirement. The SDO has no part in this legal process other than documenting the consensus-based limits for the properties cited in the specification. Many states and the EPA have programs in the United States to sample and test gasoline for various properties of interest. Many fuel producers do the same. These programs are used by authorities for enforcement to ensure conformance with the legally required specifications adopted as law.

4.7 How Specifications Vary

Because gasoline and gasoline-ethanol blends work in sparkignition engines by volatilizing in air, it is important that gasoline evaporates sufficiently to deliver a mixture that can ignite with a spark. This volatilization must occur across a wide range of weather conditions including sub-zero artic temperatures and extremely hot days with temperatures above 100°F. To allow this performance across a wide range of conditions, some of the volatility specification values for gasoline and gasoline-ethanol blends will vary with geography and time of year. For example, low volatility gasoline is used in hotter climates during the summer season to reduce evaporation and air pollution. Higher volatility gasoline is used in colder areas during the winter to ensure effective starting and warm-up of engines. We will cover more detail on these variable volatility properties in section 4.9.

4.8 Octane Number

For a spark-ignition engine to perform as designed, it is important for the gasoline or gasoline-ethanol blended fuel to resist spontaneous ignition until the spark event. When a fuel has insufficient ability to resist spontaneous ignition, the fuel is said to "knock" in the engine due to auto-ignition. This ability to resist spontaneous ignition is determined by its octane number. If the fuel in an engine is prone to auto-ignition, modern engines will compensate (to a point) to avoid knocking by effectively "detuning" the engine reducing power and efficiency (e.g., miles per gallon, or MPG). Lower octane number gasoline also limits the ability of engine designers to reduce fuel consumption by "downsizing" the engine displacement while attempting to ensure the same or greater horsepower by increasing compression ratio because knocking is more pronounced with higher compression ratios. This is becoming more widespread as authorities in the United States, Western Europe, and elsewhere strive to reduce fuel consumption and greenhouse carbon dioxide gas emissions.

As mentioned earlier, there are several types of "octane numbers." The research octane number (RON) and the motor octane number (MON) are determined in single-cylinder test engines designed for that purpose. The RON test engine is run a bit slower, with cooler air intake compared to those of the MON test conditions. The RON is measured using ASTM **D2699** [**3**] and the MON by ASTM **D2700** [**4**] standard test procedures. As noted earlier, the AKI is the arithmetic average of the RON and MON (i.e., [RON+MON]/2).

In the United States and Canada, authorities have adopted the AKI as the posted requirement for octane number value of the gasoline sold. In some areas of the country, 87 AKI is the minimum octane number requirement for regular gasoline and is often set by state law. Higher octane number grades (e.g., midgrade and premium) offer greater octane number levels to those that wish to use them. In the higher altitude areas of the United States, a lower 85 regular grade AKI is marketed. The reduced AKI value for higher altitudes is an active area of study. The minimum octane number requirement for a vehicle or engine is found in the owner's manual published by the engine manufacturer. Since about 2005, vehicle owner's manuals have had an 87 AKI or higher minimum requirement.

In most other countries, the RON is the posted octane number—though sometimes with a minimum MON required in the specification. European specification for gasoline EN 228 has this requirement.

Recent research and development (R&D) by automotive companies, gasoline suppliers, and other stakeholders have indicated that the RON is more important to modern engine performance in resisting knock than the AKI or MON. This is an area of active research that may drive changes in how octane number type and limits are cited in future revisions of specifications. In summary, the specification for minimum octane number is important for the smooth running of gasoline engines and their avoidance of pre-ignition knock.

4.9 Volatility

Of all the specifications (specs) in place for fuels, the ASTM D4814 [2] gasoline volatility specifications are by far the most complicated and difficult to comprehend. For the fuel suppliers, volatility specifications have a material impact on manufacturing costs at their refineries. For engine makers, the volatility of gasoline has a key influence on the ability of the engine to start, warm up, and run well. For regulators, volatility has a significant impact on air pollution from the evaporation and combustion of the gasoline.

To begin to understand volatility, it is important to be familiar with the properties and terms used to measure and control it. For instance, volatility specifications fall within three major fuel properties: vapor pressure, distillation, and vapor lock protection. Within these, there are seven metrics that fuel and engine experts have identified that all U.S. gasoline must meet in order to deliver satisfactory vehicle performance. These are vapor pressure, distillation points (T10 maximum, T50 minimum and maximum, T90 maximum, and final boiling point maximum), and the vapor lock index (Tv/l = 20 minimum). The term "T10" is the temperature at which the first 10 % of the gasoline sample that is being distilled is recovered.

Volatility of gasoline is important because gasoline needs to vaporize to burn. In the winter, the composition of gasoline needs to be adjusted to have higher volatility so that it will vaporize more readily at lower temperatures to start the engine and provide good performance. The explanation that follows describes how volatility is quantified.

4.9.1 VAPOR PRESSURE

Reid vapor pressure (RVP) is defined as the absolute vapor pressure exerted by a liquid at 100°F. But in ASTM D4814 [2], RVP is no longer used because the test method involves the fuel making contact with water, which does not work for gasoline-ethanol blends. The test method used most today (ASTM D4814-16) specifies several vapor pressure standard test methods-ASTM D4953 [5], ASTM D5191 [6], ASTM D5482 [7], or ASTM D6378 [8]. It uses a simple instrument that heats a small amount of gasoline to 100°F in a confined cell and measures the resulting pressure. The value reported is called the dry vapor pressure equivalent (DVPE). The value is further defined by regulating agencies that may stipulate correlation calculations depending on region and season (i.e., EPA RVP, ASTM vapor pressure, or California Air Resources Board [CARB] RVP). With regard to motor vehicles, vapor pressure is important for vehicle performance and for minimizing environmental impact. For example, in winter, higher vapor pressure is needed for cold engine starting. If the pressure is too low, the fuel will not ignite properly. During summer, lower vapor pressure is needed to reduce environmental impact, particularly ozone air pollution. Vapor pressure is a measure of how easily gasoline hydrocarbons will vaporize into the environment and become air pollution precursors for-especially-summertime ozone air pollution.

In the United States, there are six ASTM seasonal vapor pressure classes that vary by month and by geography, as shown in Table 4.1.

Vapor pressure (or RVP) is regulated during the summer by authorities concerned about air pollution. The EPA regulates RVP (federal equation) for gasolines and gasoline-ethanol blends during the summer season, which is defined as June 1 through September 15. CARB expands this RVP (CARB equation) control period for California.

4.9.2 DISTILLATION

Distillation is defined by the temperature at which a certain volume percentage of a liquid has evaporated and has been recovered by cooling. The ASTM Standard Test Method is **D86** [9]. Generally, gasoline fuel is a multicomponent blend of hydrocarbons (with several hundred discrete chemicals), typically with ethanol. Each chemical has a specific boiling point but, collectively, the liquid has its own distillation profile. ASTM **D4814** [2] specification distillation limits include the maximum temperature for distilled gasoline at 10 % recovered (abbreviated T10) as well as both

TABLE 4.1 Six ASTM seasonal vapor pressure classes

Summer	Spring/Autumn	Winter
AA—7.8 psi	B—10.0 psi	D—13.5 psi
A—9.0 psi	C—11.5 psi	E—15.0 psi

minimum and maximum temperature limits at 50 % recovered (T50), the maximum at 90 % recovered (T90), and the maximum final boiling point (FBP) after which no additional material can be distilled.

The T10 maximum limit ensures that there is a proper amount of high volatility light-end materials in the fuel to start the engine and operate at low temperatures to warm up (just enough but not too much).

The T50 minimum limit ensures good warm up and drivability performance. The T50 maximum limit ensures an adequate volume of gasoline in the middle gasoline range, which also delivers good drivability performance (i.e., idling quality, start-up time, good cold start, and warm-up).

The T90 max limit ensures a limited amount of high boiling components in gasoline that could lead to rough engine performance and engine deposits.

The FBP (also known as the "end point" or T100) restricts the amount of high boiling distillate range materials that can be used. Similar to T90, a high FBP indicates heavy components that can cause engine oil dilution, exhaust smoke, engine deposits, fuel injector problems, and so on. Small amounts are acceptable, but too much causes problems.

There is also a maximum drivability index (DI) limit composed of weighted T10, T50, and T90 combined values and a term reflecting the influence of ethanol, up to 10 % by volume.

DI = 1.5 (T10) + 3.0 (T50) + T90 + 2.4 (ethanol volume %) (4.1)

DI reflects the gasoline's ability to deliver adequate cold start and warm-up performance in a vehicle's engine. Of all the distillation specs, ethanol has the greatest impact on T50 and, as a result, significantly impacts the DI index value. Some of these distillation limits and DI vary with vapor pressure and distillation class, and some do not (ASTM's DI maximum limits range from 1250°F in summer to 1200°F in winter).

4.9.3 VAPOR LOCK

Vapor lock is a condition where gasoline vaporizes in a fuel tank or fuel line before being injected into the cylinder, preventing an engine from starting. The engine fuel handing equipment is designed to deliver a liquid not vaporized gasoline. Today's fuel injected engines encounter hot-fuel handling drivability problems (hot starting, stumble, surge, backfire, and stalling) rather than true vapor lock. Vapor lock protection is a specification limit on the *minimum* temperature for a gasoline vapor-liquid ratio of 20:1 (called $T_{V/L=20}$); $T_{V/L=20}$ is measured in an instrument similar to the vapor pressure instrument. This is ASTM test method **D5188** [10]. The 20:1 ratio was chosen because test data showed this ratio had the best correlation that would prevent vapor lock from occurring. There are six $T_{V/L=20}$ grades that (like vapor pressure) also vary with month and geography (typically by state or areas within a state).

The U.S. limits for volatility are set in ASTM **D4814** [2] based on decades of historic geographic and annual temperature profiles corrected for altitude. A more detailed explanation of how volatility limits are determined is contained in Section 5.2.1 of ASTM **D4814** [2]. In summary, the volatility of gasoline and the specification limits that are set to control it are very important to the cold start and warm-up, smooth running, and avoidance of hot-start problems of gasoline.

4.10 Composition

Several components of gasoline that are made in the refining process are limited by specifications to deliver certain performance and environmental objectives. Sulfur is limited by the EPA, CARB, the European Union, and many other individual countries for environmental reasons. Sulfur, when burned in an engine, creates sulfur dioxide gas, which can absorb on the precious metal catalyst in a modern vehicle's exhaust after-treatment system and temporarily render the catalyst less effective, increasing emissions of pollutants. With the recent Tier 3 Vehicle Emission and Fuel Standards Program, the EPA will regulate sulfur in U.S. gasoline on average from the current 30 ppm to 10 ppm beginning in 2017. Many other countries and the European Union also have regulations limiting gasoline sulfur content.

The aromatic molecule benzene also is limited by environmental regulations because the EPA [11] and other authorities have characterized benzene as a toxic chemical. (Details of EPA gasoline benzene regulations, including requirements, dates, bank and trading, and enforcement are provided in Parts 80.1220 through 80.1363 of Title 40 of the Code of Federal Regulations.)

Metals in gasoline are also sometimes limited by regulation. Years ago, the lead alkyls (tetramethyl lead, tetraethyl lead, and their mixtures) were used as octane number enhancing additives. However, the impact of lead on humans was discovered, and regulations prohibiting the addition of lead to gasoline were promulgated by many countries. The addition of other metallic additives, such as the octane-number-booster methylcyclopentadienyl manganese tricarbonyl (MMT), has been restricted in certain gasolines (e.g., U.S. reformulated gasoline). MMT is permitted in U.S. conventional (i.e., non-reformulated) gasoline, but automakers strongly discourage using gasoline with MMT.

Thus having specifications set to control the composition of certain materials and elements in gasoline allows the fuel to be safer to handle and helps reduce emissions.

4.11 Storage and Stability

The ability of gasoline and gasoline-ethanol blends to maintain freshness and quality upon storage over a period of months is important. It is common for gasoline to be left in fuel tanks of recreational and lawn and garden equipment over the winter. Gasoline, like all hydrocarbon-based materials, can oxidize over time by the reactions of some components in gasoline with oxygen in the air. Higher temperatures or certain metals—such as copper, zinc, or iron—or both can accelerate these reactions and form higher boiling materials called "gums." These materials will clog engine fuel distribution equipment and render an engine hard or impossible to start. To test the oxidation resistance of gasoline, there is a specification limit on the accelerated oxidation resistance of gasoline using the standard test method ASTM **D525** [11].

Once gasoline has begun to oxidize, there is a test to detect the resulting gum content, ASTM D381 [12]. Gums can be tested by evaporating a sample of gasoline, leaving residue. This residue is called unwashed gums and consists of everything in gasoline that would not evaporate. The residue can then be washed with a nonpolar solvent (heptane); the washed material that is left is called solvent-washed gums and is the material remaining undissolved in the solvent. Both the unwashed and the solventwashed gum contents tell us about high boiling materials in the gasoline (not just oxidized material) and those that are soluble. Such high boiling materials in the gasoline will concentrate upon evaporation of the lighter gasoline material and can cause engine problems such as valve sticking and deposits. ASTM D4814 [2] has a maximum solvent-washed gum limit of 5 mg/100 mL. Note that part of the unwashed gum includes beneficial deposit control additives.

The storage properties and limits on the amounts of undesired materials in gasoline are controlled by the specifications for oxidation resistance and gum content.

4.12 Workmanship

Because there cannot be a specification limit on every possible contaminant, there is a workmanship statement in many gasoline specifications that does not allow any undesired components in the fuel. This is called the workmanship requirement. The fuel is expected to be visually clear and bright with no visible particles or water droplets present. Workmanship also prohibits any contaminants that would cause poor performance in an engine. An example would be silicone compounds that, when burned in an engine, form silicon dioxide (i.e., sand) that interferes with the operation of the emission system. This specification is important to ensure fit-for-purpose fuel is made and delivered.

4.13 Corrosion

Gasoline and gasoline-ethanol blends are shipped, stored, and delivered in metallic pipes and tanks. The fuel handling system in vehicles is mostly made of metals. Thus, the ability of fuel to be noncorrosive to metals is an important property. There are ASTM specifications for the corrosion propensity of gasoline to silver and copper. Many pipelines and fuel producer internal specifications also contain limits on corrosion of iron (steel). Silver corrosion is important for gasoline because some fuel tank level sensing components are made from silver alloys. Sulfur compounds in fuelespecially hydrogen sulfide, light mercaptans, and dissolved elemental sulfur-each and in combination can corrode and tarnish these silver alloy sensing elements and result in erroneous fuel level readings. Likewise, these sulfur compounds can also tarnish and corrode copper-containing alloys such as brass. Both the silver (ASTM D7667 [13] or ASTM D7671) [14] and copper (ASTM D130) [15] tests are performed using test procedures that expose metallic strips to fuel for a specified time under controlled conditions. Corrosion of steel and iron is determined by the National Association of Corrosion Engineers (NACE) test. This test exposes a steel billet polished by a specific procedure to water and fuel to determine the extent of corrosion on the billet at specified test conditions. The greater the coverage of rust, the more corrosive the fuel. These three specifications put limits on corrosion and help protect the metallic fuel-handling equipment and storage tanks.

4.14 Blending Components and Additives

Components in gasoline, for the purpose of this discussion, are those materials that are intentionally added to gasoline. These components can be additives such as oxidation stability improvers, engine-cleaning detergent additives, and the like. Additives in gasoline typically are introduced at a very low level, such as parts per million (PPM). Other components can be blending components, such as oxygenates. Examples of oxygenates are aliphatic ethers (e.g., methyl tert-butyl ether [MTBE]) and alcohols (e.g., ethanol). These components are added at the percentage levels.

Engine-cleaning detergent additives (also called deposit control additives) are necessary for keeping deposits on critical engine parts at low levels. Deposits on intake valves or fuel injectors can cause performance problems and can increase emissions. Thus, in the United States, the EPA and CARB have specified that all motor gasoline must contain a minimum level of an approved depositcontrol additive. Some U.S. automotive companies have specified a higher level of deposit-control additive for a voluntary program called "Top Tier" that recognizes those fuel marketers that comply with these requirements.

Other additives are also used in gasoline to impart desired features, such as improved oxidation stability using antioxidants and better corrosion resistance using corrosion inhibitors and dispersants. These additives are used to help meet the specifications for those associated properties (e.g., corrosion inhibitors to improve the NACE corrosion rating of the fuel).

In the 1990s, the EPA also required the use of oxygenates in U.S. gasoline to reduce the cold-start tailpipe emissions of smog-producing unburnt hydrocarbons and carbon monoxide emissions. Both MTBE and corn-based ethanol were used for this purpose. As ambient air quality improved along with vehicle emission controls, these regulations were sunset. However, the United States, European Union, and other countries promulgated laws requiring the use of renewables in fuels, such as ethanol in gasoline. As of this writing, about 95 % of all U.S. gasoline contains 10 volume percent ethanol to meet the federal specification for use of renewables. The use of MTBE in U.S. gasoline has ceased due to many state laws and bans. MTBE has been found to be a groundwater pollutant, and this has resulted in significant litigation. The use of ethers such as MTBE continues elsewhere, such as in Europe.

4.15 Specifications for Emission Regulations

As part of the U.S. Clean Air Act Amendments, in the 1980s, the EPA and the automobile and fuel industries undertook a massive

vehicle, fuel, and emissions test program known as "auto/oil" to better understand the effects of gasoline on vehicle emissions. This program provided the technical basis for emissions regulations that were promulgated in the 1990s for vehicles and fuels. For the first time, the EPA required a special type of gasoline in areas that did not meet ambient ozone standards. This gasoline is known as "reformulated" gasoline (RFG). One of the requirements for the RFG rule was that it contain an oxygenate, such as MTBE or ethanol.

And, for the first time, using models, the EPA required the gasoline to be made not only to compositional specifications limits but to the predicted emission limits. First, a "simple" model was required and then a "complex" model followed. These were used to calculate the predicted emissions and to demonstrate conformance with the RFG specifications. California developed their own model for predicting emissions and required gasoline manufacturers to use the model to demonstrate conformance with their emissions limits specifications. More details about these models may be found in ASTM's "Research Report on U.S. Reformulated Spark Ignition Engine Fuel and the U.S. Renewable Fuels Standard" [16].

For non-reformulated gasoline, emission requirements also included an "anti-dumping" specification. This gasoline is called "conventional" and has EPA requirements for its not being blended with the higher emission components taken from the RFG. The fuel specification emission rules in their entirety are very complex, and a good summary is in the previously mentioned ASTM RFG Report [16].

4.16 Specifications for Renewables Use

In the United States, the European Union, and other countries, there are requirements for blending renewable components into transportation fuels. The objectives for these mandated programs are reduction of petroleum use, increased use of renewable fuels with reduced greenhouse gas emission impacts, and providing economic benefit to agricultural interests.

In the United States, these renewable use mandates originated from the Energy Independence Security Act of 2007, which specified minimum volumes of renewable fuels to be used in the total gasoline and diesel fuels. The EPA created the renewable fuel standard (RFS) to provide the framework for this mandate and required increasing amounts of renewables to be included in U.S. fuel. The program's goal was to encourage the use of corn-based ethanol and biodiesel and to provide incentives for cellulosic and so-called second-generation biofuels, beginning in 2008. However, the development of these second-generation biofuels was delayed for various reasons, and the RFS requirements are now under review for revision.

California has promulgated a low carbon fuel standard (LCFS), which is a regulation that requires use of low- and reduced-carbon fuels to address greenhouse gas emission concerns focused on global warming. Other states are considering similar legislation. These specifications for gasoline and

other fuels in California will affect the composition and use of renewables in fuels.

4.17 Conclusion

From the previous discussion, it should now be apparent that modern gasoline is a highly regulated and tightly specified product with many stakeholders involved in the process of setting its specifications. In comparison, the gasoline specification from the early 1970s, ASTM **D439**, was only several pages long. However, the current version, ASTM **D4814-16** [2], now approaches 30 pages in length, reflecting the development and improvements in specifications for this important commodity.

This specification serves to benefit the millions of motorists who, on any given day, fuel their vehicles with the full expectation of trouble-free transportation while it also meets the larger societal goals of emissions reduction and increased use of renewable fuels.

References

- British Petroleum, "Statistical Review of World Energy 2014," www.bp.com/statisticalreview (accessed January 19, 2015).
- [2] ASTM D4814-16, Standard Specification for Automotive Spark-Ignition Engine Fuel, ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [3] ASTM D2699-13b, Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel, ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [4] ASTM D2700-14, Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel, ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [5] ASTM D4953-06(2012), Standard Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method), ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [6] ASTM D5191-13, Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method), ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [7] ASTM D5482-07(2013), Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method—Atmospheric), ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [8] ASTM D6378-10, Standard Test Method for Determination of Vapor Pressure (VPX) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method), ASTM International, West Conshohocken, PA, 2010, www.astm.org
- [9] ASTM D86-12, Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [10] ASTM D5188-14, Standard Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber and Piston Based Method), ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [11] ASTM D525-12a, Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method), ASTM International, West Conshohocken, PA, 2012, www.astm.org

- [12] ASTM D381-12, Standard Test Method for Gum Content in Fuels by Jet Evaporation, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [13] ASTM D7667-10e2, Standard Test Method for Determination of Corrosiveness to Silver by Automotive Spark-Ignition Engine Fuel—Thin Silver Strip Method, ASTM International, West Conshohocken, PA, 2010, www.astm.org
- [14] ASTM D7671-10e1, Standard Test Method for Corrosiveness to Silver by Automotive Spark—Ignition Engine Fuel—Silver Strip Method, ASTM International, West Conshohocken, PA, 2010, www.astm.org
- [15] ASTM D130-12, Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [16] Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants, Research Report D02–1347, "Research Report on U.S. Reformulated Spark Ignition Engine Fuel and the U.S. Renewable Fuels Standard," ASTM International, West Conshohocken, PA, 2015, www.astm.org

Chapter 5 | Discussion on Uses of the Specification for Fuel Ethanol for Blending (ASTM **D4806**)

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5.1 Introduction

The first gallons of ethanol used as a motor fuel were procured by a world famous automotive engineer, Henry Ford, back in 1908 [1]. In the United States, the years of prohibition virtually eliminated all ethanol production for beverage and automotive use. But due to significant air quality and energy security concerns, the U.S. government now has required the use of gasoline oxygenates and renewable energy motor fuel components such as ethanol. Ethanol's use as a motor fuel has expanded greatly since the first publication of a proposed ASTM ethanol specification in 1984. Fast forward to today—nearly all unleaded gasoline in the United States is blended with ethanol at some level, and this trend is expected to grow over the next decades.

ASTM D4806, Standard Specification for Denatured Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel (referred to here simply as ASTM D4806), outlines key information identified by experts in motor fuel and automotive industries, government officials, and by consumers. The key performance properties are discussed in greater detail and emphasis to ensure the expected performance of ethanol as a motor fuel component in spark-ignition engines fuels. Since first published as a specification in 1988, ASTM D4806 has been subjected to a continuous review and updating process due to the constantly changing technology of spark-ignition automotive engines, the changing regulatory requirements, and even due to the technical data identifying concerns with ethanol's fit for use as a motor fuel component. ASTM D4806 may be used for applications beyond motor fuel use if agreed upon by consenting parties. It is important to recognize that the performance requirements included in this specification have been identified as parameters needing a level of control to ensure acceptable use as a motor fuel blend component and may or may not reflect all of the necessary parameters for other applications. As an example, ASTM D4806 may identify many of the attributes needed for denatured fuel ethanol to be used in industrial solvent applications. Further, parameters and corresponding limits identified in ASTM D4806 are germane to the use of ethanol as a blending component in gasoline but not necessarily as a predominate fuel component in ethanol flex fuels such as E85-a blend made up of 51 % to 85 % (volume) denatured fuel ethanol

with the balance hydrocarbons, which is a motor fuel that can be used only by flexible fuel vehicles.

5.2 History of ASTM D4806

ASTM International's first efforts to develop specifications for denatured fuel ethanol started as a cooperative discussion between ASTM's Committee D02 on Petroleum Products, Lubricants, and Fossil Fuels and Committee E44 on Solar, Geothermal, and Other Alternative Energy Sources. The initial collection of expectations as proposed by the broad representation of experts from the ethanol, oil, automotive, and industry consultants resulted in the development and publication of ASTM D02/E44 Proposal P 170, *Denatured Fuel Ethanol to be Blended with Gasolines For Use as an Automotive Spark-Ignition Engine Fuel* (P 170) in 1984 [2]. The initial P 170 publication outlined key parameters for denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 5–10 % by volume. In 1986, Proposal P 170 was withdrawn due to imminent replacement of this information with a standard specification.

The format of the first ASTM denatured fuel ethanol specification has evolved over time. The most recent version includes important information such as performance properties, regulatory aspects (e.g., acceptable denaturants, effective sampling techniques, etc.), and other information for denatured fuel ethanol from production through its offering to consumers.

5.3 Performance Requirements

The intention of ASTM **D4806** is to outline the necessary properties that a solution of very high concentration fuel ethanol and a suitable denaturant must have in order to ensure acceptable attributes and performance when blending with gasoline for ultimate use as spark-ignition engine fuels. The intent of ASTM **D4806** is very different from other motor fuel specifications—such as ASTM **D4814**, *Standard Specification for Automotive Spark-Ignition Engine Fuel*. ASTM **D4814** describes the properties for a wide variety of finished motor fuel blends that include gasoline and similar fuels composed of hydrocarbons blended with alcohols, ethers, and so on. The finished fuels provide acceptable performance and combustion properties. ASTM **D4814** does not define

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the properties for an individual fuel component; ASTM D4806 describes a singular motor fuel component, anhydrous denatured fuel ethanol. To clarify, the term "fuel ethanol" means a grade of undenatured ethanol with components common to its production as compared to a refined, undenatured ethanol that has undergone several distillation steps to improve its odor and taste as expected when destined for beverage or industrial use. Undenatured ethanol may perform acceptably as a gasoline additive; however, the U.S. Alcohol and Tobacco Tax and Trade Bureau (or TTB, formerly Alcohol Tobacco and Firearms) assesses a substantial liquor excise tax on all undenatured ethanol (currently set at \$27 per gallon), creating a substantial economic disincentive. Ethanol produced for beverage applications may also perform acceptably as a motor fuel; however, TTB liquor tax liability and additional manufacturing costs associated with the multiple distillation steps to improve purity create compounding economic disincentives.

A minimum ethanol content is specified in ASTM D4806 to ensure blenders of ethanol can accurately achieve targeted ethanol concentrations in the final gasoline/ethanol blend. A consistent concentration of ethanol can be identified with a laboratory instrument (such as a gas chromatograph) as outlined in ASTM D5501, Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20% Ethanol by Gas Chromatography [3]. Ethanol purity has been included in ASTM D4806 since its first publication in 1988. Section 4.3 of the 1988 publication stated "Total fuel ethanol content of denatured fuel ethanol, including impurities as limited in 4.2, must be not less than 95 volume %." This limit has changed very little over the past 25 years; a minimum of 92.1 volume % ethanol is required in the most recent version (2015). Fuel grade ethanol is expected to have minor quantities of water, other alcohols, and denaturants. Organic alcohols and esters common to the ethanol fermentation production process, such as methanol, n-propanol, and isoamyl alcohol (3-methy-1-butanol), are allowed by ASTM D4806; quantities of these organic compounds are restricted indirectly in the specification through limits specified on the remaining other major components (water, methanol, denaturant). Small amounts of methanol can be corrosive to components in the fuel handling system and greatly affect vapor pressure in fuel blends; consequently, methanol content in ASTM D4806 is limited to no more than 0.5 volume %.

The allowable water content in ASTM **D4806** has been restricted to 1.0 volume %, 1.25 mass %, since the very inception of a denatured fuel ethanol specification. The water content limit is accompanied by a precautionary statement that the water content may be further restricted if very low temperature storage and handling concerns are present for the ultimate gasoline ethanol fuel blend. This precautionary statement is focused on preventing gasoline/ethanol phase separation when unacceptable levels of water contamination may be present. Karl Fischer titration, both coulometric and potentiometric, has been used successfully to determine the water content of denatured fuel ethanol.

Several parameters listed in Table 1, Performance Requirements of ASTM **D4806**, are intended to mitigate any contribution to corrosion ethanol may cause. Maximum chloride content allowed in ASTM **D4806** was originally set at 40 parts per million (ppm) by mass due to grave concerns about the strong relation of chlorides to certain instances of metal corrosion. Current ethanol manufacturing practices do not utilize any processing aides that would create any measurable level of chloride; this specification targets any incidental exposure to chlorides throughout the distribution system. Automotive industry experts indicate a greater chance of corrosion with increasing conductive properties in motor fuels-thus the presence of a limit for chloride in ASTM D4806. The original test method used to detect chloride in denatured fuel ethanol was a modified method of Procedure C within the ASTM D512 Test Methods for Chloride Ion in Water. In 2008, ASTM members considered new technology and data regarding acceptable levels of chloride in ethanol blended fuels. Improvement to the analytical methods, namely the development and publication of ASTM D7319, Test Method for Determination of Total and Potential Sulfate and Inorganic Chloride in Fuel Ethanol by Direction Injection Suppressed Ion Chromatography, and ASTM D7328, Test Method for Determination of Total and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection, allowed laboratories to significantly improve the accuracy of chloride detection. This analytical advancement enabled a reduction in the limit of chlorides as data from General Motors came forward indicating that 2 ppm mass chloride spiked into ethanol fuel blends used by flexible fuel vehicles demonstrated damaging effects [4]. The ASTM D4806-08a version of the specification reduced the allowed chloride level to 10 ppm mass maximum, and this limit continues in the most recent version approved in 2015, which ensures a contribution of no more than 1 ppm mass chloride from the ethanol when blending up to 10 volume % ethanol in gasoline.

A limit to the titratable acidity present in denatured fuel ethanol, restricted to 0.007 mass % maximum reported as acetic acid, limits the amounts of organic acids that could be corrosive to many metals. For just over 20 years, the only acceptable method to measure acidity levels in denatured ethanol was a standard titration method using a phenolphthalein endpoint [5]. Recent advancements in titration technology have led to the publication of ASTM D7795, Test Method for Acidity in Ethanol and Ethanol Blends by Titration (2012), introducing automatic titration methods, and to the subsequent recognition of this test method as acceptable for use when determining acidity. For many years, several compounds such as carbon dioxide and common corrosion inhibitors and detergents added to denatured fuel ethanol were known to interfere with the test methodology and resulted in the reporting of potentially inflated levels of acidity. ASTM D4806-12 includes a robust discussion as to the known carbon dioxide interference in the Appendix; and Table 1, Note 3, provides information on effects of fuel additives on titratable acidity.

A new parameter, pHe, appeared in ASTM **D4806-99**, coupled with the publication of ASTM **D6423**, *Standard Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85)*. General Motors [6,7] provided convincing evidence of fuel pump failures when the pHe of ethanol used as a fuel for automotive spark ignition engines is below 6.5. Fuel pump plastic part failures were recorded when the pHe of denatured fuel ethanol was above 9.0. Creation of the term

"pHe" and the establishment of an acceptable range of 6.5 to 9.0, coupled with a published standard test method allowed ASTM Subcommittee D02.A on Gasoline and Oxygenated Fuels to address this concern swiftly. This performance specification continues to appear in the latest version of ASTM D4806.

An open forum on sulfates in ethanol and their effects in the service station filter plugging was held at the June 2005 meeting of Section 1 of Subcommittee D02.A on Gasoline and Oxygenated Fuels. The forum included speakers from the oil, automobile, and ethanol industries; the oil industry presentations identified filter plugging issues at retail service stations and meter deposit issues at terminals, while the automobile industry disclosed a spike in fuel injector repair rates at dealership service departments in several markets. The ethanol industry presentation raised the concerns of failure to present evidence of direct cause and effect from sulfates present in denatured fuel ethanol. Subcommittee D02. A's Balanced Technical Advisory Panel (BTAP) was used as a clearinghouse for any sulfate data submitted, and it eventually succeeded in developing a consensus position by all stakeholders to add a maximum limit of 4 ppm mass sulfate to ASTM D4806. The sulfate parameter was later modified to "existent sulfate" to better reflect the type of sulfates of concern in motor fuels. Supplemental information in the Appendix (X1.1.9) states that the presence of small amounts of inorganic sulfates in denatured fuel ethanol under the right conditions can contribute to turbine meter deposits, premature plugging of fuel dispenser filters, and fuel injector sticking.

ASTM **D4806** also contains general requirements to ensure spark-ignition engine fuel quality expectations such as limits to the amount of sulfur, nonvolatile matter (solvent-washed gums), and copper, as well as a requirement for visual inspection of the fuel's appearance. The U.S. Environmental Protection Agency (EPA) regulates the amount of sulfur that can be present in motor fuels.

5.4 Regulatory Aspects

There are two major U.S. regulatory agencies for denatured fuel ethanol: the TTB and the EPA. There are several facility permit options for ethanol production facilities; however, onerous restrictions on the storage and handling of undenatured ethanol by the TTB compel industry to denature ethanol prior to release from a production facility. The TTB publishes a list of authorized materials suitable for use as denaturants when ethanol is intended for fuel use. (Refer to the regulatory requirements as listed in Title 27 Alcohol, Tobacco Products and Firearms, Part 19, Subpart X, specifically §19.746.) It is important to recognize that the addition of denaturants does not improve the performance of ethanol for motor fuel use; the presence of denaturant strictly eliminates alcohol excise tax liability. The TTB has authorized materials as denaturants for fuels that ASTM D4806 prohibits for use in spark-ignition engine fuels. As a note, the TTB has only approved hydrocarbons produced from crude oil as authorized denaturants, thus bringing environmental concerns regarding the presence of sulfur and benzene that are germane for petroleum-based fuels to denatured fuel ethanol. The quantity of denaturant allowed, both a minimum and a maximum concentration, is strictly regulated by the TTB and EPA, and both are addressed in ASTM requirements.

Detailed information on denaturants appears in Section 5 of ASTM **D4806** and in the Appendix, Section X3.

Whether ethanol is used in oxygenated fuels, reformulated gasoline, or in conventional gasoline, there are certain regulatory parameters that must be considered, mainly sulfur content. The EPA regulates the amount of sulfur present in all motor fuels; denatured fuel ethanol is included in these requirements. Historical data indicate that very little sulfur (less than 2 ppm mass on average) is present in fuel grade ethanol. The EPA acknowledged the sulfur content present in denatured fuel ethanol is attributable to the TTB requirement for a hydrocarbon denaturant [8].

Due to the broad recognition of ASTM **D4806**, many states as well as the model fuel regulations in National Institute of Standards and Technology (NIST) Handbook 130, *Uniform Engine Fuels and Automotive Lubricants Regulation*, adopted by the National Conference on Weights and Measures—require denatured fuel ethanol to meet the ASTM specification. Subcommittee D02.A on Gasoline and Oxygenated Fuels attempts to include any unique requirements by state-level fuel regulations, such as those of the California Air Resource Board (CARB), and this information appears in the Appendix, Section X2.1.

5.5 Workmanship Expectations

The workmanship clause in ASTM **D4806** has been developed to address concerns about atypical production or handling that could render the product unfit for use in finished motor fuel. Denatured fuel ethanol is expected to be a clear, colorless liquid over a broad range of temperatures; color or foreign matter present in an ethanol sample may indicate inappropriate storage or handling conditions needing further investigation.

5.6 Storage Handling and Sampling

Denatured fuel ethanol is expected to be a stable product over long periods of time when protected from environmental effects and ignition sources; these product storage conditions are very similar to those used when handling flammable products. Section 7 of ASTM **D4806** outlines considerations that must be well understood not only to ensure that denatured fuel ethanol samples are collected appropriately for the intended analysis but also to eliminate any contamination of the ethanol by the sample container.

References

- U.S. Energy Information Administration, "Biofuels: Ethanol and Biodiesel *Explained*," U.S. Department of Energy, Washington, DC, 2015, http://www.eia.gov/Energyexplained/Index.cfm? page=biofuel_ethanol_home (accessed March 1, 2016).
- [2] Gibbs, L. M., Basis for ASTM **D4806** Property Limits, written communication to ASTM task group, August 14, 2007.
- [3] ASTM D5501, Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20 % Ethanol by Gas Chromatography, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [4] Clark, S. and Studzinski, W., "Flex Fuel Vehicle Performance and Corrosion Study of E85 Fuel with Chloride Addition," SAE Technical Paper 2010-01-2088, 2010, doi:10.4271/2010-01-2088.
- [5] ASTM D1613, Standard Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [6] Barnes, G. J., "Ethanol Use in the U.S. Motor Fuels Market," presented at the *Renewable Fuels Association, National Ethanol Conference on Ethanol Policy and Marketing*, General Motors Corporation, Chicago, IL, February 1997.
- [7] Halsall, R. and Brinkman, N. D., "U.S. Fuel Ethanol Quality and Its Effects on Vehicle Durability," presented at the SAE International Fall Fuels & Lubricants Meeting, Tulsa, OK, October 1997.
- [8] U.S. EPA, "Control of Air Pollution from Motor Vehicles: Tier 3 Motor Vehicle Emission and Fuel Standards, V. Fuel Program, G. Standards for Oxygenates (Including Denatured Fuel Ethanol) and Certified Ethanol Denaturants," *Federal Register*, Vol. 79, No. 81, April 28, 2014.

Chapter 6 | Discussion on Uses of the Specification for Ethanol Fuel Blends (ASTM **D5798**)

Kristin A. Moore¹

6.1 Introduction

Ethanol debuted as the primary component in certain motor fuel blends in the early 1990s. These high-ethanol-content fuel blends are restricted for use in flexible-fuel vehicles, sometimes referred to as "dual-fueled vehicles" or "variable fuel vehicles." A flexible-fuel vehicle (FFV) is one that can operate on gasoline containing no ethanol, fuel blends of 85 % by volume denatured fuel ethanol, or any combination of the two [1]. Describing the performance and compositional characteristics for a predominantly ethanol motor fuel is the goal of ASTM D5798, Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines (referred to as Specification D5798 or more simply ASTM D5798). The title purposely includes the term "ethanol fuel blends," which was created by ASTM International's D02 Petroleum Products, Liquid Fuels, and Fossil Fuels Committee and was the direct responsibility of Subcommittee D02.A on Gasoline and Gasoline-Oxygenate Blends, specifically to distinguish this predominately ethanol motor fuel from denatured fuel ethanol, which is described by ASTM D4806.

6.2 History of ASTM D5798

ASTM D5798 was first drafted in 1995 and describes an automotive fuel blend that is "nominally 75 to 85 volume % denatured fuel ethanol and 25-15 additional volume % hydrocarbons." ASTM D5798 contains the necessary details to blend a fit-for-purpose motor fuel for flexible-fuel vehicles while providing guidance on regulatory requirements for alternative fuels and identification of key considerations to ensure acceptable performance for consumers. The U.S. Energy Policy Act of 1992 (EPAct 1992) established the alternative fuel definition for denatured ethanol as "mixtures containing 85 percent or more (or such other percentage, but not less than 70 percent) ... is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits" [2]. ASTM D5798 was modeled after requirements developed by stakeholders promoting the use of E85, a blend of 85 % denatured fuel ethanol and 15 % hydrocarbons which are typically gasoline, and the thorough research completed by

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General Motors on the properties needed for high-ethanol and high-methanol-content fuels [3]. ASTM D5798 was originally created to outline the performance properties and limits for a high blend of ethanol as an alternative fuel; the specification captured the market term "E85" but used the more descriptive term "Ed85." EPAct 1992 allowed for variation of the alternative fuel component to provide for requirements relating to cold start, safety, or vehicle function; ethanol has an extremely low vapor pressure that must be elevated for spark-ignition fuel applications. A specification for a predominately methanol motor fuel blend (M85), ASTM D5797, preceded the development of ASTM D5798. Elements of the M85 specification influenced many of the requirements that were included in the ASTM D5798 specification, including the maximum ethanol content of 85 % denatured fuel ethanol [4]. ASTM D5798 has evolved over multiple decades on a path of continuous improvement.

The first efforts at ASTM International related to ethanol fuel blends were based on the performance, storage, and handling information that was published by numerous government and industry studies; this was an admirable effort to aggregate this information into a single document. Experts in the field realized early on that the properties described in the ASTM Specification D4806 [5] for fuel ethanol as a gasoline additive were insufficient in describing all of the properties needed when ethanol is used as the primary fuel component. The California Air Resources Board (CARB) published one of the initial fuel specifications for E85, circa 1992. Another publication of important E85 properties and limits was the research outlined in the SAE Technical Paper 940764: "The Development of Improved Fuel Specifications for Methanol (M85) and Ethanol (Ed85)" by General Motors engineers. Importantly, many of the early prescribed attributes of E85 were mirrored after data and insight gained with the development of M85, a blend of 85 % by volume methanol and 15 % by volume hydrocarbons. In order to ensure acceptable and safe vehicle performance of E85, cold start and flammability concerns were a primary area of focus for both M85 and E85.

Comparison of the 1995 and most current version of ASTM **D5798** indicates a significant increase in the understanding of the performance needs of ethanol fuel blends by the vehicles designed to operate on this fuel. Referenced documents in Section 2 of the 2014 version of ASTM **D5798** show extensive development of new

standard test methods for high ethanol fuel blends. In the early years, many petroleum-based test methods were used when analyzing high ethanol fuel blends; sometimes great modification to the method elements were needed due to the chemical differences between hydrocarbons and alcohols. Significant progress in both the understanding of the chemical properties and advancements in analytical technology have improved the analytical techniques available to characterize these fuel blends.

The nomenclature describing a high-ethanol-based fuel has evolved over the years from the historical designation "E85" to the modern day "ethanol flex fuel." The first term for a predominately ethanol motor fuel was "Fuel Ethanol (Ed75-Ed85)" or simplified in the marketplace to "E85." The former term, Ed75-Ed85, indicated the ethanol (capital E) was denatured, lower case d, and followed by the maximum volume percentage of ethanol in the blend. When the maximum denatured ethanol content was 75 % by volume, the term Ed75 would be used. In 2010, a broad-based stakeholder group-including ASTM Subcommittee D02.A, developed the term "ethanol flex fuel" in coordination with the expansion of the allowable ethanol content in ASTM D5798. The U.S. Department of Energy's Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends, a widely used reference for blenders, adopted the "flex fuel" label as of the 2013 version [6]. The National Conference of Weights and Measures incorporated the name "ethanol flex fuel" into its model regulations in 2014.

It is important to remember that denatured fuel ethanol is required to contain between 2 and 5 % by volume of an approved denaturant to avoid any beverage alcohol tax implications [5]. The denaturant volumes present in ethanol fuel blends are ultimately combined in the total hydrocarbon volume of the blend. Undenatured ethanol may perform acceptably in FFVs when combined with gasolines; however, the U.S. Alcohol and Tobacco Tax and Trade Bureau (TTB, formerly Alcohol Tobacco and Firearms [ATF]) assesses a substantial alcohol excise tax on all undenatured ethanol (currently set at \$27 per gallon), creating a significant economic disincentive to distribution and to the use of undenatured alcohol.

6.3 Performance Requirements

ASTM **D5798** outlines the properties of a high-ethanol fuel blend necessary to ensure acceptable vehicle performance under a broad range of geographies and varying climates. Determining acceptable volatility of the ethanol fuel blend for all of the various geographies and climatic conditions has been an ongoing challenge over the years [7]. In order to provide proper performance while mitigating cold start and flammability concerns, the volatility of ethanol fuel blends must be adjusted based on historical climate conditions and altitude. Numerous industry-sponsored vehicle studies over the last 20 years [8] have continued the evolution of improvements to the allowed ethanol content and required vapor pressures. Similar to the seasonal volatility changes required of gasolines, ethanol fuel blends follow a "seasonal and geographical volatility" schedule (see Table 3 of ASTM **D5798** to identify the appropriate seasonal class in the United States). Vapor pressure of the ethanol fuel blend is increased at lower temperatures and decreased at warmer temperatures to ensure adequate vehicle operability. Based on the volatility of the hydrocarbons used in the blend, the ratio of ethanol and hydrocarbons is adjusted to meet the vapor pressure requirements of the final fuel blend.

The concentration of ethanol in the flex fuel blend affects many different attributes: volatility, water solubility, establishment of proper air/fuel mixture for optimum vehicle operation, and flammability. Performance effects are discussed in greater detail later in this chapter. Expanding on the flammability concerns-all flammable liquids vaporize, creating a headspace that could possibly ignite under optimal temperature. In this case, flammability concerns stem from the possibility that certain ethanol fuel blends have low enough vapor pressures that a flammable mixture could result in the headspace of an enclosure at lower temperatures. The volatility classes included in ASTM D5798 require high volatility fuel in low temperature conditions, thus mitigating the probability of flammable vapors at sufficient concentration to allow ignition. Auto manufacturers have also taken steps to mitigate any possibility of vehicle tank ignition, including the installation of flame arrestors in fuel filler neck and using non-ignitable electronic fuel system components.

The initial version of ASTM **D5798** allowed three seasonal volatility classes in the United States:

- Class 1, with a minimum of 79 % ethanol by volume for summer temperature conditions
- Class 2, with a minimum of 74 % ethanol by volume for spring/ fall temperature conditions
- Class 3, with a minimum of 70 % ethanol by volume for cold winter temperature conditions

The three seasonal class designations continued in the ASTM **D5798** specification with very minor changes over the years. However in 2010, ASTM Subcommittee D02.A undertook a significant review of the specification. The resulting 2011 version of ASTM **D5798** expanded the allowable ethanol content range, added another volatility class, and improved the volatility information in the appendix of the specification (see **Table 6.1**).

The most significant change in the 2011 version was the reduction of the minimum ethanol content to 51~% by volume for

TABLE 6.1	Comparison of ASTM D5798 specification versions
	1995 and 2011.

ASTM D5798 Specification Version	Seasonal Classes	Vapor Pressure, kPA (psi)	Ethanol Content
1995	Class 1	38-59 (5.5-8.5)	79 % vol., minimum
	Class 2	48-65 (7.0-9.5)	74 % vol., minimum
	Class 3	66-83 (9.5-12.0)	70 % vol., minimum
2011	Class 1	38-59 (5.5-8.5)	51-83 %
	Class 2	48-65 (7.0-9.5)	
	Class 3	59-83 (8.5-12.0)	
	Class 4	66-103 (9.5-15.0)	

all volatility classes, thereby eliminating the per class minimum ethanol requirement. This major overhaul of the volatility requirements of ASTM **D5798** was initiated by a realization that summertime gasoline volatility has significantly decreased over time, affecting ethanol fuel blend's volatility and creating a marketplace inability to meet minimum vapor pressure requirements under the constrains of prescribed ethanol content [9]. ASTM Subcommittee D02.A, specifically the D5798 Task Force, remained true to the spirit of this specification, retaining predominately ethanol fuel blends for all classes. Through consideration of available marketplace hydrocarbon gasoline and gasoline blendstocks, expected seasonal volatility class requirements led to the standardization of 51–83 % ethanol content by volume for each seasonal volatility class.

The concentration of ethanol can be identified with a laboratory instrument such as a gas chromatograph as outlined in ASTM D5501, Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20 % Ethanol by Gas Chromatography [10]. Ethanol content has been included in ASTM D5798; however, the test method for ASTM D5501 was modified in 2012 to include ethanol blends with a minimum of 20 % ethanol by volume. Organic alcohols and esters common to the ethanol fermentation production process, such as n-propanol and isoamyl alcohol (3-methy-1-butanol), are allowed by ASTM D5798; early versions of ASTM D5798 limited the "higher alcohols" to a maximum 2 % by volume, which was ultimately deemed unnecessary. Small amounts of methanol can be corrosive to components in the fuel handling system and greatly affect vapor pressure in fuel blends; methanol content in ASTM D5798 is limited to no more than 0.5 % by volume.

The components used to blend ethanol fuel blends are restricted to denatured fuel ethanol and hydrocarbon blendstock. The hydrocarbon blendstock may be gasoline, gasoline blendstock for oxygenated blending (BOB), natural gasoline, or other hydrocarbons in the gasoline boiling range. Table 2 of the 2014 version of ASTM D5798 lists volatility requirements including knowing the vapor pressure of the hydrocarbon blendstock used in the fuel. The blender of the ethanol flex fuel will need to know the hydrocarbon vapor pressure in order to choose a suitable blend ratio to ensure performance attributes of the final ethanol flex fuel blend. When using gasoline that is blended with ethanol as the hydrocarbon blendstock (e.g., E10), the blender will need to make an adjustment for this additional ethanol content in the final blend ratio. Importantly, there are currently no ASTM or other analytical methods to accurately measure the hydrocarbon content in the finished ethanol flex fuels.

The maximum water content in ethanol fuel blends has been restricted to 1.0 mass % maximum since the very inception of ASTM **D5798**. The water content limit is an effort to reduce the potential for water-related contamination that may cause vehicle operability problems. Water contamination far in excess of this specification limit would also lead to gasoline-ethanol phase separation concerns. Karl Fischer titration, both coulometric and potentiometric, has been used successfully to determine the water content of ethanol fuel blends.

Several parameters listed in Table 1 of the ASTM D5798 performance requirements are intended to mitigate corrosion to vehicle fuel systems, specifically acidity and chlorides. Titratable acidity is restricted to 0.005 % by mass maximum reported as acetic acid; this limits organic acids that could be corrosive to metals. For more than 20 years, the only acceptable method to measure acidity levels in denatured ethanol was a standard titration method using a phenolphthalein endpoint [11]. Recent advancements in titration technology have led to the publication of ASTM D7795, Test Method for Acidity in Ethanol and Ethanol Blends by Titration (2012), which introduces automatic titration methods and establishes them as acceptable for use when determining acidity. The maximum chloride content allowed in ASTM D5798 is 1 mg/kg. Current ethanol manufacturing practices do not utilize any processing aides that would create any measurable level of chloride ions; this specification targets any incidental exposure to chlorides throughout the distribution system. Automotive industry experts [12] indicate a greater chance of corrosion with increasing conductive properties in motor fuels-thus, the presence of a limit for chloride in ASTM D5798. Improvement to the analytical methods, namely the development and publication of ASTM D7319, Standard Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography and ASTM D7328, Standard Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection, allowed laboratories to significantly improve the accuracy of chloride detection.

The acid strength (or "pHe") requirement appeared in ASTM **D5798-99**, which was coupled with the publication of ASTM **D6423**, *Standard Test Method for Determination of pHe of Denatured Fuel Ethanol and Ethanol Fuel Blends. General Motors* **[13,14]** provided convincing evidence of fuel pump failures when the pHe of ethanol used as a fuel component for automotive spark-ignition engines was below 6.5. Fuel pump plastic part failures were recorded when the pHe of denatured fuel ethanol was above 9.0. Creation of the term "pHe" and establishment of an acceptable range of 6.5 to 9.0 with a published standard test method allowed ASTM Subcommittee D02.A on Gasoline and Oxygenated Fuels to address this concern simultaneously in both ASTM **D4806** and ASTM **D5798**. This performance specification continues to appear in the latest version of ASTM **D5798**.

ASTM **D5798** also contains general requirements to meet spark-ignition engine fuel quality expectations such as limits to the amount of sulfur, nonvolatile matter (solvent-washed gum content and unwashed gum content), and copper, as well as a requirement for visual inspection of the fuel's appearance. The U.S. Environmental Protection Agency (EPA) regulates the amount of sulfur that can be present in motor fuels. Importantly, users of both ASTM **D4806** and ASTM **D5798** must recognize the similarities and the subtle differences in each of these specifications. Both specifications are ethanol-related specifications; however, the specifications are mutually exclusive in application and contain independent performance table requirements. As an example, a denatured fuel ethanol meeting the limits for chloride content in ASTM **D4806** with maximum limit of 10 mg/kg may not be suitable for blending a predominately ethanol fuel blend meeting ASTM **D5798** with a maximum limit of 1 mg/kg.

6.4 Regulatory Discussion

Ethanol fuel blends can be considered an alternative fuel as defined by the Department of Energy [15]; U.S. federal fleets are required to use alternative fuels when available. To qualify as an alternative fuel for federal fleet usage, the ethanol blend is required to meet one of the definitions for ethanol as an alternative fuel. For ethanol, EPAct 1992 [15] defines a fuel "containing denatured ethanol as a volume of 85 percent or more (or such other percentage, but not less than 70 percent as determined by the Secretary, by rule, to provide for requirements relating to cold start, safety or vehicle functions)..." An alternative fuel, as defined by the Department of Energy, "is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits." Implied in this definition is the volume of denaturant that must be subtracted from the total denatured ethanol volume for a more accurate reporting of the total ethanol content.

Due to the broad recognition of ASTM **D5798**, many states as well as the model fuel regulations in NIST Handbook 130 *Uniform Engine Fuels and Automotive Lubricants Regulation* adopted by the National Conference on Weights and Measures require ethanol fuel blends to meet the ASTM **D5798** specification.

6.5 Ordering Information

To ensure the appropriate seasonal class of ethanol flex fuel is ordered, the purchasing agency must indicate the ultimate geographical use of the product and time of delivery to ensure the appropriate volatility class of fuel is blended and delivered. Management of inventory turnover must also be a consideration when ordering ethanol fuel blends, particularly if slow-moving inventory will result in inappropriate volatility in the season it is ultimately consumed. Primarily, a cold, winter concern, slow inventory turnover must be taken into account when ordering deliveries to anticipate a seasonal volatility change when inventory is anticipated to be consumed.

6.6 Workmanship Expectations

ASTM **D5798**'s Workmanship section requires that ethanol flex fuels be visibly free of sediment and suspected matter; this requirement is designed to guard against contamination that may clog fuel filters, fuel lines, and other fuel system components. A broad statement regarding the avoidance of adulterants and contaminants is intended to prevent any negative consequences of using materials unacceptable for spark-ignition engines. Ethanol flex fuels must not be blended from silicon-containing materials; silicon contamination of motor fuels has led to fouling of vehicle components such as spark plugs, exhaust oxygen sensors, and catalytic converters.

6.7 Sampling, Containers, and Sample Handling

Ethanol fuel blends are expected to be stable over long periods of time when protected from environmental effects and ignition sources. These product storage precautions are very common when handling flammable products. ASTM **D5798** outlines considerations that must be well understood to ensure not only that samples are collected appropriately for the intended analysis but also to eliminate any contamination by the sample container. A minimum sample quantity of 1 litre is recommended as a starting point for general analysis.

References

- [1] U.S. Department of Energy, Energy Efficiency & Renewable Energy, "Flexible Fuel Vehicles: Providing a Renewable Fuel Choice," DOE/GO-102010-3002, U.S. Department of Energy, Washington, DC, 2010.
- [2] U.S. Department of Energy, Energy Efficiency & Renewable Energy, Alternative Fuels Data Center, "Key Federal Legislation," 2014, http:// www.afdc.energy.gov/laws/key_legislation (accessed March 1, 2016).
- Brinkman, N., Halsall, R., Jorgensen, S., and Kirwan, J., "The Development of Improved Fuel Specifications for Methanol (M85) and Ethanol (Ed85)," SAE Technical Paper 940764, 1994, doi:10.4271/940764
- [4] ASTM D5797, Standard Specification for Fuel Methanol for Use in Spark-Ignition Engines, ASTM International, West Conshohocken, PA, 2007, www.astm.org
- [5] ASTM D4806, Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [6] U.S. Department of Energy, Energy Efficiency & Renewable Energy, Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends, DOE/GO-102013-3861, U.S. Department of Energy, Washington, DC, 2013.
- [7] Reynolds, R., "The Importance of Seasonal Volatility Adjustments for E-85 Ethanol Gasoline Blends," Information Paper 980202, Renewable Fuels Foundation, Washington, DC, 1998.
- [8] Coordinating Research Council, "2008 CRC Cold-Start and Warmup E85 Cold Ambient Temperature Driveability Program," CRC Report No. 654, Coordinating Research Council, Alpharetta, GA, 2009.
- [9] Renewable Fuels Association, "E85 Fuel Ethanol Industry Guidelines, Specifications, and Procedures," Renewable Fuels Association, Washington, DC, 2009.
- [10] ASTM D5501, Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20 % Ethanol by Gas Chromatography, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [11] ASTM D1613, Standard Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products, ASTM International, West Conshohocken, PA, 2012, www.astm.org

- [12] Clark, S. and Studzinski, W., "Flex Fuel Vehicle Performance and Corrosion Study of E85 Fuel with Chloride Addition," SAE Technical Paper 2010-01-2088, 2010, doi:10.4271/2010-01-2088
- [13] Barnes, G. J., "Ethanol Use in the U.S. Motor Fuels Market," presented at the *Renewable Fuels Association, National Ethanol Conference on Ethanol Policy and Marketing*, General Motors Corporation, Chicago, IL, February 1997.
- [14] Halsall, R. and Brinkman, N. D., "U.S. Fuel Ethanol Quality and Its Effects on Vehicle Durability," presented at the SAE International Fall Fuels & Lubricants Meeting, Tulsa, OK, October 1997.
- [15] H.R. 776–102nd Congress, Energy Policy Act of 1992, U.S. Department of Energy, Title III, Section 301.

Chapter 7 | Discussion on Uses of the Specification for Butanol for Gasoline Blending (ASTM **D7862**)

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7.1 History of ASTM Specification ASTM **D7862**

It has been critical to the successful development of gasoline and gasoline-powered vehicles to have consensus among refiners, vehicle manufacturers, and other interested parties on the characteristics of gasoline necessary for satisfactory performance and reliable operation. This consensus is reached in the United States under the auspices of ASTM International (formerly the American Society for Testing and Materials). The Butanol Task Group under ASTM Section D02.A.02, Oxygenated Fuels and Components, was created in December 2010 in response to a request to establish a fuel quality standard governing the use of butanol in motor fuels. An ASTM collaboration site was set up to coordinate the development. The Butanol Task Group developed numerous drafts that were circulated for review and comment. Teleconferences were held to discuss the various proposed changes to wording and content. After a number of ballots and negative resolutions, ASTM issued a new specification ASTM D7862-13, Standard Specification for Butanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel [1].

The new specification covers butanol intended to be blended with gasoline at 1 to 12.5 % by volume for use as an automotive spark-ignition engine fuel. The new specification establishes performance requirements and test methods for butanol content, water content, acidity, inorganic chloride, solvent-washed gum, sulfur content, and total sulfate. The U.S. Environmental Protection Agency (EPA) under its "substantially similar" rule, permits the addition of butanol up to a maximum 2.7 % by mass oxygen. Consequently, the limits of some trace contaminants in butanol listed in Table 1 of ASTM D7862 [1] are predicated on a maximum of 12.5 % by volume butanol usage in gasoline. Registration is pending before the EPA to permit the addition of higher levels of butanol in gasoline as an allowable oxygenate in gasoline. If and when such permission is granted, this specification would be re-balloted to allow a higher concentration of butanol, with correspondingly lower limits for some contaminants.

When written, ASTM D7862 [1] included test methods for water content, acidity, solvent-washed gum, and sulfur content.

When ASTM **D7862** [1] was adopted, two ASTM analytical test methods, ASTM **D7319** [2] and ASTM **D5501** [3]—then applicable to denatured ethanol—were being updated to provide for the inclusion of butanol.

However, because butanol initially was not included in the scope of the methods, as an interim measure, two annexes were provided to enable a test method for determining levels for limits outlined in Table 1 of ASTM **D7862** [1]. Those two annexes were:

- Annex A1, "Test Method for Determination of Butanol and Acetone Content of Butanol for Blending with Gasoline by Gas Chromatography"
- Annex A2, "Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography"

Both of those annexes subsequently were removed from ASTM **D7862** [1] because the specifications passed the appropriate ASTM **D02** analytical testing methods subcommittees. The two annexes were converted into the following ASTM specifications:

- Replacement of Annex A1 with ASTM **D7875**, *Standard Test Method for Determination of Butanol and Acetone Content of Butanol for Blending with Gasoline by Gas Chromatography* [4]
- Replacement of Annex A2 with ASTM D7319, Standard Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography [2]

7.2 History of Butanol

Butanol production via anaerobic bacteria fermentation has been observed since 1861, when it was witnessed by Pasteur [5]. During anaerobic bacteria fermentation processes, butanol is a single product among many. Another result is the production of acetone, which was first witnessed in 1905 by Schardinger [6]. By the beginning of the twentieth century, interest in butanol had risen sharply. This was due to butanol's involvement in the solution to a material shortage of natural rubber that had struck society, resulting in efforts being undertaken to make a synthetic rubber. It was found that butadiene or isoprene rubber could be synthesized from butanol or isoamyl alcohol, another fermentation product.

^{&#}x27;Gevo, Inc., 345 Inverness Dr. South, Englewood, CO 80112 DOI: 10.1520/MNL6920150007

This discovery stimulated great interest in anaerobic fermentative processes for compound production.

Between 1912 and 1914, Chaim Weizmann, a chemist, performed one of the first microorganism screenings to study microbiology in hopes of better understanding the fermentation process [7]. One species he isolated, *Clostridium acetobutylicum*, was able to yield more acetone and butanol than previous species while feeding on a larger range of biomass.

The next advancement occurred during World War I, when the British army needed to produce smokeless gun powder in far larger amounts than importing could handle. In order to produce the smokeless powder, or cordite, acetone was required as a colloidal solvent. To solve the problem, the British army sought the help of Weizmann. He designed a system to increase acetone production via fermentation, which was later adopted by Great Britain and implemented at the Royal Naval Cordite Factory. Once the United States joined the war, a joint project of the United States and Great Britain was undertaken to produce acetone in the U.S. Midwest. The result was the opening of two acetone production facilities that closed in less than a year.

After World War I ended, large stockpiles of butanol had been built up as a by product of the acetone production. This stockpile was used by E.I. du Pont de Nemours & Co. as a solvent for a nitrocellulose lacquer, which was a quick-drying automobile finish. Also, the acetone production facilities that had been used during the war were purchased and reopened in order to produce butanol.

When Weizmann's patent expired in 1936, a flood of anaerobic fermentation plants were opened. Molasses fermentation processes grew in popularity as new microorganisms were isolated. Every company had its own unique patented microorganism that was able to produce acetone and butanol from molasses in great amounts.

The next spike in fermentation utility occurred during World War II, when acetone was again needed for munitions production [8]. Acetone production from molasses was set to the highest sustainable rates—and even higher, in some places. Great Britain actually had to import its molasses, and the United States eventually reverted to corn mash. Other companies involved in acetone production included India, Australia, South Africa, and Japan. Fermentation processes finally began to experience a decline after the end of World War II and came to a screeching halt in the United States by the 1960s. By this time, petrochemical production of solvents became much easier and cheaper, and farmer interests caused molasses prices to increase dramatically. The combination of these events made fermentative production of acetone and n-butanol inefficient and uneconomical. The use of butanol in gasoline goes back to the 1970s–1980s and has been approved under Section 211(f) of the Clean Air Act through the "Arconol," "DuPont," and "Octamix" waivers. At that time, tert-butyl-alcohol (TBA), a man-made material, was the prime butanol used, although research suggests that isobutanol was also being evaluated. These butanols were produced from petroleum processes: Both n-butanol and isobutanol were produced using a hydroformylation process (also referred to as the oxo process), and TBA was a by-product of the propylene oxide process.

7.3 Isomers

Butanol has four different isomers. However, only three are commercially important for the fuel space because t-butanol is a solid at room temperature and currently is not included in the scope of ASTM **D7862** [1]. The three isomers (Fig. 7.1) included in the scope are 1-butanol (n-butanol), isobutanol (2-methyl-1-propanol), and sec butanol (2-butanol) (Table 7.1).

7.4 Performance Requirements

ASTM D7862 [1] establishes performance requirements and test methods for butanol content, water content, acidity, inorganic chloride, solvent-washed gum, sulfur content, and existent sulfate. In formulating the new standard specification, the consensus of the ASTM Butanol Task Group was that the sources of butanol most likely to be used for gasoline blending are fermentation-based processes generally similar to those employed for the production of fuel-grade ethanol. Accordingly, the task group took guidance from ASTM D4806, Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel [9], in identifying contaminants most likely to be of concern and in setting specification limits for those contaminants. Because the scope of this proposed new specification permits blending up to 12.5 % by volume, the levels of specified contaminants were adjusted relative to ASTM D4806 [9] (which currently considers blends of up to 10 % by volume). For impurities expected in butanol but not present in fuel ethanol, the task group took input from its membership based on relevant historical experience and used that for the limits as explained here.

 Butanol, vol % min—Level set consistent with current capabilities of manufacturing processes and permitted impurities. As is the case with ASTM D4806, there is no explicit limitation on fusel oil content, but the specification of major and minor components effectively limits the fusel oil concentration.





TABLE 7.1	Comparison o	f butanol	isomers inclu	ded in ASTM D7862 .
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Comparison of Butanol Isomers [10-12]			
Property	1-Butanol	2-Butanol	2-Methyl-1-propanol
CAS Number	71-36-3	78-92-2	78-83-1
Other (non IUPAC) Names	n-butyl alcohol	sec-butyl alcohol	Isobutyl alcohol
Density (kg/m ³)	809.8	806.3	801.8
Research Octane Number (RON)	96	101	113
Motor Octane Number (MON)	78	82	94
Melting Point (°C)	-89.5	-114.7	-108
Boiling Temperature (°C)	117.7	99.5	108
Enthalpy of Vaporization at $T_{\rm boil}$ (kJ/kg)	584	550	564
Flash Point	35°C (95°F)	24ºC (75ºF)	28°C (82ºF)
Autoignition Temperature	345°C (653°F)	406ºC (763ºF)	415ºC (779ºF)
Flammability Limits			
Lower Limit (Vol %)	1.4	1.7	1.2
Upper Limit (Vol %)	11.2	9.8	10.9

Note: CAS (Chemical Abstracts Services) Registry Number is assigned to a substance when it enters the CAS REGISTRY database and is a numeric identifier that can contain up to 10 digits.

IUPAC (International Union of Pure and Applied Chemistry) nomenclature is developed so that any compound can be named under one set of standardized rules to avoid repeat names.

Because the different isomers are chemically different, the identification of the isomer mix is specified as a report item. In regards to t-butanol, no limit is directly placed on the isomer, but an indirect maximum limit of less than 4 % by volume does exist due to the specifications in Table I for all other species.

- Methanol, vol % max—ASTM D4806 [9] permits a maximum of 0.5 % by volume. Setting this specification at 0.5 vol % max ensures that a 12.5 vol % blend of butanol with gasoline will have no more methanol than a 10 vol % blend of ethanol with gasoline.
- Water, vol % max—ASTM D4806 [9] permits a maximum of 1.0 % by volume. To protect against the phase separation of dissolved water at colder temperatures, this same level was maintained for the butanol specification.
- Acidity, mass % max—This is set at the same limit as ASTM D4806 [9].
- Inorganic chloride, mg/kg max—ASTM **D4806** [9] limits inorganic chlorides to 10 mg/kg. Setting this specification at 8 mg/kg max ensures that a 12.5 % by volume blend of butanol with gasoline will have no more chlorides than a 10 vol % blend of ethanol with gasoline.
- Solvent washed gum, mg/100mL max—This specification is set at the same level as ASTM D4814 [13] and ASTM D4806; hence, no adjustment for blend percentage is required.
- Sulfur, mg/kg max—The 30 mg/kg max specification matches the average sulfur requirement for U.S. gasoline as set by current EPA regulations. This has been set to protect against engine wear, deterioration of engine oil, corrosion of exhaust system parts, and a temporary reduction in the efficiency of the converter catalyst.
- Existent sulfate, mg/kg max—This specification is set at the same limit as ASTM D4806 [9].

TABLE 7.2 ASTM D7862 Table 1 requirements.

Property	Limit	Method
Butanol, volume %, min	96.0	ASTM D7875
1-Butanol, volume %	Report	ASTM D7875
2-Butanol, volume %	Report	ASTM D7875
2-Methyl 1-propanol, volume %	Report	ASTM D7875
Methanol, volume % max	0.4	ASTM D7875
Water content, volume %, max	1.0	ASTM E203 or ASTM E1064
Acidity (as acetic acid CH ₃ COOH), mass % (mg/L), max	0.007 (56)	ASTM D1613
Inorganic chloride, mg/kg (mg/L), max	8 (6)	ASTM D7319
Solvent-washed gum, mg/100 mL, max	5.0	ASTM D381
Sulfur, mg/kg (mass ppm), max	30	ASTM D2622 , ASTM D5453
Existent sulfate, mg/kg (mass ppm), max	4	ASTM D7319

The Table 1 requirements in ASTM D7862 [1] are shown here in Table 7.2.

7.5 Regulatory Discussion

ASTM **D7862** [1] will further the commercialization of a new renewable fuel and will provide a fuel-quality standard to govern the production and marketing of butanol. Butanol has a number of benefits as a blending agent in gasoline and is compatible with existing vehicles and refueling infrastructure. Butanol offers a high blending value due to its low vapor pressure, high octane number, and distillation properties.

In 2005, Congress passed the Energy Policy Act (EPACT), which required the establishment of renewable fuel standards (RFS). In December 2007, Congress passed the Energy Independence and Security Act of 2007 (EISA), which changed the categories and volumes of renewable fuels required under the RFS (commonly referred to as RFS2). RFS2, mandated by EISA, requires that annual renewable fuel use in the transportation sector be at least 15.2 billion gallons in 2012 and at least 36 billion gallons by 2022. One item to note is that the gallon requirement as stated is not actually liquid gallons of renewable fuel, but it allows for an energy density factor when calculating the compliance through a renewable identification number (RIN). Some folks will commonly refer to the gallons as RIN gallons because they take into account the energy density of the renewable fuel. Due to its energy density, butanol received 1.3 RINs per liquid gallon. Under the RFS program, butanol can either qualify as a conventional, advanced, or cellulosic biofuel depending on the feedstock (corn, sugarcane, and lignocellulosics) used to produce the butanol.

In 1981, the EPA issued the "substantially similar" rule, recognizing that the use of certain types of oxygenates was safe below specified oxygen content. The rule, as revised in 1991, allows aliphatic alcohols (excluding methanol, but including butanol) to be blended into gasoline up to a concentration that would result in 2.7 mass percent oxygen in the blend. The rule requires the finished blend to possess all the physical and chemical characteristics of an unleaded gasoline specified by ASTM **D4814-88** for at least one of the seasonal and geographic volatility classes.

A manufacturer of an additive for use in motor vehicle gasoline may not sell, offer for sale, or introduce into commerce such additive unless it has been registered by the EPA in accordance with the regulations at 40 CFR 79. Any fuel or fuel additive registered with the EPA must have a supplemental registration involving toxicity that may require additional toxicity testing. Oxygenates that were not initially registered now will require full toxicity studies to be completed before they can be used. According to the EPA's public Web site, there are various companies who have registered isobutanol and n-butanol (40 CFR Part 79) for use in on-road motor vehicle gasoline. (Tier I and Tier II testing is not listed on the EPA Web site; please check with the manufacturer regarding their part 79 registration and any limitations.)

The EPA regulations also created a process by which a waiver could be granted for an oxygenate recipe that an applicant has demonstrated will not cause or contribute to the failure of any emission control device or system. Under this waiver system, the EPA has granted waivers for blends of gasoline and gasoline grade tertiary butyl alcohol (TBA) up to 3.5 mass percent oxygen content (16 volume percent TBA) and for various blends of methanol and gasoline-grade TBA or other higher molecular weight alcohols (cosolvents). An EPA waiver is not an exemption from the registration requirements under 40 CFR Part 79, including—but not limited—to Tier I and Tier II toxicology testing.

Underwriters Laboratories Inc. (UL) has approved isobutanol for fuel storage and dispensing products certified to UL Subject 87A. This is up to 16 percent isobutanol by volume (iBu16), and the isobutanol must be compliant with ASTM **D7862**.

7.6 Workmanship Expectations

The intent of a workmanship statement regarding additives to gasoline is to make sure the final blend meets the criteria as stated in ASTM **D4814**, "To be free of adulterant or contaminant that may render the fuel unfit for purpose" [**13**]. To help ensure the end gasoline is visually free of undissolved water, sediment, and suspended matter, the butanol undergoes a visual quality check by the butanol manufacturer. The sample is placed in a clear glass jar and inspected for undissolved water, sediment, and suspended matter. For gasoline, the inspection is done at ambient temperature or 21°C (70°F), whichever is higher. Acceptable butanol is reported to be clear, bright, and free of suspended material.

Silicon is a contaminant and, depending on where the contamination occurs along the supply chain, the repercussions can be engine problems. Manufacturers and importers of butanol must avoid butanol contaminated by silicon-containing materials. Silicon contamination of gasoline-oxygenate blends has led to fouled vehicle components (for example, spark plugs, exhaust oxygen sensors, and catalytic converters) requiring parts replacement and repairs.

There are two main commercial technologies deployed in the world to ferment sugar into butanol. One way is through direct fermentation of the sugar to isobutanol. Another way is through a process involving acetone–n-butanol–ethanol that is called "ABE." This process uses bacterial fermentation to produce three products instead of one in the same fermentation broth. It was developed by the chemist Chaim Weizmann and was the primary process used to make acetone during World War I [7]. Because acetone contamination of gasoline-oxygenate blends can degrade elastomers used in fuel system components as well as paint and clearcoat finishes used on vehicles, manufacturers and importers of butanol must avoid butanol contaminated by acetone.

7.7 Storage Handling

Butanol should always be kept away from fire, sparks, and heated surfaces. No smoking should be allowed near areas where butanol is stored or handled. The butanol should only be stored and handled in areas with an intrinsically safe electrical classification. Flammable liquids such as pure butanol can act as a non-conductive flammable liquid (or static accumulator) and may form ignitable vapor-air mixtures in storage tanks or other containers. Precautions to prevent static-initiated fire or explosion during transfer, storage, or handling include but are not limited to:

- Containers should be grounded and bonded during product transfers. Grounding and bonding may not be adequate protection for preventing ignition or explosion of hydrocarbon liquids and vapors that are static accumulators.
- (2) Special slow load procedures for "switch loading" must be followed to avoid the static ignition hazard that can exist when higher flash point material (such as fuel oil or diesel) is loaded into tanks previously containing low flash point products (such as gasoline or naphtha).

(3) Storage tank level floats must be effectively bonded. For more information on precautions to prevent staticinitiated fire or explosion, see the National Fire Protection Association's NFPA 77, *Recommended Practice on Static Electricity* (2007) and the American Petroleum Institute's (API) *Recommended Practice 2003, Protection against Ignitions Arising Out of Static, Lightning, and Stray Currents* (2008).

Additional precautions include keeping away from flame, sparks, excessive temperatures, and open flame and using only approved containers. Containers should be kept closed and clearly labeled at all times. Empty or partially full product containers or vessels may contain explosive vapors. Do not pressurize, cut, heat, weld, or expose containers to sources of ignition, and store them in a well-ventilated area. The storage area should comply with NFPA 30, *Flammable and Combustible Liquid Code*. The cleaning of tanks previously containing this product should follow the API's recommended practices (RPs), *Cleaning Mobile Tanks in Flammable and Combustible Liquid Service* (2013) and *Cleaning Petroleum Storage Tanks* (2015).

References

- ASTM D7862-13, Standard Specification for Butanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel, ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [2] ASTM D7319-13, Standard Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography, ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [3] ASTM D5501-12e1, Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20 % Ethanol by Gas Chromatography, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [4] ASTM D7875-14, Standard Test Method for Determination of Butanol and Acetone Content of Butanol for Blending with Gasoline by Gas Chromatography, ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [5] Jones, D. T. and Woods, D. R., "Acetone-Butanol Fermentation Revisited," *Microbiological Reviews*, Vol. 50, No. 4, 1986, pp. 484–524.
- [6] Reilly, J., Hickinbottom, W. J., and Henley, F. R., "The Products of the 'Actone: n-Butyl Alcohol' Fermentation of Carbohydrate Material with Special Reference to Some of the Intermediate Substances Produced," *The Biochemical Journal*, Vol. 14, No. 2, 1920, pp. 229–251.
- [7] Weizmann, C. "Improvements in the Bacterial Fermentation of Carbohydrates and in Bacterial Cultures for the Same," *British Patent* 4945, 1915.
- [8] Wilkins, M. R. and Atiye, H., "Fermentation," Nurhan Turgut Dunford, Ed., Food and Industrial Bioproducts and Bioprocessing, New York, Wiley, 2012, p. 195.

- [9] ASTM D4806-15, Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [10] World Health Organization, International Chemical Safety Card, http://www.ilo.org/dyn/icsc/showcard.home, 1-Butanol (accessed January 28, 2015).
- [11] World Health Organization, International Chemical Safety Card, http://www.ilo.org/dyn/icsc/showcard.home, 2-Butanol (accessed January 28, 2015).
- [12] World Health Organization, International Chemical Safety Card, http://www.ilo.org/dyn/icsc/showcard.home, 2-Methyl-1-Propanol (accessed January 28, 2015).
- [13] ASTM 4814-15a, Standard Specification for Automotive Spark-Ignition Engine Fuel, ASTM International, West Conshohocken, PA, 2015, www.astm.org

Bibliography

- Aakko-Saksa, P., Rantanen-Kolehmainen, L., Koponen, P., Engman, A., and Kihlman, J., "Biogasoline—Options Possibilities for Achieving High Bio-Share and Compatibility with Conventional Cars," *SAE International Journal of Fuels and Lubricants*, Vol. 4, No. 2, 2011, pp. 298–317, doi:10.4271/2011-24-0111
- Alasfour, F. N. "The Effect of Using 30 % Iso-Butanol-Gasoline Blend on Hydrocarbon Emissions from a Spark-Ignition Engine," *Energy Sources*, Vol. 21, No. 5, 1999, pp. 379–394.
- Bata, R. M., Elrod, A. C., and Lewandowskia, T. P., "Butanol as a Blending Agent with Gasoline for I. C. Engines," SAE Technical Paper 890434, 1989, doi:10.4271/890434
- Baustian, J., and Wolf, L., "Cold-Start/Warm-Up Vehicle Performance and Driveability Index for Gasolines Containing Isobutanol," SAE Technical Paper 2012-01-1741, 2012, doi:10.4271/2012-01-1741
- Bechtold, R., and Pullman, J., "Driving Cycle Economy, Emissions and Photochemical Reactivity Using Alcohol Fuels and Gasoline," SAE Technical Paper 800260, 1980, doi:10.4271/800260
- Cooney, C., Wallner, T., McConnell, S., Gillen, J. C., Abell, C., Miers, S. A., and Naber, J. D., "Effects of Blending Gasoline with Ethanol and Butanol on Engine Efficiency and Emissions Using a Direct-Injection, Spark-Ignition Engine," presented at the ASME 2009 Internal Combustion Engine Division Spring Technical Conference, Milwaukee, WI, May 3–6, 2009, Internal Combustion Engine Division, ASME, New York, NY.
- Gautam, M. and Martin, D. W. II, "Combustion Characteristics of Higher-Alcohol/Gasoline Blends," *Journal of Power and Energy*, Vol. 214, No. 5, 2000, pp. 497–511.
- Gautam, M., Martin, D. W. II, and Carder, D., "Emissions Characteristics of Higher Alcohol/Gasoline Blends," *Journal of Power and Energy*, Vol. 214, No. 2, pp. 165–182.
- Gui, F., Sridhar, N., and Peters, M., "Compatibility of Carbon Steel with Isobutanol," presented at the *NACE Corrosion 2011 Conference & Expo*, March 13–17, 2011, Houston, TX, NACE International, Stafford, VA.
- He, X., Ireland, J., Zigler, B., Ratcliff, M., Knoll, K. E., Alleman, T. L., and Tester, J. T., "The Impacts of Mid-level Biofuel Content in Gasoline on SIDI Engine-out and Tailpipe Particulate Matter Emissions," SAE Technical Paper 2010-01-2125, 2010, doi:10.4271/2010-01-2125

Hull, A., Golubkov, I., Kronberg, B., and Marandzheva, T., "An Alternative Fuel for Spark Ignition Engines," *International Journal of Engine Research*, Vol. 7, No. 3, 2006, pp. 203–214.

Irimescu, A., "Performance and Fuel Conversion Efficiency of a Spark Ignition Engine Fueled with Iso-Butanol," *Applied Energy*, Vol. 96, 2012, pp. 477–483.

Kim, D. H., Lee, J. M., Park, E. H., Song, J. H., and Park, S. I., "Engine Performance and Toxic Gas Analysis of Biobutanol-Blended Gasoline as a Vehicle Fuel," *International Journal of Automotive Technology*, Vol. 12, No. 3, pp. 409–416.

Kimura, K., Wolf, L., Baustian, J., and Haskew, H., "Hydrocarbon Permeation in Gasoline Vehicle Fuel Systems Using Isobutanol Blends," SAE Technical Paper 2012-01-1582, 2012, doi:10.4271/2012-01-1582

Kortum, D. J. and Miller, M. G., "Oxygenated Fuel Strategies to Combat Air Pollution, a Federal Overview," presented at the *American Chemical Society (ACS) National Meeting*, Washington, DC, August 21–26, 1994, American Chemical Society, Washington, DC.

Lachenmeier, D. W., Haupt, S., and Schultz, K., "Defining Maximum Levels of Higher Alcohols in Alcoholic Beverages and Surrogate Alcohol Products," *Regulatory Toxicology and Pharmacology*, Vol. 50, No. 3, 2008, pp. 313–321.

Mays, M. A., "The Use of Oxygenated Hydrocarbons in Gasoline and Their Contribution to Reducing Urban Air Pollution," *Pure & Applied Chemistry*, Vol. 61, No. 8, 1989, pp. 1373–1378.

McCabe, L. J., Fitch, F. B., and Lowther, H. V., "Future Trends in Automotive Fuels and Engine Oils," SAE Technical Paper 830935, 1983.

Merola, S., Tornatore, C., Valentino, G., Marchitto, L., and Corcione, F., "Optical Investigation of the Effect on the Combustion Process of Butanol-Gasoline Blend in a PFI SI Boosted Engine," SAE Technical Paper 2011-24-0057, 2011, doi:10.4271/2011-24-0057

Moss, J. T., Berkowitz, A. M., Oehlschlaeger, M. A., Biet, J., Warth, V., Glaude, P-A, and Battin-Leclerc, F., "An Experimental and Kinetic Modeling Study of the Oxidation of the Four Isomers of Butanol," *Journal of Physical Chemistry*, Vol. 112, No. 43, 2008, pp. 10843–10855.

Pechout, M., Mazac, M., and Vojtisek-Lom, M., "Effect of Higher Content N-Butanol Blends on Combustion, Exhaust Emissions and Catalyst Performance of an Unmodified SI Vehicle Engine," SAE Technical Paper 2012-01-1594, 2012, doi:10.4271/2012-01-1594

Popuri, S. and Bata, R., "A Performance Study of Iso-Butanol-, Methanol-, and Ethanol-Gasoline Blends Using a Single Cylinder Engine," SAE Technical Paper 932953, 1993, doi:10.4271/932953

Regalbuto, C., Pennisi, M., Wigg, B., and Kyritsis, D., "Experimental Investigation of Butanol Isomer Combustion in Spark Ignition Engines," SAE Technical Paper 2012-01-1271, 2012, doi:10.4271/2012-01-1271

Rice, R. W., Sanyal, A. K., Elrod, A. C., and Bata, R. M., "Exhaust Gas Emissions of Butanol, Ethanol, and Methanol—Gasoline Blends," *Journal of Engineering for Gas Turbines and Power*, Vol. 113, No. 3, 1991, pp. 377–381. SAE J1297-2007-07, Alternative Automotive Fuels, SAE International, Warrendale, PA, 2007, www.sae.org

Schultz, M., Clark, S., Honary, L. Conconi, C., and Dean, S. W., "Vehicle Emissions and Fuel Economy Effects of 16 % Butanol and Various Ethanol Blended Fuels (E10, E20, and E85)," *Journal of ASTM International*, Vol. 8, No. 2, 2011, pp. 1–19.

Serras-Pereira, J., Aleiferis, P. G., Richardson, D., and Wallace, S., "Characteristics of Ethanol, Butanol, Iso-Octane, and Gasoline Sprays and Combustion from a Multi-Hole Injector in a DISI Engine," SAE International Journal of Fuels and Lubricants, Vol. 1, No. 1, 2009, pp. 893–909.

Smith, J. D. and Sick, V., "The Prospects of Using Alcohol Based Fuels in Stratified Charge Spark Ignition Engines", SAE Technical Paper 2007-01-4034, 2007, doi:10.4271/2007-01-4034

Stansfield, P., Bisordi, A., OudeNijeweme, D., Williams, J., Gold, M., and Ali, R. "The Performance of a Modern Vehicle on a Variety of Alcohol-Gasoline Fuel Blends," *SAE International Journal of Fuels* and Lubricants, Vol. 5, No. 2, pp. 813–822, 2012, doi:10.4271/2012-01-1272

Wallner, T. and Frazee, R., "Study of Regulated and Non-Regulated Emissions from Combustion of Gasoline, Alcohol Fuels and Their Blends in a DI-SI Engine," SAE Technical Paper 2010-01-1571 2010, doi:10.4271/2010-01-1571

Wallner, T., Shidore, N., and Ickes, A., "Impact of Ethanol and Butanol Oxygenates on SIDI Engine Efficiency and Emissions Using Steady-State and Transient Test Procedures," presented at the 16th Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, September 27–30, 2010, Office of Energy Efficiency & Renewable Energy, U.S. Department of Energy, Washington, DC.

Wasil, J. R., McKnight, J., Kolb, R., Munz, D., Adey, J., and Goodwin, B., "In-Use Performance Testing of Butanol-Extended Fuel in Recreational Marine Engines and Vessels," SAE Technical Paper 2012-32-0011, 2012, doi:10.4271/2012-32-0011

West Virginia University, "The Economical Production of Alcohol Fuels from Coal-Derived Synthesis Gas Contract No. DE-AC22-91PC91034," *Quarterly Technical Program Report Number 4*, U.S. Department of Energy, Washington, DC, 1995.

Yacoub, Y., Bata, R., and Gautam, M., "The Performance and Emissions Characteristics of C1-C5 Alcohol-Gasoline Blends with Matched Oxygen Content in A Single-Cylinder Spark Ignition Engines," *Journal of Power and Energy*, Vol. 212, No. 5, 1998, pp. 363–379.

Yanowitz, J., Christensen, E., and McCormick, R. L., "Utilization of Renewable Oxygenates as Gasoline Blending Components," Office of Scientific and Technical Information, U.S. Department of Energy, Washington, DC, 2011.

Yasunaga, K., Mikajiri, T., Sarathy, S. M., Koike, T., Gillespie, F., Nagy, T., Simmie, J. M., and Curran, H. J., "A Shock Tube and Chemical Kinetic Modeling Study of the Pyrolysis and Oxidation of Butanol," *Combustion and Flame*, Vol. 159, 2012, pp. 2009–2027.

Chapter 8 | Discussion on Uses of the Specifications for Aviation Turbine Fuels (ASTM **D1655**) and Aviation Gasoline (ASTM **D910**)

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8.1 Aviation Fuels: Jet Fuel

8.1.1 INTRODUCTION AND BRIEF HISTORY OF MAIN GRADES

The primary requisites of a jet fuel property and the accompanying specification limit are to ensure satisfactory and acceptable performance without compromising flight safety. Air travel, in particular, demands stringent global safety standards to win public trust, leading to conservatism in design and a cautious iterative approach to technological development of both aircraft and engines. A similar cautious approach applies to jet fuel specifications that have been derived over time and are a compilation of experience along with a history of satisfactory use. Over time, property specifications and limits have been added to counteract specific problems usually associated with improved technological changes to engines and airframes.

Time flies-both figuratively and literally. Consider this: In 1903, the Wright brothers successfully flew a plane for a whopping 59 seconds. Thirty-eight years later, in 1941, the Japanese used flight to bomb Pearl Harbor. And only 28 years after that, Apollo 11 landed on the moon in 1969. Jet fuel's beginnings started with gas-turbine-powered aircraft developed and built just before and during World War II. Illuminating kerosine-traditionally produced and used for oil lamps-was the first fuel used by the English developers to power aircraft turbine engines during World War II. At the time, it was selected because of a gasoline shortage but, as refining practices changed during World War II, gasoline became plentiful; to maximize fuel for wartime use, the U.S. Air Force switched to a "wide cut" fuel. ("Wide cut" fuels are a combination of a kerosine fraction plus a lighter naphtha fraction taken off the refinery's primary distillation column. "Wide cut" jet fuels have a low flash point and safety issues have led them to virtually disappear from worldwide use.) It is interesting and illustrative to note that the first fuel used in the United Kingdom (in the Frank Whittle designed Gloster Meteor jet engine) was a kerosine plus 1 % light oil in 1940-the light oil being needed to ease lubricity concerns in pumping the fuel. Subsequent material and design changes to high-pressure gear pumps enabled the need for the oil to be dropped. But later, as the pumping pressures required to inject fuel into the higher pressures of the combustion zone increased and as more severely hydrotreated fuels entered the market, the requirement for jet fuel to have good lubricity returned and remains with us today. At this time, however, the equipment and accessory parts manufacturers are capable of producing components that can operate with relatively severely hydrotreated fuels and with pumps capable of producing injection pressures into combustion chambers as high as 1400 psig. An indication of the pressure and temperature adjustments that accompanied engine technology changes over the last 40 years is given in **Fig. 8.1**.

At the end of World War II, a wide cut fuel called JP-4 began to be used by the U.S. Air Force. Wide cut fuel is a hydrocarbon mixture with a boiling temperature range between that of gasoline and kerosine and could be made available in high quantities, which is an important criteria in times of war. Traditionally, in the twentieth century, supply requirements for war were made up of 80 % fuel, with 20 % being armaments, men, food, and other supplies. Fuel was the largest supply segment measured either by weight or volume. Therefore, fuel availability was a critical element of national security and still is today. Wide cut jet fuel has a higher volatility and much lower flash point than kerosine jet fuel, and that higher volatility caused problems with safety in storage. Wide cut fuels are much more likely to catch fire and possibly explode if an aircraft is hit by enemy fire. Wide cut fuels also have problems in rapid boil-off and vaporization in the high rate of climb of military aircraft. So the air force began to switch back to kerosine-type fuel during the 1970s and now essentially uses only the kerosine-type jet fuel. The U.S. military kerosine jet fuel was designated JP-8. However, at present, the U.S. military is moving rapidly toward using the commercial jet fuel, Jet A, in the United States and Jet A1 outside the United States. Jet A1 is very similar to JP-8 but without the fuel system icing inhibitor (FSII), corrosion control additives, and static dissipater additive required and specified in JP-8 military contracts. Perhaps this would also be a convenient point to mention that, since the 1950s, a high flash point kerosine-type fuel (JP-5) has been used for jets stationed aboard the U.S. Navy's aircraft carriers, where the risks and consequences of a fire are considered greater, especially on nuclear-powered aircraft carriers. The flash point of JP-5 is 60°C minimum, whereas the commercial fuels Jet A and Jet A1 have a flash point of 38°C minimum.

¹ 374 Martinez Pl., Pagosa Springs, CO 81147 DOI: 10.1520/MNL6920150015 FIG. 8.1 Engine technology changes in the last 40 years.



Kerosine-type fuel was also selected for use by commercial airlines during the initial development of extended and scheduled passenger services in the mid to late 1950s. The general public had to be assured of safe operations, and media coverage of large fireballs following a crash were not acceptable to the fledgling commercial passenger air services with a forward vision of increased expansion to transatlantic and global flights. The kerosine-type fuels used by commercial aircraft are classified in two grades: Jet A, with a freeze point of -40° C maximum, and Jet A1, with a freeze point of -47° C maximum. Jet A is used in the continental United States, whereas Jet A1 is used in the rest of the world. Both Jet A and Jet A1 are specified and covered in ASTM D1655, *Standard Specification for Aviation Turbine Fuels* [1].

In particularly cold climates, such as Alaska and Canada, a wide cut commercial fuel know as Jet B (similar to the military's JP-4) is sometimes used because of its low freezing point and its increased volatility—allowing for easier starting of an aircraft or helicopter; but its use is very limited. Jet B is covered in ASTM **D6615**, *Standard Specification for Jet B Wide Cut Aviation Turbine Fuel* [2]. Additionally, some refineries in Alaska and Canada make a product called Jet A 50, with a freeze point temperature of approximately –46°C.

8.1.2 THE "LANGUAGE" OF ASTM SPECIFICATIONS

It is instructive to understand the care and precision that goes into the wording of ASTM specifications and test methods and, in particular, to understand how the words "shall," "should," and "may" are used to qualify requirements and actions. The specific meaning of these words is as follows:

- "Shall" is used when the provision is mandatory.
- "Should" is used when the provision is recommended but not mandatory.
- "May" is used when the provision is entirely optional.

8.1.3 THE SET-UP OF ASTM D1655—TABLES 1, 2, AND 3, AND ANNEXES AND APPENDICES

In ASTM **D1655**, *Standard Specification for Aviation Turbine Fuels*, there are three important tables, one annex, and three appendices. Each will be discussed in this chapter but with most of the emphasis on Table 1 of ASTM **D1655**—its properties and specification values.

Table 1, "Detailed Requirements of Aviation Turbine Fuels," is the main table of the specifications properties and limits for Jet A and Jet A1. Along with each property, there is an assigned ASTM test method (or methods) detailing how the property is to be measured. And, of course, there is a limit (a maximum or minimum or range) associated with the property. For example, the flash point is set at 38°C minimum as measured by ASTM D56, *Standard Test Method for Flash Point by Tag Closed Cup Tester*. Sometimes, there are alternative methods allowed for determining the property to be measured, such as in the case of the flash point. For flash point, the alternative method ASTM D3828, *Standard* *Test Method for Flash Point by Small Scale Closed Cup Tester*, can be used. Many times, when more than one method is allowed, then one of the methods is designated a referee method. In cases of a dispute of the value of the property, the referee method will be the one used to determine the property value.

Table 1 of ASTM D1655 is not the only place where the required quality level is stated in order for the product to be acceptably labelled as jet fuel. In ASTM D1655, Table 1 is referred to in Paragraph 6, "Detailed Requirements," but there is a subsequent paragraph that must also be met-Paragraph 8, "Workmanship, Finish, and Appearance." There is a critical statement in this paragraph that, "The aviation fuel specified in this specification shall be visually free of undissolved water, sediment, and suspended matter. The odor of the fuel shall not be nauseating or irritating....No substance of known dangerous toxicity under usual conditions of handling and use shall be present, except as permitted in this specification" [1]. Unlike many other middle distillate fuel specifications, there is no actual measurement of water and sediment required for jet fuel, instead ASTM D1655, Standard Specification for Aviation Turbine Fuels, relies on the wording in Paragraph 8. The requirements of Paragraph 8 must not be ignored.

Table 2 of ASTM **D1655** is entitled, "Detailed Information for Additives for Aviation Turbine Fuels." The table is split into two sections. One section is for "Fuel Performance Enhancing Additives" and the other section is for "Fuel Handling and Maintenance Additives." The additives in this table are discussed in more detail in section 8.1.9 of this chapter, headed "ASTM **D1655** Table 2 Detailed Information for Additives for Aviation Turbine Fuels."

Table 3 of ASTM D1655 is entitled "Incidental Materials" and is a relatively new addition to the specification. As of this writing, it carries a single reference and that is to fatty acid methyl ester as a known possible contaminant of jet fuel. Incidental materials are chemicals, metals, molecules, or components that can occur in turbine fuels as a result of production of crude oil, processing and refining operations, or from being picked up during subsequent distribution and storage. Table 3 lists specific materials that have an agreed limit, and further guidance concerning these materials is given in ASTM D1655, Appendix X1.16, "Incidental Materials." These incidental materials are considered unavoidable from a practical viewpoint even though they are unwanted in jet fuel. It is not deemed necessary to test each batch of turbine fuel for compliance with the limit in Table 3. However, a rigorous management of change (MOC) scheme should be conducted to show that the limit in Table 3 is not exceeded, and conducting an MOC is required for the specification to be met.

It is important to understand the differences between an annex and an appendix. Annexes are mandatory information and notated with an "A." Whereas, appendices are non-mandatory information and notated with an "X." Appendices are there to provide useful additional information and usually to help clarify a point, but they are not mandatory. ASTM **D1655** includes Annex A1, "Fuel from Non-Conventional Sources." These so-called "alternative fuels" will be dealt with in a separate chapter in this book.

• ASTM **D1655**, Appendix X1, "Performance Characteristics of Aviation Turbine Fuels": This section provides similar

information to that contained in this chapter. The appendix was written only after due process and consensus had been reached through the voting process used by ASTM. It is worthwhile to read and understand this appendix.

- ASTM D1655, Appendix X2, "Control of Processing Additives and Distribution": Although the specification requires that only approved additives are used, confirming that non-approved additives are totally absent is difficult. Questions arise about what analytical method should be used and the lowest limit of detection and precision of such equipment. Plus, there is no available data relating processing additive concentrations to aircraft system performance sufficient to set no-harm levels. As stated previously, an acceptable way around this is to conduct a rigorous management of change (MOC) that thoroughly evaluates the impact of processing changes, including process additive usage, and to make sure these changes will not adversely affect finished product quality.
- ASTM D1655 Appendix X3, "Form for Reporting Inspection Data on Aviation Turbine Fuels": As jet fuel travels through the distribution system, it is inspected and certain quality control tests are undertaken-some of which duplicate the tests required by the specification. Most often these quality control tests are conducted to ensure there has not been any contamination during handling. For example, the distillation test may be run to check that there are no heavy ends in the jet fuel as a result of contamination with diesel. It is advantageous, and often a requirement of the quality control authority, to check these test results against the original certificate of quality produced for the batch at the refinery. To aid these checks, it is helpful if all quality reporting at the refinery (or outside laboratory) and subsequent reporting done during distribution are written up on a standardized form and that form is detailed in Appendix X3.

The reader is referred to these appendices (Appendix X1, X2, and X3), and they are not covered further in this chapter [1].

8.1.4 HOW DO WE GO ABOUT CHOOSING THE PROPERTIES TO BE INCLUDED IN THE SPECIFICATION AND SETTING THE LIMIT?

The ASTM International Committee D2 on Petroleum Products, Lubricants, and Biofuels is "responsible" for fuel specifications and test methods. The specification properties and associated limits for jet fuels represent a consensus among the members of ASTM International, Committee D02, and Subcommittee J on Aviation Fuels. Subcommittee J is the main group that discusses and sets the jet fuel specifications, and it is made up of engine manufacturers (e.g., General Electric, Pratt and Whitney, Rolls Royce, and Honeywell), airframe manufacturers (e.g., Boeing and Airbus), airlines, the Federal Aviation Administration (FAA), refiners, jet fuel traders and suppliers, pipeline companies, laboratory testing companies, test equipment manufacturers, additive companies, aviation fuel consultants, and other interested parties. Gaining consensus among this wide group is a time-consuming process but one that is driven by a common goal of enhancing the flying experience and setting the specifications for aviation fuels that meet performance goals and provide a safe flying environment. Subcommittee J does go out of its way to listen to and be guided by the original engine manufacturers and airframe manufacturers. Participation in ASTM technical committees is open to any individual or organization on a global basis. Aviation jet fuel specifications can be found in ASTM D1655, Standard Specification for Aviation Turbine Fuels, and ASTM D6615, Standard Specification for Jet B Wide Cut Aviation Turbine Fuels. Other countries have jet fuel specifications; notably, in the UK, there is Defence Standard 91-91 (Def Stan 91-91) [3], which is similar to ASTM D1655 Jet A1, and in Russia, there are several different specs including GOST 10227-86 Grade TS-1. The military (particularly in the United States) also has jet fuel specifications, notably Mil DTL 5624, covering JP-4 wide cut jet fuel and JP-5 high flash point jet fuel, and Mil DTL 83133, covering JP-8 kerosine jet fuel. Some pipeline companies also have their own jet fuel specifications that essentially are derived from ASTM D1655 but often with more restrictive limits, such as on the thermal stability test and flash point test.

When a member of the aviation community believes a change is necessary in the specification-either a change in regard to a new property or to the limit, method, or wording currently in place for defining an existing property-that change is brought before Subcommittee J and is discussed and evaluated for technical merit. If there is a group consensus that the change is worthy of consideration, a carefully worded ballot is put before the full committee membership. If the ballot passes, then it moves onto a vote at the main ASTM D02 Committee level and, if it passes that, it moves on to become a change in the printed specification. There are other checks and balances along the way to ensure openness and a balanced consensus approach. Of particular note, if there are any negatives posted on the ballots-either at the subcommittee or main committee level, they must be adjudicated by Subcommittee J and responses formed and provided to the negative voter in writing. Only by a consensus vote with a two-thirds majority can the negative be held as being nonpersuasive and the proposed specification change proceed forward. If the negative vote is found to be persuasive, the proposed change does not go forward and does not cause a change to the specification. Adjudication of the negatives is a major undertaking; all voices are heard and, within the model of ASTM, they usually can be suitably resolved. But the process does require openness, respect for others' opinions, and a willingness to strive for the best possible resolution for the industry as a whole and for the flying public.

The ASTM specification limits generally apply at the point of manufacture, and there is an implied assumption that the properties are stable from manufacture through to the skin of the aircraft. Where properties are known not to be stable, such as with the microseparometer ratings, then there is a note in the specification stating where the limit applies.

8.1.5 COMPOSITION OF JET FUEL

There are two ways to describe a material—by its chemical composition or by its performance properties. Both viewpoints can be instructive. Jet fuel is a complex mixture, but substantially it is a 100 % hydrocarbon mixture. Any given fuel may contain several thousand individual hydrocarbon compounds. Aviation gasoline,

within its narrow boiling range, may contain as many as 300 individual hydrocarbons; whereas JP-4, with its wide boiling range, may contain as many as 5000 hydrocarbons. Jet A and Jet A1 would have somewhat fewer hydrocarbons than JP-4. Modern analytical techniques are getting closer to being able to detect specific compounds in the kerosine boiling range. The additional constraint of a freeze point of -40°C for Jet A and -47°C for Jet A1 also reduces the number of acceptable hydrocarbons. Current instruments are not quite powerful enough so we do not know how many different molecular species there are, but a good guess is that there could be around 4000 hydrocarbons in Jet A and a slightly lower number in Jet A1. The range of the sizes (molecular weight or carbon number) is restricted by the distillation, freezing point, and-in some cases-by the aromatics, naphthalenes, and smoke point requirements. Kerosine-type jet fuel has a distribution between 8 and 16 carbon numbers; the distribution of wide cut jet fuel is between about 5 and 15 carbon numbers. The distribution of hydrocarbons found in petroleum-derived fuel varies from one crude oil source to another and the refiner must control and monitor the refining processes at his disposal to meet all the physical and chemical property requirements for aircraft use and as specified in ASTM D1655. Only very small quantities, rarely exceeding 1 % of non-hydrocarbon compounds, are likely to be present in petroleum-derived aviation fuel. An exception would be ASTM D6277, Standard Specification for Unleaded Gasoline Containing a Non-Hydrocarbon Component; in this spec, ethers may be present.

The hydrocarbons found in jet fuels can be divided into four major classes:

- Paraffins
- Cycloparaffins
- Aromatics
- Olefins

8.1.5.1 Paraffins and Cycloparaffins

Paraffins have a chain-like structure of carbon atoms, and cycloparaffins contain rings of carbon atoms—with the rings usually composed of five or six carbon atoms. Examples of these compounds are illustrated in **Fig. 8.2**.

Paraffins and cycloparaffins are very similar in most of their properties, and together they make up 75 % to 90 % of most aviation fuels. They are stable in storage and clean-burning, and they do not attack any normal construction materials. The paraffins are the least dense of the hydrocarbons and have the highest heats of combustion per unit weight and the lowest per unit volume. Cycloparaffins are denser than straight chain paraffins, but their densities do not approach those of aromatics, which are discussed in the following paragraph.

8.1.5.2 Aromatics

Aromatics are those hydrocarbons that contain the characteristic six-member benzene ring. The aromatics can be described in three classes: single-ring aromatics, multi-ring aromatics with no two rings sharing a single carbon atom, and multi-ring aromatics with two rings sharing two common carbon atoms; see Fig. 8.3.



All members of the multi-ring aromatics have boiling points above 200°C (400°F), as do some members of the single-ring aromatics when a long side chain is attached.

The concentration of aromatics of all classes is limited to a maximum of 25 vol. % in jet fuel specifications, but typically jet fuels contain about 10 % to 16 % total aromatics and 0.5 % to 3.0 % of the multi-ring type. Most of the multi-ring aromatics are of the type in which two carbon atoms are shared by two rings, and these compounds are referred to as naphthalenes. Naphthalenes are specifically limited in jet fuel because they will take longer to react with oxygen in the combustion zone (compared to other hydrocarbons) before they can be totally burned out to carbon dioxide and water. Because the speed of gas flow through the combustion zone is so fast, these double-ring naphthalenes are not always burned out; where additional relatively cooler air is introduced into the combustion zone to keep the liner surfaces and inlet to the turbine at around 1000°C, this can lead to a minor quenching effect. As a result, deposition made up of unburned hydrocarbon/carbon on the cooler combustor can liners-which in turn leads to hot spots and differential heating and stress of the liners and solid particles-can lead to erosion of turbine blades. Additionally, combusting the carbon-carbon double bond can lead to radiant heat being produced, and this too can result in additional heat load on the liners. Consequently, naphthalenes are limited in the specification to 3.0 vol. % maximum. Aromatics are stable in storage, tend to be smoky in burningespecially in older equipment, have high solvency powers, and tend to swell many elastomers. As a class, the aromatics have the highest densities of the hydrocarbon compounds and have the lowest heats of combustion per unit weight and the highest per unit volume. Because jet fuel is sold on a volume basis, high densities are generally preferred by purchasers.



8.1.5.3 Olefins

An olefin is a hydrocarbon that has a characteristic carbon-tocarbon double bond—this bond being more reactive chemically than the single bonds in straight chain paraffins or the resonance stabilized double bonds in aromatic ring hydrocarbon structures. The carbon atoms in the molecule may be arranged in a chain (aliphatic olefins), in a ring (cycloolefins), or on a chain attached to an aromatic ring (aromatic olefins). Some olefins may have two or more carbon-to-carbon double bonds, in which case they are called poly-olefins (usually there are just two carbon-to-carbon double bonds, and these types of molecules are called diolefins). See Fig. 8.4.

Olefins were at one time limited in jet fuel specifications by a maximum bromine number, but this has been dropped and the olefins are indirectly limited by the specification requirements for meeting the accelerated gum test. Some types of aromatic olefins and diolefins are very reactive and, in the presence of a catalyst, will polymerize to form higher molecular weight gums. Some trace metals can act as catalysts in these gum-forming reactions. If these highly reactive olefinic hydrocarbons are present, it is in very low concentrations—below 0.2 %. Olefins are nearly as clean burning as paraffins and are intermediate between paraffins and cycloparaffins in such properties as density and heating values on both a weight and volume basis.

8.1.5.4 Non-Hydrocarbons

Non-hydrocarbon compounds that may be present in aviation jet fuels are compounds containing sulfur, oxygen, or nitrogen. Sulfur compounds are found in greater concentrations than oxygen or nitrogen compounds. Oxygen and nitrogen gases from contact



with air are also dissolved in jet fuel. The current ASTM **D1655** specification for jet fuel limits the total sulfur content to a maximum of 0.30 % by mass (3000 ppm). It is anticipated that, as more data is gathered on sulfur deposition/pollution at ground level and more especially at higher altitudes, there may be calls to reduce the sulfur in jet fuel. Right now, jet fuel can be considered a relatively "dirty fuel" from a refining, fuel storage, and transportation perspective when compared to gasoline and diesel where the sulfur levels in many areas of the world are set at 50 ppm and 10 ppm, respectively. Sulfur in jet fuel may be present as thiophenols, mercaptans, sulfides, disulfides, thiophenes, thiophanes, and even traces of free sulfur.

Thiphenols and mercaptans are slightly acidic and are usually removed during refining operations by caustic washing or hydrotreating. Thiophenol is an unlikely component in adequately processed jet fuel, and mercaptan sulfur is limited in ASTM **D1655** to a maximum of 0.003 % by mass. Mercaptans are undesirable components of jet fuel because of their disagreeable odor and corrosive tendencies toward cadmium plating, which is used on rivets on some aircraft. Butyl mercaptan is what you smell in the United States when a skunk is killed on the road. Other sulfur compounds mentioned in the previous paragraph are believed to be innocuous in the concentrations encountered, as far as aircraft operations are concerned, but all sulfur contributes to air pollution at ground level and at altitude.

Oxygen may be present in very small quantities as phenols or naphthenic acids. The latter compounds may have some objectionable corrosive properties and also will react with alkaline materials to form soaps and surfactants that can build up and disarm filter water separators. Caustic washing will help in removing naphthenic acids. The only limit placed on naphthenic or any

other acids is in the total acidity test, which has a limit of 0.10 mg KOH/g maximum in ASTM D1655. This ASTM specification limit is high in comparison to the acidity limit in Def Stan 91-91 where the limit is set at 0.015 mg KOH/g. The significant difference between these specifications has been reviewed with a look to harmonization of the specifications. European standards organizations are not inclined to raise their 0.015 mg KOH/g maximum specification to the level in ASTM D1655. And conversely, ballots to tighten the ASTM specification have failed, with refiners claiming that lowering the number (tightening the specification) could lead to certain crudes not being acceptable for use in certain refineries. Although no good evidence appears to exist for the lower number of 0.015 mg KOH/g, there are some indirect accounts that link higher acid number with molecular species that can be detrimental to thermal stability [4]. The original concerns with acid levels were related to metal corrosion and an adverse effect on water separating properties. In 1971, the UK's Aviation Fuel Committee agreed to amend the jet fuel specification DERD 2494 in Issue 6 with a limit of 0.012 mg KOH/g. DERD 2494 was the forerunner to the UK's Ministry of Defence Standard 91-91 (Def Stan 91-91). This level was chosen as a result of a wide survey showing that the 0.012 mg KOH/g limit precluded harmful fuel, yet that level was generally achievable by refiners in Europe. In 1978, the limit in DERD 2494 was increased to 0.015 mg KOH/g in order to standardize with U.S. military specifications at the time. ASTM requires a technical reason usually related to performance in an aircraft to make changes to the specifications. Just because refiners generally could meet a given limit was not deemed an acceptable reason for moving away from the traditional higher limit in ASTM specifications of 0.10 mg KOH/g. For ASTM balloting to prevail, there has to be a strong performance reason before changing a specification limit.

Nitrogen compounds are present in aviation jet fuels in trace quantities only, although somewhat higher levels of nitrogen compounds can be found in jet fuel derived from shale oil. There is evidence that these compounds contribute to gum formation. In the case of diesel fuel, one of the well-established mechanisms by which insolubles are formed is the acid-catalyzed conversion of phenaleones and indols to complex indolylphenalene salts. These types of reactions were found in the work of the U.S. and British navies and were described by Pedley, Hiley, and Hancock [5]. And while this body of work on diesel fuel is associated with much larger and higher boiling molecules than those found in jet fuel, some similar mechanisms are suspected to possibly occur in the heavy ends of jet fuel.

Fuel gum consists of high-molecular weight, nonvolatile organic compounds containing hydrogen, carbon, oxygen, and possibly sulfur and nitrogen. Gum is found in marketed fuels only up to the limit permitted by specification, which in ASTM **D1655** is existent gum 7 mg/100ml maximum or about 0.01 % by weight. Additional gum may form during storage because of the presence of reactive materials and trace metal catalysts. Gum compounds may be soluble or insoluble and, in the latter case, may cause filter clogging and sticking in servo valves. Within the limits of current specifications, there is no indication that gum will affect the combustion process.

8.1.6 HOW TO FIND WHERE THE TESTS IN ASTM D1655 ARE DISCUSSED WITHIN THIS CHAPTER

In Table 8.1, the left-hand column gives the individual properties that are specified in ASTM D1655, and the right-hand column lists the chapter section in which the property is discussed. Hopefully, this will ease the way of finding information associated with the test property.

8.1.7 JET ENGINE OPERATIONS AND THE FUEL SYSTEMS ON AIRCRAFT

To understand the performance requirements of jet fuel as described in this chapter, it is helpful to understand-at least in general terms-the operation of an aircraft gas turbine engine. The simplest gas turbine engine is comprised of a compressor, a combustion chamber (combustor), a turbine (or turbines), an

TABLE 8.1 Location guide.

Detailed Requirements of Aviation Turbine Fuel	Test Method	Chapter Section Where the Requirement Is Discussed	
Workmanship, finish, and appearance	See Para. 8 of ASTM D1655	8.1.3 The Set-Up of ASTM D1655 —Tables 1, 2, and 3, and Annexes and Appendices	
		8.1.8.6 Fuel Metering (Water Affects Capacitance Measurements)	
		8.1.8.11 Dirt, Particulates, Surfactants, and Other Contaminants	
ASTM D1655 Table 1 Specification Requirements			
Acidity, total 0.10 mg KOH/g max	ASTM D3242	8.1.5.4 Non-Hydrocarbons	
Aromatics 25 vol % max	ASTM D1319	8.1.5.2 Aromatics 8.1.8.4 Combustion	
Aromatics 26.5 vol %	ASTM D6379	8.1.5.2 Aromatics 8.1.8.4 Combustion	
Mercaptan sulfur 0.003 mass % max	ASTM D3227	8.1.5.4 Non-Hydrocarbons 8.1.8.8 Other Metal Contaminants	
Sulfur, total 0.30 mass % max	ASTM D1266 ASTM D2622 ASTM D4294 ASTM D5453	8.1.5.4 Non-Hydrocarbons 8.1.8.7 Corrosivity	
Distillation Temperatures	ASTM D86	8.1.8.4 Combustion (Distillation Used in Calc. of Specific Energy)	
10 % recovered 205°C max 50 % recovered report	ASTM D2887	8.1.8.5 Volatility and Flammability	
90 % recovered report			
Pinal boiling point 300°C max			
Loss % 1.5 max			
Flash point 38°C min	ASTM D56	811 Introduction and Brief History of Main Grades	
	ASTM D3828	8.1.8.5 Volatility and Flammability	
Density at 15°C, 775 to 840 kg/m ³	ASTM D1298 ASTM D4052	8.1.8.6 Fuel Metering	
Freezing point, Jet A –40°C max	ASTM D2386	8.1.8.1 Low Temperature Properties	
Jet A1−47°C max	ASTM D5972		
	ASTM D7153		
	ASTM D7154		
Viscosity at -20°C, 8.0 mm²/s max	ASTM D445	8.1.8.1 Low Temperature Properties	
Net heat of combustion 42.8 MJ/kg min	ASTM D4529	8.1.8.4 Combustion	
	ASTM D3338		
Compustion criteria (plus aromatics of 25 vol % max)	ASTM D4809	818.4 Compustion	
EITHER	ASTM D1822	8.1.8.4 Combustion	
Smoke point, 25 mm min		8.1.5.2 Aromatics	
OR		8.1.8.4 Combustion	
Smoke point, 18 mm min			
and			
Naphthalene, 3.0 vol % max			
Copper strip corrosion, 2 h at 100°C, No. 1 max	ASTM D130	8.1.8.7 Corrosivity	

(Continued)

TABLE 8.1 Location guide (Continued).

Detailed Requirements of Aviation Turbine Fuel	Test Method	Chapter Section Where the Requirement is Discussed
Thermal stability (2.5 h at control	ASTM D3241	8.1.8.3 High Temperature Oxidation and Deposit Formation
temperature of 260°C min)		8.1.8.7 Corrosivity (Copper Contamination Effects)
Filter pressure drop 25 mm Hg max		8.1.9 ASTM D1655 Table 2 Detailed Information for Additives in Aviation
Tube deposit less than 3		Turbine Fuels
No peacock or abnormal color deposits		
Existent gum 7 mg/100 ml max	ASTM D381	8.1.5.3 Olefins
	IP540	8.1.5.4 Non-Hydrocarbons
Microseparometer rating:	ASTM D3948	8.1.8.10 Static Electricity
Without electrical conductivity additive, 85 min		8.1.8.11 Dirt, Particulates, Surfactants, and Other Contaminants
With electrical conductivity additive, 79 min		
Additives	ASTM D2624	8.1.8.10 Static Electricity
Electrical conductivity (if additive is used)		8.1.8.11 Dirt, Particulates, Surfactants, and Other Contaminants
50–600 pS/m under the conditions at delivery		

exhaust nozzle, and a fuel system. This arrangement is called a "turbo-jet engine." Refer to Fig. 8.5 showing the "core engine" components of a turbo-jet engine: the high-pressure compressor, combustion chamber, high-pressure turbine, and the high-pressure shaft connecting the turbine to the high-pressure compressor. There can also be a low-pressure turbine connected to a low-pressure compressor with its connecting shaft running inside the high-pressure shaft.

The compressor takes in air and compresses it through a series of stages. Each stage contains a rotating row of blades, called "rotors," followed by a row of stationary blades called "stators." Air enters the front end, is compressed, and is also heated by the compression as it flows through the rotor of each stage. As the air exits the rotor, it also has a swirl angle associated with it. The job of the stators is to turn the compressed air back to an axial direction (parallel to the engine centerline axis), which increases the flow area as it flows to the next rotor row. Very early (1940s) compressors had five or six stages and overall compression ratios of about four. By the 1960s, compressors had 12 to 17 stages and overall compression ratios of nine to twelve, with commensurate increases in air temperature as the airflow reached the combustor. Current engines have fewer stages, but each stage compresses more efficiently, so the final pressure rise through all the stages is higher.

Fig. 8.6 shows the combustor (the older type combustion chamber is often called a "can") that was designed originally as a single can with a single fuel nozzle or fuel injector. On the very early jet engines, there were a number of cans that encircled the engine centerline and took in the air from the compressor. By the 1960s, can designs were giving way to full annular combustor designs that were lighter in weight, less expensive to fabricate, and that were longer-lived with greater growth potential for higher inlet air temperatures and higher exit gas temperatures. The combustor is made up of an inlet system to accept the compressor discharge airflow, a dome structure with swirl cups and fuel nozzles to provide a sheltered region to stabilize the combustion process,

inner and outer liners with film holes to cool the liner structure, and larger holes to add airflow to the combustion process and to help shape the inlet temperature profile of the combustor discharge airflow to maximize turbine efficiency. There is an igniter located just downstream of the dome to start or restart the combustion process. Fuel is added through the injector nozzle to a portion of the air coming from the compressor and is ignited; it then burns at a very high temperature in the region just downstream of the fuel injection point. More compressor air is then added to ensure all the fuel is burned, to cool the combustor structure, and to reduce the gas temperature down to a level suitable for the turbine. The remainder of the compressor air flows to the turbine section to be used as a cooling flow for those parts. The level of combustor exit gas temperature is limited by the turbine flow path materials and whether or not the turbine hardware is air cooled and surface coated for additional temperature protection.

The turbine, like the compressor, is composed of a number of stages, each stage having a stator followed by a rotor. The blade arrangement is just the reverse of a compressor, as is the action. The stator is called a "turbine nozzle." Its purpose is to take the incoming combustor flow, turn it sharply away from the axial direction (inducing about 30 degrees of angle change or swirl), and accelerate it to Mach 1.0 as it leaves this part of the stage. The blades of the rotor portion of the stage are called "buckets." The high-speed swirling airflow hits these buckets, driving them in the direction of rotation and giving up kinetic energy and temperature, basically expanding the combustion gases to a lower pressure and temperature. The curvature of the buckets turns the flow back to axial, setting up the correct angle for flow to the next turbine stage. The energy extracted from the airflow by the buckets is used to drive the compressor by means of a drive shaft connected through the center of the core between the turbine and the compressor. Additionally, the drive shaft supplies power to the engine generator and to various pumps on the engine.

The nozzle, normally a static part, accepts the air flow from the last turbine stage and accelerates the flow to Mach 1.0 (or nearly so)





FIG. 8.6 Computer model of a full annular combustor mounted in an engine casing. (Courtesy of Dr. San-Mou Jeng, University of Cincinnati, Mechanical Engineering Department.)



to provide the exhaust momentum, which—minus the airflow inlet momentum (to the compressor)—becomes the actual thrust produced by the engine.

Fig. 8.7 shows the engine fuel system, which starts where fuel is received from the aircraft wing tanks. This fuel flow is directed to a pump or a series of pumps, through the engine fuel filters and on to the engine control system, and then to the combustor. A portion of the fuel is split off in the control for other uses. For example, fuel is used as a hydraulic medium to move the compressor actuators that rotate compressor stator vanes to optimize

airflow angles that increases compressor efficiency at various power settings. Fuel also flows to fuel-oil coolers for engine oil cooling, airframe hydraulic fluid coolers, and for electronic hardware cooling fluid radiators. Normally, a relatively large fraction of fuel from these cooling uses goes back into the aircraft wing fuel tanks by recirculation, which helps to disperse the fuel heat load. **Fig. 8.7** is described in more detail later in this section.

This is a fundamental description of how an engine works. Unlike a piston engine, the combustion process is continuous. The engine thermal efficiency is greater than that of a piston



FIG. 8.7 Jet engine fuel supply system.

engine, which loses a lot of the combustion energy to internal water cooling and heat energy remaining in the exhaust gases.

From the crude turbo-jet engines of the late 1930s and up through the 1940s, engine architecture gradually became more sophisticated, more complicated, and more efficient. To the basic core engine, fan systems were added, driven by low-pressure turbine systems that sat behind the core engine high-pressure turbine system, **Fig. 8.8**. The fan has fewer stages than does the compressor, but they are larger in diameter, much larger in inlet area, and therefore move much more airflow but at lower velocities, generating substantial increases in engine thrust. Fan systems can be front-mounted on an engine or aft-mounted, but convention favors front-mounted. A portion of the fan air flows into the core engine inlet. The rest of the fan flow travels aft over the outside of the core engine and exits through a fan (exhaust) nozzle that increases the flow velocity. The large mass of the fan air, at moderate velocity, has significant momentum and, hence, thrust (Thrust = Δ [mass x velocity]/g Δ T). The term "bypass ratio" defines the fan size relative to the core size in terms of airflow. If the bypass ratio of an engine is 7:1, that means that seven times the core airflow actually flows through the fan and out the fan exhaust. Total airflow to the fan inlet is eight times the core airflow. High fan flow at low velocity helps to reduce the engine noise signature by surrounding the high velocity core flow and acting as an absorber of the velocity noise.

To increase the efficiency of the fan engine, booster stages can be placed in the core inlet duct, behind the fan, and in front of the core compressor inlet (see the low-pressure compressor shown in **Fig. 8.5**) to increase the air pressure flowing into the core engine.

For military engines in fighters and bombers, the fan system is normally much smaller in total airflow and bypass ratios of about one are typical, but the fan system may have two or three stages to increase the fan discharge air pressure for both the core and the bypass air to keep the engine diameter small for the thrust produced. These engines may also have an augmenter system between the last stage of the low-pressure turbine system and the exhaust nozzle (which will be a variable area nozzle to control the engine thrust when the augmenter is in operation and when it is not in operation).

The augmenter is an atmospheric combustor located aft of the engine turbine system and ahead of the exhaust nozzle. In the core engine, less than half the available oxygen is consumed in the

FIG. 8.8 Cutaway of a typical turbo fan engine (CFM 56-7), not nacelle mounted, so air inlet duct and exhaust nozzles are not shown. (Courtesy of GE Aviation and the Energy Institute [6]).



combustor so, downstream of the engine turbines, fuel can still be added and the remaining oxygen can be burned. This is especially true if the military engine is a fan engine because the fan air can be mixed with the vitiated core air and fuel added to stoichiometric (100 % oxygen consumption) levels. Except for the nozzle, higher temperatures are less of a concern because there is no more flow path structure to worry about. Using augmentation choked to sonic flow at the nozzle discharge can increase an engine's thrust level by about 40 %. An augmenter is normally comprised of fuel spray bars with 20 or 30 mil holes (one-thousandth of an inch) instead of fuel nozzles. The augmenter combustion length is about 1.5 engine diameters (this gives ample time to burn the fuel). In addition to the spray bars, there are an igniter system, vee gutter flame holders to stabilize the combustion process, and an aircooled liner to protect the engine casings. Because the augmenter system is basically a big open pipe, the liner will also have air hole patterns to quell combustion vibration patterns that sometimes are generated during operation. These acoustic patterns (called "screech" due to their frequency level) can be axial, radial, or circumferential in mode-or a combination of these three basic modes. These frequencies can be high enough that hardware that is mechanically synchronous can be destroyed in seconds.

It is also constructive to understand how the engines operate during a normal flight cycle. Most civil turbo-fan engines spend most of their operating time at a cruising power setting. A typical engine operating cycle would be to start and come up to an idle power setting at the airport gate; idle power continues during taxi-out for takeoff (this could range from ten minutes in Cincinnati to an hour in New York); high-level takeoff power would last for about 3-5 min, followed by a slightly lower throttle setting for climb-out power for about 25 min or more to reach cruising altitude; then the throttle setting is further retarded to cruise power for an hour and a half to eight hours or even much longer on some intercontinental flights, followed by power reduction for letdown to landing (about 30 min) and throttle back to flight idle setting in preparation for landing (about 15 min). This is followed by approach power prior to the runway and, after landing, 30 to 40 sec thrust reverse (80 % power) before returning to idle and taxi-in to the ramp (another 15 min). Even most of the military aircraft accumulate similar experience-except fighters and bombers executing real or simulated combat missions in which the engines might experience 200 or more throttle movements in an hour's worth of flight.

The key area in which the fuel has to live up to its combustion requirements is during engine transient operation (such as throttle bursts and sudden chops), in-flight engine starting after an upset that causes the engine to shutdown (such as a stall caused by non-uniform airflow into the engine inlet), a sudden slug of icy water in a storm, or similar situations. Fuel cannot be burned until it is in a vapor state, and it cannot be ignited until the ratio of the fuel vapor to the air is about 3.5 % (0.035) or greater. But once combustion has started, the design of the combustor and fuel delivery system must be such that the combustion process can be sustained below a fuel-air ratio of 0.5 % (0.005) to account for engine deceleration during a throttle chop. Some of the key fuel characteristics that can help sustain the process of combustion are distillation, fuel freezing

temperature, density, viscosity, and flash point. These are discussed in the next section.

Jet fuel is stored primarily in the wings of the aircraft (considered the safest place), also in the center tanks in the fuselage, and sometimes in the tail section of the aircraft (where fuel weight is used to trim the aircraft). The fuel is picked up by a low-pressure boost pump and may pass through an air conditioning heat exchanger and then into the engine pump assembly. A lowpressure pump supplies a high-pressure gear pump that passes the fuel to the main fuel control module and from there to the fuel flow meter. There is also a bypass of extra fuel from the fuel control back to the low-pressure side of the high-pressure pump. This fuel is cold relative to the hot lubricating oil being circulated through the engine bearings. The colder fuel is used to take heat out of the oil and cool it in the fuel oil heat exchanger. After the fuel is metered for engine requirements as decided by the pilot's thrust lever position and computer management systems, the fuel passes to the integrated generator drive (IGD), where the fuel is used to cool oil in the IGD. Depending on the speed of the engine and, as a consequence, the fuel flow rate, the temperature of the fuel can be subjected to a significant rise in temperature. After the IGD, the fuel moves to the fuel manifold and from there to the individual nozzles in each combustor. This is a very simplified description, and there are many variations on how the fuel is supplied and on thermal management of the fuel during its supply route to each engine combustion zone. Each engine manufacturer has its own variation on the fuel supply system shown in Fig. 8.7.

8.1.8 PERFORMANCE REQUIREMENTS OF JET FUEL AND THEIR IMPLICATIONS

Jet fuel specifications are primarily based on performance tests rather than on closely defined product composition. Some product composition requirements, such as aromatics being limited to 25 vol. %, are in the specification. These have been discussed in the previous "Composition of Jet Fuel" section and will be discussed further in the "Combustion" section. The performance requirements are now dealt with under the following section headings:

- Low Temperature Properties
- Low Temperature and Water Related Effects
- High Temperature Oxidation and Deposit Formation
- Combustion
- Volatility and Flammability
- Fuel Metering
- Corrosivity
- Other Metal Contaminants
- Lubricity
- Static Electricity
- Dirt, Particulates, Surfactants, and Other Contaminants

8.1.8.1 Low Temperature Properties

Aviation jet fuels must perform over an extremely wide temperature environment. They must operate on fuel exposed to high temperatures in the wing tanks of aircraft when the aircraft sits for long periods in the sun under hot desert conditions. Under these conditions, fuel temperatures approach and can even exceed 40°C. In the aircraft certification process administered by the Federal Aviation Administration (FAA), aircraft are tested with fuel at a temperature of 50°C and are subjected to a rapid rate of climb to see if fuel vaporization and boiling in the tanks and lines is a cause for concern in maintaining pumping pressures for the fuel. And just as much care is given to low temperature exposure. Jet fuel is exposed to very low temperatures due to operating conditions at altitudes up to 60,000 ft. Civil aircraft flights generally operate in the 35,000 to 42,000 ft. range to be above tropospheric weather conditions and to provide passengers with a smooth flight. Significant data has shown that the optimal place for storing fuel on an aircraft is in the wings. In many large transport aircraft, the ratio of maximum fuel weight to total aircraft gross weight can be as much as 50 %. This can be compared to about 5 % fuel weight for the typical automobile. In the wing tanks, the fuel is in direct contact with the lower wing skin, which is exposed to ambient temperatures that, at high altitude, can be as extreme as -100°C (-148°F), although temperatures at 40,000 feet more normally approach -60°C. At these low temperatures, the long straight chain paraffinic molecules come out of solution from the fuel. These paraffins have the highest crystallization temperatures of the hydrocarbon molecules normally found in jet fuel. The long chains tend to align themselves and form a wax crystal matrix, which then forms as a wax layer along tank walls where fuel is on one side and ambient air is on the other. The wax layer will continue to thicken over time during the flight. (See Fig. 8.9 and Fig. 8.10.) In addition, the solid wax crystal particles can form in the body of the fuel and then flow with the fuel, which can clog filters and prevent fuel flow to the boost pump inlet and to the engine. They can even

FIG. 8.9 Wax buildup on tank walls. (Adapted from Fig. 8.6 in *Aircraft Fuel Systems* [7].)



significantly limit the flow area of fuel pipes that are exposed to cold temperatures as the wax clings to the inside surface of the pipe. (See Fig. 8.10.)

In-flight aircraft operation is not usually permitted below a fixed fuel temperature differential above the specification maximum freezing point. This limit is stated in the flight manuals of each aircraft. For Boeing aircraft, the differential is 3°C, and for Airbus aircraft, the differential is 4°C. In other words, as a flight proceeds, the temperature of the fuel in the wing tanks is measured. As it approaches 3°C in a Boeing aircraft or 4°C in an Airbus, of the specification freeze point of -47°C for Jet A1 and -40°C for Jet A, the pilot is alerted and must take action to raise the temperature of the fuel in the wing tank. The pilot can fly faster, thereby raising the temperature of the wing by increased friction over the wing; he can reroute the aircraft around a particular cold weather cell; or he can decrease altitude. (On some occasions, warmer temperatures can be found at higher altitudes—especially for very high flying aircraft traveling through the tropopause. Above the tropopause, the temperatures increase-rather than decrease-with altitude, as they do within the troposphere.) This need to increase bulk fuel temperatures can be a serious problem when operating in polar regions (if operating Mach number margins are small) because descending may not necessarily mean locating any warmer air. In each case, the action to increase the fuel temperature results in greater fuel usage and cost of operations. To reduce the need for pilots having to find warmer conditions on polar flights out of Chicago and San Francisco going to Beijing or Hong Kong, some airlines will measure the actual freeze point of the fuel loaded on board the aircraft. This is usually done by sampling the fuel as it is loaded and running ASTM D5972, Standard Test Method for Freezing Point of Aviation Fuels (Automatic Phase Transition Method). Once the results are known, the actual freeze point of the fuel is transmitted to the aircraft, which has usually left and is in flight. The actual freeze point temperature of the loaded fuel is put into the aircraft computer system and evasive action to find warmer air is not

flow testing.

Photograph of wax buildup in a wing tank during cold

FIG. 8.10



required unless the fuel temperature drops to within 3°C or 4°C of the actual freeze point of the fuel aboard the aircraft.

The measurement of freezing point is done by ASTM **D2386**, *Test Method for Freezing Point of Aviation Fuels*, which is the referee method. Other methods are ASTM **D5972**, ASTM **D7153**, and ASTM **D7154**. For further information on these and other test methods, refer to the actual methods in the *ASTM Book of Standards* [1,2,8,9].

In addition to the freeze point, another important low temperature property is viscosity. Viscosity is limited in ASTM D1655 to 8.0 mm²/sec (cSt) at -20°C. Viscosity is important in terms of the auxiliary power unit (APU) ground cold start operations and restarts at altitude. The APU is a small gas turbine usually located in the upright support structure for the stabilizer wings on the rear of the aircraft (i.e., in the empennage, or tail section). The primary purpose of an aircraft's APU is to provide electrical power to start the main engines. The main turbine engines must be accelerated to a suitable rotational speed in order to provide sufficient air compression for self-sustaining operation. The APU is also used to provide energy for functions other than propulsion. Aircraft APUs generally produce 15 V alternating current (AC) at 400 Hz (rather than 50/60 Hz in mains supply) to run the electrical systems of the aircraft; others can produce 28 V direct current (DC). As well as electric power for the electric motors used for startup and for turning the main engine, electric power is needed for the igniters in the combustion zone. In extended twin engine operations, the APUs must be capable of operating at all times, and the igniters may be required to fire continuously or intermittently during the entire flight. APUs must start up on command regardless of altitude and temperature. They can sometimes endure long cold soak periods (15 h or more) at 40,000 ft and, as a consequence, the fuel in the unheated lines leading to the APU are believed to approach -40°C and even lower. APUs do not have inlet fuel-oil heat exchangers, and the lines going up to the tail section from the cabin are not heated. Additionally, APUs have simple pressure

atomizers that are sensitive to the fuel viscosity property—unlike the main turbine engines, which have airblast atomizers that are much less sensitive to fuel properties. Fuel viscosity has a significant effect on spray formation and droplet size in the atomization process. APU cold starting is atomization limited and, therefore, viscosity limited. In order to get sufficient atomization to start the turbine in the APU, the viscosity of the jet fuel must not exceed 12 cSt. Studies by Honeywell in cold soak ground tests have shown that there is insufficient atomization to allow for droplet evaporation and the ability to start when the viscosity of the jet fuel reaches around 13 mm²/sec (cSt). See Fig. 8.11.

In the last few years, questions have arisen as to just what the viscosity of current in-service jet fuels are at -40° C. Extrapolations from viscosity measurements by ASTM **D445** at -20° C are not thought to be reliable enough and, in fact, jet fuels typically could be above or at least approaching the 13 cSt level at -40° C. And fuels that were at the specification limit of 8.0 mm²/sec (cSt) at -20° C would be at the 12 mm²/sec operating design limit at a temperature of -30° C, well above the actual anticipated working temperature of -40° C. Work is ongoing to look into the actual temperatures surrounding the APU and the temperatures of the fuel lines feeding the APU. As information is collected, a decision may be made to change the viscosity limit to 12.0 mm²/sec at -40° C.

8.1.8.2 Low Temperature and Water Related Effects

All hydrocarbons can dissolve a limited amount of water. The amount of dissolved water at a given temperature varies significantly depending on the composition of the fuel and on additives that may be present in the fuel. Saturation limits for both kerosine type and wide cut type jet fuels, along with aviation gasoline, are shown in **Fig. 8.12**. As water-saturated fuel in the wing tanks is cooled during the flight, water comes out of solution as free water. Low levels of water from the fuel are not a problem, but they are cumulative to water that is pulled into the tanks by breathing of humid air. It is required by quality control and

FIG. 8.11 Fuel viscosity affects spray droplet size. (Courtesy of Honeywell.)





FIG. 8.12 Water solubility versus temperature for aircraft fuels. (See Figs. 2-33 in [10].)

handling procedures to minimize as far as practical the free water content of fuel. However, any slugs of water formed in the fuel handling and storage system must not be transferred and delivered on board aircraft. To do so could be catastrophic because water transferred to the engine could cause a flameout and loss of power. With good ground handling practices, water is kept out of the fuel put on board. However, as an aircraft descends at the end of its flight, the tanks that at altitude are at a low pressure with dry air will now pull warm moist air in through the vent system to balance the pressure between the ullage and the outside pressure. The moisture in this incoming air condenses onto the cold aircraft structures in the fuel tanks and, eventually, this water mixes with the fuel. This water exists either in suspension within the fuel or collects as a puddle at the bottom of the tank and can be problematic not just to the engine but to the gauging system in a number of ways. One way is the difference in dielectric constants for water and fuel. These are approximately 2.1 for fuel and 80 for water. Water suspended in fuel will therefore increase the dielectric of the fuel between the electrodes of the capacitance-reading probes used to gauge the fuel volume in each tank. Measurement accuracy can be significantly affected.

Another problem posed by free water is the formation of ice during very long flights and which may not even melt between flights. Ice formed in tanks and in fuel piping during a long flight has been shown to be a significant problem requiring mitigation strategies in design and fuel handling onboard aircraft. As the aircraft reaches its destination and descends through much warmer air, the ice can be released into the fuel but not melt immediately and can then block filters or the intake area of the fuel-oil heat exchanger, causing fuel flow to be severely reduced and a loss of power, as occurred on January 17, 2008, when a British Airways (BA) Flight 38, a Boeing 777-236ER traveling from Beijing to London, lost power as it approached Heathrow Airport. The BA pilot was credited with doing an excellent job in landing the plane even though he landed short of the runway. The subsequent investigation by the National Transportation Safety Board (NTSB) found that ice released from the fuel system accumulated on the fuel-oil heat exchanger, leading to reduced fuel flow. Modifications have been developed and implemented to prevent the problem from recurring. Additionally, airframe manufacturers have instituted stricter ice accretion tests to check aircraft designs to avoid large ice buildups. See Fig. 8.13.

8.1.8.3 High Temperature Oxidation and Deposit Formation

The thermal stability of petroleum-based jet fuel currently is a limitation on engine design. Improving the efficiency of jet engines follows the laws of thermodynamics and invariably means moving to higher temperatures. However, the temperature at which jet fuel breaks down is already being closely approached within the fuel supply system to the engines. As fuel is supplied to the engines, it is pumped to high pressures and metered into the combustion chamber. The high pressures are necessary because the combustion chamber pressure can be as high as 1000 psig. As the fuel moves from the fuel tank via the low-pressure boost pump, it will move through a fuel to oil heat exchanger. In this unit, the fuel is used as a heat sink to cool the oil needed to lubricate bearings operating under extremely high temperatures. The fuel then passes through a high-pressure pump that delivers the fuel to the fuel manifold and fuel nozzles for injection into the combustion chamber; the fuel lines may pass through the hot compressed air section. As the fuel passes through the system, it will pick up heat and, while well below the petroleum-based fuel's breakpoint temperature limit, it will move closer toward temperatures where carbon deposits and varnish-like material can begin to be formed. These varnish-like deposits can begin to coat surfaces, causing restrictions. If the fuel



FIG. 8.13 Fuel oil heat exchanger inlet—ice crystals partially blocking the inlet.

temperature exceeds 175°C (350°F), this can lead to coking of the fuel nozzles with attendant loss of performance. In the worst cases, carbon deposits in injectors can lead to poor spray patterns that can then result in very high temperatures and more radiant heat causing burn-through of combustor cans and high temperatures on exit from the combustion zone can lead to failure of the turbine blades. The thermal problem is exacerbated when operating at high altitude cruise conditions where engine rotational speed, which governs pump speed, is relatively high but fuel flow and consumption are low, resulting in a lot of hot recirculated fuel and undesirable heat generation. In some aircraft designs, hot fuel from the engine is fed back to the aircraft fuel tanks as a cooling measure but also as a way to keep the fuel in the tanks warm.

The need to be able to measure and understand the thermal stability of jet fuel started in the 1950s when military aircraft with the J57 engine suffered plugged nozzle filter screens as a result of carbon deposits. In the J57 engine, the manifold was subject to high temperatures; better designs compensated for this, but manifolds and the nozzles themselves are still subject to high temperatures—particularly on shut down of the engine when engine heat soak-back occurs and there is no fuel flow.

The thermal stability problems occurred again with varnish formation on the main engine controls (MEC) on Boeing 747s where fuel temperatures were higher than on previous aircraft. **Fig. 8.14** shows the increased level of deposits on MECs from a Boeing 747 versus a DC 10 aircraft. The B747 MEC with high-fuel temperatures had operated for only 7,483 hours time since new (TSN) as compared to the DC10 MEC with lower fuel-operating temperatures and 10,378 hours TSN.

The thermal stability specification requirement is measured by ASTM **D3241**, *Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels*. In this sensitive test, fuel is pumped over a heated tube at a set pressure and flow rate; the heat from the tubes (the tubes are electrically heated) causes fuel to

FIG. 8.14 Effects of thermal stability on main engine controls. Varnish buildup on B747 hydro-mechanical units expedited the need for an improved measure of thermal stability.



FIG. 8.15 A tube with brownish lacquer deposits (indicated by blue arrow; quarter for scale): (a) Standard Color Code for the ASTM Jet Fuel Thermal Oxidation Tester (JFTOT)™; (b) The brownish lacquer on the tube is compared visually to the colors on the rating guide to determine where the lacquer color best fits on the scale.



breakdown and leave a deposit on the tube. (See Fig. 8.15). The fuel exits the heated area and is passed through a 17 micron screen. Both the heated tube and screen are maintained at 260°C (500°F), which is considered a relatively high temperature but is used to accelerate the test and stress the fuel. The tube deposit color is compared to standard reference colors and visually rated. The pressure drop across the screen is also measured. To pass this test, the tube deposit must be less than 3 on the nondimensional JFTOT[™] tube rating scale, and the pressure drop cannot exceed 25 mm of Hg. Research has indicated that certain molecules and catalysis with metals will exacerbate the oxidation reactions leading to the deposits. Heteroatoms containing sulfur or nitrogen (or both) are mainly responsible for the breakdown of the fuel, resulting in the formation of higher molecular weight materials that are insoluble and deposit out onto hot surfaces or in the materials being carried with the fuel to be deposited on the test filter. The catalytic reaction of copper is very detrimental to this test, and as little as 14 ppb of copper will cause some jet fuels to have higher levels of deposit, exceeding the specification limit of less than 3 on the nondimensional JFTOT[™] tube rating scale.

The visual rating of the deposits on the tube is a limitation of this very sensitive test; two methods recently have been added to ASTM **D3241** to measure the thickness and amount of the deposit. One method uses an ellipsometric technique, while the other uses interferometry. Pass–fail is based on a specific peak depth of 85 nm. It is hoped that by placing these methods in the specification that information can be gathered on their effectiveness in improving test precision.

8.1.8.4 Combustion

A diagram of a typical aviation gas turbine is shown in Fig. 8.5 and Fig. 8.8, and the combustion zone is enlarged and shown in Fig. 8.6. A combustion zone or combustion chamber (combustor) is needed to contain the flame and allow for suitable combustion to take place. Modern combustors tend not to be single individual cans arranged in a group of combustor cans (typically on older designs with nine or ten cans) in a ring around the core of the engine but are annular or double annular designs. The design and operation of the combustor has already been described relative to Fig. 8.6 in section 8.17, "Jet Engine Operations and the Fuel System on Aircraft."

Unlike a gasoline engine where the fuel is tested by a standardized combustion technique in a standardized engine to give a scaled reading we call the octane number, it is impractical to test jet fuel in a large turbine engine. So instead we "judge" the combustion characteristics of jet fuel in a series of relatively simple tests. These are:

- Smoke point: ASTM D1322, Standard Test Method for Smoke Point of Kerosine and Aviation Turbine Fuel
- Naphthalenes: ASTM D1840, Standard Test Method for Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet Spectrophotometry
- Aromatics: ASTM D1319, Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Absorption

All three of these tests are antiquated and in need of replacement by more up-to-date methods. This has been recognized by the aviation industry and by ASTM Subcommittee J. Newer improved methods are being developed; already the measurement of aromatics by ASTM D6379, Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates-High Performance Liquid Chromatography Method with Refractive Index Detection, is included in the specification and is being used to a limited extent. Despite the age of the tests, they have stood and still do stand in good stead. In particular, the smoke point test does give a good indication of the burning properties of a fuel even though it is an old and subjective test. The new video method for determining flame shape and height has reduced the subjectivity. The test is still much in need of replacement. Unfortunately, to date, a better test has not been established. The smoke point is correlated with flame radiation, hot parts life, engine soot, and smoke formation-as the smoke point goes up, the parts life increases. There is a "cliff" effect in that below a smoke point of 18 mm (height of the flame where smoking does not occur), the radiation increases significantly and turbine parts life decreases dramatically. The hot parts life of a turbine engine can be halved if operated on a 16-mm smoke point fuel compared to an 18-mm smoke point fuel. The smoke point specification for jet fuel is set at a 25 mm minimum, although lower smoke points are permitted provided naphthalene and aromatic volume percent contents are met. This provision for a lower smoke point is explained later in this chapter.

Naphthalenes are double-ring aromatics and, as explained in the composition section of this chapter, they can have a detrimental effect on turbines and parts life. Because of the carbon-carbon double bond being "isolated" inside the ring, it is difficult for the oxygen atoms (from air) to reach them and burn the carbon to carbon dioxide in the milliseconds that the combustion process takes before the gases expand, exit the combustion area, are diluted with relatively cooler air, and forced onto the highpressure turbine blades that rotate the shaft (which in turn rotates the high-pressure compressor blades, compressing the incoming air). The naphthalene content in the specification is set at 3.0 vol. % maximum.

Aromatics content is a gross measure of combustion quality and is set in jet fuel specifications at 25 vol. % maximum. (Aromatics effects on compatibility and system elastomers and effects on hardness and "set" of elastomers used in sealing applications will be discussed later in the "Aromatics" section of the chapter.) Although ASTM D1319, Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption, usually is used to determine the aromatic content of jet fuel, the specification does also allow the use of ASTM D6379, Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection; when this method is used, the specification level is set at 26.5 vol % maximum to account for a perceived bias. Whether this is a real bias is currently under investigation.

Taking all three of these methods, the acceptable combustion property of jet fuel is set by a combination of these properties:

Aromatics, vol. % 25 maximum (or 26.5 vol. % by ASTM D6379) AND

EITHER Smoke point, mmm	25 minimum
OR Smoke point, mm and	18 minimum
Naphthalene, vol. %	3.0 maximum

Military jet fuels have specifications requiring a smoke point of 19.0 mm minimum for JP-5 and JP-8, with a 20.0 minimum for JP-4. Military specifications will also allow hydrogen content of 13.4 mass % minimum to replace the smoke point in JP-5 and JP-8. For JP-4, the hydrogen content is set at 13.6 mass % minimum. Hydrogen content was looked at as a combustion parameter for civil jet fuel, but engine tests clearly showed that engine design overrides fuel effects, and the civil aviation industry preferred to remain with the basket of tests (aromatics, smoke point, and naphthalenes) to "judge" the quality of combustion.

The main purpose of the jet fuel is to be burned and furnish energy, and what customers ultimately pay for is the energy from the fuel. The minimum heat content or specific energy is set at a net heat of combustion of 42.8 MJ/kg minimum. Other parameters in the specification control the molecular makeup of the jet fuel so that the hydrogen to carbon ratio is always high enough that the specification for net heat of combustion is always met. It would be hard for jet fuel to fail this specification. The net heat of combustion of a fuel can be measured by ASTM D4809, Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method), but this test takes very precise thermometry and calorimetry and is not used very much. So instead the heat of combustion is nearly always estimated based on equations using other pertinent fuel characteristics. ASTM D3338, Standard Test Method for Estimation of Net Heat of Combustion of Aviation Fuels, is the method most commonly used. This estimation method uses values for density, distillation temperatures, and aromatic content-along with a sulfur correction-as the variables, and all of these properties have to be measured anyway in certifying jet fuel against ASTM D1655. The second estimation method that is allowed is ASTM D4529, Standard Test Method for Estimation of Net Heat of Combustion of Aviation Fuel, and this method uses the density, aniline point, and sulfur as variables; because of the use of aniline and toxicity concerns, this method is somewhat out of favor.

As mentioned earlier, an aromatics requirement was originally limited in jet fuel because aromatics were considered detrimental and led to combustor deposits and smoking. With the very high pressures and temperatures in today's engines, carbon hot spot deposits and smoking are far less of a problem. However, aromatics are a concern in regard to compatibility with elastomers.

Aromatics will "react" with elastomers used in airframes and engines. Elastomers used for sealing must be capable of operating over a wide temperature range, with normal fuel temperatures in the wing tanks ranging from -60°C to +40°C and higher temperatures in the fuel delivery system. Rotating seals can be particularly difficult to maintain under these wide temperature conditions. The seal materials Buna N and Nitrile rubbers are often used because of their compatibility with fuels. However, all seals are affected to some extent by petroleum products, and the aromatics can penetrate the sealing material, creating additional swelling. All O-ring and gasketed joints are designed to seal well when clamped together. As long as reasonably consistent aromatics levels are "seen" by the aircraft, there are no problems. However, if the aromatic level drops, then the swelling and hardness and what is called the "set" of the O-ring or elastomer sealing face on older materials that have been in service for a while will change, often accompanied by shrinkage. This is a concern when switching to some of the alternative fuels that have high levels of iso-paraffins but no aromatics. Consideration was given to including a minimum level for aromatics in jet fuel of 8.0 vol. % minimum, but this was felt unnecessary for inclusion in ASTM D1655 because aircraft uplift a wide mixture of fuels and not a single-sourced fuel. However, this limit was put into the extended requirements of Table 1 of ASTM D7566, Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons [8].

Fig. 8.16 shows what happened during a test program with NASA's Alternative Aviation Fuel Experiment (AAFEX) to look into the emissions reductions from aircraft engines when operating on an alternative fuel derived from the Fischer-Tropsch process of gas to liquids (GTL). The GTL aviation fuel with no aromatics in it was left in the plane overnight, and the next morning the engine was found to be leaking fuel due to seal shrinkage. After changing to new seals, there were no further leaks.

8.1.8.5 Volatility and Flammability

Volatility is a measure of the tendency to evaporate. How quickly a liquid fuel evaporates at a given temperature is important in regard to starting the process of combustion and sustaining it. It is important to remember that a liquid will not burn—the liquid must evaporate into the vapor phase to allow oxygen molecules to move into contact with the hydrocarbon molecules that are going to be transformed into oxidized materials in the process we call combustion and in the process release heat energy. In the case of hydrocarbons in the combustion process, the hydrogen is transformed into water and the carbon to carbon dioxide. Both reactions are exothermic and give out sufficient heat to be self-sustaining combustion reactions once an ignition source has been applied to the oxygen (air) hydrocarbon vapor mixture to ignite (spark) the combustion.

Jet fuel volatility is normally gaged by two tests—flash point and the initial portion of the distillation curve. Wide cut jet fuel has a sufficiently high enough volatility that the flash point is so low as to make it inappropriate for measurement, so instead the volatility is measured by a third test—vapor pressure.

Jet A1 and Jet A kerosine-type fuels must have a high enough volatility to allow for sufficient evaporation at all normal ground FIG. 8.16 The emissions testing on alternative fuels that demonstrated leakage after the seals shrunk when in contact with neat alternative fuels with no aromatics. (a) NASA's Alternative Aviation Fuel Experiment (AAFEX) emissions testing portion;
(b) The emissions testing on alternative fuels that demonstrated leakage occurred with neat alternative fuels with no aromatics in the fuel. After changing the seals there were no further leaks.



temperatures and at the temperatures at altitude to allow the turbine engines to be restarted in the event of a flameout. But having too high a volatility is also a problem. If the fuel is too high in volatility, it can lead to the fuel boiling in the aircraft tanks during rapid rates of climb. Boiling occurs as the vapor pressure exerted by the liquid exceeds the atmospheric pressure in the ullage of the tank. Large sudden releases of vapor in the fuel can cause problems with pumping and gaging.

There is also a linkage from volatility (flash point, distillation, and vapor pressure) to safety. The lower the volatility, the safer the product is in terms of handling and storage.

The boiling range of Jet A and Jet A1 is defined in ASTM **D1655** by ASTM **D86**, *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure*, and is as follows:

- 10 % recovered 205°C maximum
- 50 % recovered report
- 90 % recovered report
- Final boiling point 300°C maximum

Although we are discussing volatility and flammability, at this juncture it is convenient to point out that at the high temperature end, the final boiling point of 300°C set in the specification is rarely, if ever, reached with petroleum-based jet fuels because molecules that boil at the 300°C temperature will have freezing points above the specification limit of -47°C, which is the freezing point of Jet A1. The Jet A fuels used in the United States with a freeze point of -40°C are not as severely undercut, but nonetheless, they too are undercut on the end point in order to meet the freeze point. Perhaps it is also convenient to point out here that distillation of jet fuel is also used as a quality control test to show that there has not been any contamination with heavier boiling materials such as diesel fuel. Typical distillation curves are shown in Fig. 8.17. The flash point is also used as a quality control test to show there has not been any contamination with lighter boiling materials such as gasoline.

FIG. 8.17 Distillation curves for typical aviation turbine fuels and avgas [10].



The distillation can also be done by ASTM **D2887**, *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*. Results obtained by ASTM **D2887** have to be converted to estimated ASTM **D86** results by using the correlation given in Appendix X5 of method ASTM **D2887**.

For wide cut jet fuels, the vapor pressure is measured by ASTM D323, Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method), or alternatively, ASTM D5191, Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method). The vapor pressure is measured at 38°C and is the sum of the partial pressures of the molecular species in the fuel plus the partial pressure of dissolved air at a vapor to liquid ratio of 4:1. It is always interesting to note that, in kerosine at sea level, if the dissolved air were to be taken out as a gas volume, it would be equal to about 15 % of the volume of the liquid jet fuel. A true or absolute vapor pressure where the vapor space approaches zero can be measured at any temperature by using ASTM D6378, Standard Test Method for Determination of Vapor Pressure (VP,) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method). Although of interest to airframe manufacturers, the absolute pressure is not part of the ASTM D1655 specification and is not determined on a routine basis.

The flash point is set for Jet A1 and Jet A at 38°C minimum as measured by ASTM D56, Standard Test Method for Flash Point by Tag Closed Cup Tester-although some multiproduct pipelines will require a higher minimum to protect against a lowering of the flash point caused by trace levels of gasoline being back mixed with the kerosine. Other flash point test methods are in use but because of the differences in the test methods (volumes and heating rates), the other tests will not give results identical to the Tag flash point result, and allowances must be made for these differences. The flash point tests such as Tag, Abel, and Pensky Martens are all dynamic tests where the temperature of the sample is increased at a specific rate and the test flame is applied at specific set intervals until the flash is observed. In dynamic tests, the temperature of the sample is constantly changing, and the test flame is applied to a single charge of the sample as many times as necessary to obtain the flash.

Vapor pressure and flash point are related but do not measure the same property. The vapor pressure measures the pressure exerted by the fuel at a specified temperature, while the flash point gives an indication of the lowest temperature at which a flammable fuel/air mixture is formed under set and specified laboratory test conditions.

8.1.8.6 Fuel Metering

The measurement of fuel quantity and fuel flow is important on the ground when refueling the aircraft but even moreso for flight operations. There are no service stations in the sky so it is comforting to know you have enough fuel to finish the journey and still have something left in the tank. Product is bought, sold, and transferred on a volume basis. Although volume is more easily measured than is mass during product transfer, measuring volume comes with the need to also measure temperature to account for volume changes due to temperature. The volumes are corrected by measuring the density and temperature and then adjusting to a standardized temperature of 60°F in the United States and to either 15°C or 20°C outside the United States. Corrections to the standardized temperatures are accomplished through the use of ASTM D1250, *Standard Guide for Use of Petroleum Measurement Tables* and the

associated volumes of correction tables to standardized temperatures, which are also available from ASTM.

Onboard aircraft measurement is primarily on a mass basis whether dealing with total aircraft weight on take-off and landing or with the need to maintain the center line gravity for trim during flight or when measuring fuel flow to the engine and to the combustion system. The maximum range of an aircraft is limited either by the maximum allowable take-off weight (MTOW)—in which case it is weight limited—or by the total volume that can be handled by the tank sizes on board the aircraft—in which case it is volume limited. Modern aircraft now have onboard fuel property measurement units (FPMUs) that determine density, temperature, and volume all in one unit. A sample of the uplifted fuel passes through the unit each time the aircraft is refueled, capturing the key properties required for accurate gaging and range management associated with variable flying conditions such as wind, payloads, and actual engine fuel consumption.

Volume in the aviation industry is usually measured in U.S. gallons or in litres; whereas mass units for density are in kg/m³ at 15°C (or lb/gal at 60°F). Relative density, which is the ratio of fuel density to that of water density (usually at 15°C), is falling out of use. However, in the United States, the American Petroleum Institute (API) gravity, which is based on an arbitrary scale at 60°F, is still used extensively. The density is measured by using a hydrometer as per ASTM **D1298**, *Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method*, or by using a digital density meter and ASTM **D4052**, *Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter*.

The density of jet fuel is set with a range from 775 kg/m³ to 840 kg/m³ at 15°C. In general, density is not a limitation for refiners because distillation, flash point, freeze point, aromatics and smoke point, and naphthalenes tend to be more important in controlling the molecular makeup of jet fuel; but density is used as a control in terms of quality control testing and guarding against contamination. Additionally, in Def Stan 91-91, there is a requirement for batches manufactured at the refinery to be homogeneous; the Def Stan 91-91 specification requires there to be no more than 3.0 kg/m³ variation in density across a single batch. (See Paragraph 5.1 of Def Stan 91-91 [**3**].)

Gaging fuel quantities on board an aircraft is critical and not easily accomplished at every specific point in time because of the attitudes and steeply varying pitches of the aircraft as well as the odd shapes of the tanks. There is also the need for the fuel system to always have liquid available at the pump suction in the collecting tanks; therefore, fuel is always being pumped around, and the tank level is not static. Inside each tank in the wings and in the center tank (in the fuselage area) there are multiple capacitance type gages. These are two concentric tubes that measure the height of the fuel by changes in the electrical capacity as the fuel height varies inside the tube. To do this, it is important to know the dielectric strength of the jet fuel as precisely as possible and not to have water contamination in the fuel because this changes the dielectric strength significantly. There are as many as seven capacitance probes per tank, and the fuel heights from all the probes are used to determine the volume in each tank. This is then converted into a mass unit for input into aircraft systems for controlling fuel flow and for pumping fuel between tanks to maintain trim and metered flow to the engines. Perhaps the importance of metered flow can be better understood by realizing that the pilot has a thrust lever that he can pull to change the metered flow to the engine. As greater fuel volume enters the combustion chamber, the gas flow increases and speeds up the turbine, which rotates faster and causes more air to be pulled in and compressed. There is another gaging system on some aircraft that uses ultrasonic signals bounced off the fuel surface to measure fuel volumes in tanks. In either case, metering of the fuel to the engine is all important.

8.1.8.7 Corrosivity

There are two properties in the ASTM D1655 jet fuel specification that help to guard against corrosion in aircraft fuel systems and turbine engines. One is the limitation on sulfur and the other is the copper strip corrosion test. Sulfur also was mentioned earlier in the non-hydrocarbon section with regard to its effect on air pollution. Sulfur is also a potential problem within the turbine itself. During combustion, the sulfur in the jet fuel burns to form sulfur trioxide and sulfur dioxide. These will react with water molecules, which are formed from the combustion of the hydrocarbons, to form sulfuric and sulfurous acids. The concentrations of these acids are small relative to the mass air flows. The low concentrations and the metals used in modern aircraft turbines, which are required to withstand the high temperatures in the combustor zone and in the high- and low-pressure turbines, means that the engine components in modern designs are less prone to attack by the corrosive mechanisms of sulfurous and sulfuric acid. However, in the early days of turbine development, un-combusted carbon could combine with the sulfuric acid material forming acidic smuts that led to hot spots on combustors and to acidic attack. Accordingly, the total sulfur in ASTM D1655 jet fuel is limited to 0.30 mass %, which is determined by a number of methods. The method that seems to have the most usage is the Horiba Sulfur Analyzer used in ASTM D2622, Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry. Other manufacturer's equipment can be used in this method. The other methods allowed by the specification are: ASTM D1266 (the so-called "lamp method" that uses wet chemistry and is very much out of favor), ASTM D4294 (an energy dispersive X-ray fluorescence method), and ASTM D5453 (a UV fluorescence method).

Corrosion of aircraft fuel-system components has always been an issue, particularly with bronze pump bushings. Failures of pumps still occur when the copper in the bronze is attacked by the fuel. The primary fuel constituents involved in copper corrosion are elemental sulfur and hydrogen sulfide, although acidic components will play a part and so too will mercaptans. The most common source of hydrogen sulfide is incomplete stripping following refinery hydrotreating of heavier materials, with kerosine being taken off as a lower boiling material of the output from the hydrotreater. Elemental sulfur can form many valences and is electrochemically very active, especially in the presence of hydrogen sulfide. The reduction of water soluble sulfates in tank bottoms by

FIG. 8.18 Copper strip adjunct chart.



sulfate-reducing bacteria will lead to the formation of free sulfur in the jet fuel. Both elemental sulfur and hydrogen sulfide are corrosive to copper at levels below 5 ppm, but exact levels at which unacceptable corrosion occurs seem to be dependent on the presence of other trace materials, the mercaptan level, and possibly even the type of mercaptan—with the lower molecular weight mercaptans being more mobile and less electron stabilizing.

Because of the difficulties in measuring trace levels of sulfur or hydrogen sulfide, the aggressiveness of jet fuel toward copper is measured by ASTM **D130**, *Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test*. For jet fuel, the specification is set at a No. 1 strip maximum when the copper strip is subjected to immersion in the test sample of jet fuel for 2 h at 100°C. The appearance of the copper strip is compared to a standard color adjunct chart, and only very minimal discoloration is permitted by the limit set at less than a No. 1 on the adjunct chart. See **Fig. 8.18**.

Another good reason for avoiding copper corrosion is to stop copper from contaminating the fuel. As pointed out earlier in the section on high temperature oxidation and deposit formation, just 14 ppb of copper can adversely affect the ASTM D3241 thermal stability test. Unfortunately, passing the copper test at the refinery is no guarantee of meeting the thermal stability requirements further downstream. During the downstream distribution process, the jet fuel can dissolve copper from bronze parts in pumps and heating coils in marine tankers. Even non-direct contact can lead to trace levels of copper in jet fuel. For example, copper components are often used in impellers that pass marine tanker exhaust gasses into the ullage space of a compartment, creating the inert gas system. Jet fuel subsequently filled into that section can possibly pick up copper contamination from the compartment. Jet fuel needs to be kept away from copper and copper-containing metals to the greatest extent possible.

8.1.8.8 Other Metal Contaminants

Besides copper, perhaps the next most common and detrimental metal contaminant is zinc. Like copper, zinc will catalyze oxidation reactions and can lead to varnish-like deposits on hot metal surfaces. In addition, zinc from galvanized steel has found its way into jet fuel and formed complexes with certain additive packages. These complexes can be marginal in solubility and will tend to block filters.

The corrosion of cadmium plating on parts—and especially on rivets—has been attributed to mercaptan sulfur compounds. Mercaptan sulfur compounds are limited in jet fuel ASTM D1655 to 0.003 mass % maximum as measured by ASTM D3227, *Standard Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosine, Aviation Turbine and Distillate Fuels (Potentiometric Method).* The mercaptan sulfur determination can be waived if the fuel is tested and is found to be sweet by the doctor test method— ASTM D4952, *Standard Test Method for Qualitative Analysis for Active Sulfur Species in Fuels and Solvents (Doctor Test).*

Iron oxides (rust) are often present in jet fuels and are the result of water corrosion of mild steel tanks and pipelines. The iron will also act as a catalyst and accelerate oxidation under hot conditions, leading to fuel deposits on hot parts. Although far less active than copper or zinc, iron can be just as much a problem because it tends to be found in higher concentration levels. The fine iron oxides are also a problem because they have a huge surface area and will attract surfactants (described later) and keep the iron in suspension in the fuel. The iron oxides are removed by filtration. Generally, in aviation fuel handling, the fuel is filtered each time it is moved. The mantra of the industry is "keep it clean and keep it dry." And this is accomplished by strictly controlled filtration equipment and operations. The subject of filtration and keeping jet fuel clean and dry is extensive and only briefly touched on in this chapter. For more information, the reader is referred to EI 1550, "Handbook on Equipment Used for the Maintenance and Delivery of Clean Aviation Fuel" [11].

Although not part of ASTM **D1655**, the expectations of the original turbine manufacturers with regard to intake of metals for their engines can be understood by looking at ASTM **D7566**, *Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*. In Table A1.2 (Other Detailed Requirements), there is a list of metals. Every one of the metals must be less than 0.1 mg/kg. The list includes the following: aluminum (Al), calcium (Ca), cobalt (Co), copper (Cu), iron (Fe), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), palladium (Pd), platinum (Pt), tin (Sn), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). Essentially, the expectation is that jet fuel will be metal free. The specification ASTM **D7566** will be covered in chapter 9 of this book.

8.1.8.9 Lubricity

In a jet turbine engine, there are significant pressures built up on sliding and rotating parts and, in particular, on the gears of high-pressure pumps and in servo valves where, in both cases, the jet fuel is used as a lubricant. In some cases, the rotational speeds are not high enough to maintain hydrodynamic lubrication conditions, whereas the pressures *are* high leading to boundary lubrication conditions. The fuel viscosity alone will not prevent metal to metal contact. A layer of adsorbed polar material several microns

thick may be required to prevent excessive wear of these surfaces that are in close contact with each other. There generally is sufficient polar material found in most straight run jet fuel to meet the requirements of lubricity for today's aircraft jet turbine engine fuel systems. However, when jet fuel is manufactured under severely high pressure and high temperature hydrotreating/hydrocracking, the natural polar materials in the fuel are destroyed and the lubrication ability of the jet fuel is significantly degraded. Cases of pump failures and flameouts are known to have occurred in aircraft that consistently operated on severely hydrocracked fuel from a single source refinery.

The "lubrication ability" of jet fuel is measured using ASTM D5001, Standard Test Method for Measurement of Lubricity of Aviation Turbine Fuels by the Ball-on-Cylinder Evaluator (BOCLE). The ASTM D1655 jet fuel specification does not have a requirement for lubricity. However, fuel lubricity is covered in the standard's non-mandatory Appendix X1.10. In the case of Def Stan 91-91, there is a lubricity requirement that the wear scar diameter as measured in the ASTM D5001 BOCLE test shall not be more than 0.85 mm. Because fuels in the United States are so intermixed and aircraft uplift fuel from more than one location, it was not possible to find an aircraft that regularly and consistently saw only severely hydrotreated/hydrocracked fuel with a low lubricity and high wear scar. Therefore, the inclusion of a lubricity specification in ASTM D1655 was felt to be unwarranted. As little as 10 % straight run jet fuel will provide a 90 % severely hydrotreated/hydrocracked fuel with sufficient polar compounds to provide acceptable lubricity. Additionally, it is possible to add an acceptable and approved corrosion inhibitor additive that will also act as a lubricity improving additive (more on this appears in the additives section). The question of the need for a lubricity specification in ASTM D1655 has not gone away. As greater volumes of alternative fuels derived from relatively severe processing that contain large quantities of isoparaffins and practically no polar compounds enter the market, there is some concern that a lubricity specification should be introduced into ASTM D1655.

8.1.8.10 Static Electricity

The generation and dissipation of static electricity can create problems in the handling of aviation fuels. A considerable amount of information can be found in ASTM D4865, Standard Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems. Readers are strongly encouraged to read and understand the content of this guide. Hydrocarbons are extremely poor electrical conductors but usually contain trace levels of ionizable materials that carry charges of static electricity. When the fuel is at rest, the charges neutralize each other. But when the fuel moves, the ions of opposite charges become separated and an electric charge is generated. Either the positive or negative charges can leak off to ground, leaving the fuel positively or negatively charged. The time required for the charge to bleed off depends upon the fuel's conductivity. If the conductivity is low and the flow velocities are high, then the charge may not bleed off before the fuel is discharged into a tank or vessel and the surface in the tank can become charged. It can still bleed away, but there is also the possibility of a discharge from the fuel's surface to a conductor (with the discharge being in the form of a spark). And if the spark has sufficient energy and passes through the vapor above the tank surface, it can ignite the vapor. Then there is the possibility of an explosion with catastrophic consequences. Again the reader is referred to ASTM **D4865** for more information on this subject. Because of the use of very fine filter water coalescers in aviation fuel handling, in order to keep jet fuel clean and dry, there is the strong possibility of static buildup on the large surface areas of the filters. Therefore, it is important when designing facilities to allow for appropriately slow fuel velocities and also sufficient lengths of piping after the water filter coalescers for the static that does build up to dissipate and leak to ground. This process is called the relaxation time, and allowing sufficient relaxation time is important in designing aviation fuel facilities. See **Fig. 8.19** for the effects of static discharge in an incorrectly filled filter water separator.

In Table 1 of ASTM D1655 there is a reference (Paragraph 5.2) stating that a conductivity additive may be added to jet fuel in accordance with the allowances given in Table 2. In Table 2 of ASTM D1655 there is an allowance for the conductivity improving additive Stadis 450 to be added to jet fuel (up to a maximum level of 3 mg/l) at the point of the initial blending of the additive into the fuel. Because the additive will tend to plate out on surfaces, the conductivity can be lost over time and subsequent additions of the additive are permitted up to an accumulative maximum amount of 5 mg/l. When the initial amount of additive is unknown, only 2 mg/l more additive is permitted. If an electrical conductivity additive is used, this can only take place if the stipulations in Note M of Table 1 are met. The conductivity of the fuel shall not exceed 600 pS/m at the fuel's point of use. When an electrical conductivity additive is required by the fuel purchaser then the conductivity shall be 50 to 600 pS/m at the point of delivery. The reason for the limitations on conductivity improver dosage rates is because of the need to have a dispersant/surfactant material in the additive package. The dispersant/surfactant will coat filters, causing them to be made less effective in coalescing water and, potentially, to become disarmed.

Conductivity additives are not widely used in U.S. aviation fuels although they are used elsewhere in the world. In the United States, multiproduct pipelines are used extensively, bringing into play the possibility of surfactant contamination of the jet fuel. (See the following section on dirt, particulates, surfactants, and

FIG. 8.19 Static discharges in a filter water separator that was not filled correctly have left charring marks on the filters.



other contaminants.) Following pipeline transfers, clay treaters are widely used in the United States to remove the surfactant contaminants that can potentially be transferred into the jet fuel after other fuels (gasoline and diesel) have passed down the pipeline and left surfactants as residues on pipe walls. The clay treaters will also take the conductivity improvers out of the fuel along with other ionizable material, thereby making the conductivity of the jet fuel very low. To cope with handling low conductivity materials, there are strict guidelines on the flow velocities and piping lengths recommended for aviation fuel handling. These recommendations are well understood, widely available, and are followed in the United States, mitigating against the need for a conductivity improver.

8.1.8.11 Dirt, Particulates, Surfactants, and Other Contaminants

The philosophy in aviation fuels is that any material not originally part of the fuel is considered a contaminant and should not be there. Such emphatic guidelines are difficult to meet; therefore, in order to help comply more realistically with contaminants, Table 3 ("Incidental Materials") has been introduced into the ASTM specification (the need for this table will be discussed later in this chapter). Currently, only one incidental material is listed in Table 3 and that is fatty acid methyl ester (FAME). Following this philosophy, contaminants that should not be present in jet fuel include free water, solid materials (such as rust, dust, or sand), microbial debris, other fuels, and unapproved additives as well as other more unusual materials—such as solvents and surfactant materials. The only contaminant limited in the jet fuel specification by a quantitative number is gum.

ASTM **D1655** limits existent gum to 7 mg/100 ml as determined by ASTM **D381**, *Standard Test Method for Gum Content of Fuels by Jet Evaporation*, or by IP 540, *Determination of the Existent Gum Content of Aviation Turbine Fuel—Jet Evaporation Method*. Information on the need to maintain a low level of gum is outlined in section 8.1.5.3 on olefins.

Surfactant materials are not detrimental to the aircraft or to the turbine engine; by and large, they will burn effectively. But they are extremely detrimental to the filter water coalescers that are used to filter out dirt and water from jet fuel. These filters rely on the ability of the glass fibers of the filter to be hydrophilic and to collect water on the fiber through surface tension. The filters then allow the water to run along the fibers until there is a node where the water drops will aggregate or coalesce together reaching a size that, as they exit from the outer edge of the filter, are large enough to drop out of the fuel under gravity before the fuel exits the filter vessel via the separator, which is a hydrophobic Teflon or synthetic screen. When surfactants are present in the fuel, they will coat the glass fibers, making them hydrophobic and preventing the coalescing from taking place. The water will exit from the coalescing stage in small dispersed droplets and may not fall out of the fuel before exiting the filter water separator. In addition, when surfactants are present, the ability of the filter to hold and trap dirt will be compromised. In order to protect the filter water separators and ensure their efficacy, surfactants must be kept out of jet fuel.

To test for the presence of surfactants, jet fuel—at the point of manufacture—must meet a minimum microseparometer rating of 85, when electrical conductivity additives are not used, or a minimum of 70, if an electrical conductivity additive is used. The difference in the microseparometer rating with and without electrical conductivity additive is because the additive contains a surfactant that is needed to disperse the additive throughout the fuel. The microseparometer rating is measured by using ASTM D3948, *Standard Test Method for Determining Water Separation Characteristics of Aviation Turbine Fuels by Portable Separometer*. See Fig. 8.20.

If an electrical conductivity additive is used, then it is necessary to also measure the electrical conductivity. The specification level for electrical conductivity is set at 50 to 600 pS/m and reference to this value is given in Note M of Table 1 in ASTM **D1655**. The electrical conductivity is measured using ASTM **D2624**, *Standard Test Methods for Electrical Conductivity of Aviation and Distillate Fuels*.

Dirt, like water, is not quantitatively called out in ASTM **D1655** other than in Paragraph 8 ("Workmanship, Finish, and Appearance"). However, in Def Stan 91-91, there is a requirement to measure and report the particulate level in jet fuel at the refinery. The particulates are counted within certain micron size ranges and the units are individual channel counts and International Organization of Standardization (ISO) codes. This technology comes from the particle counting methods used to define the cleanliness of hydraulic oils. The methods used are IP 564, IP 565,

or IP 577. At present, the information is required by Def Stan 91-91 on a report basis only. Data is being gathered to decide what levels should go into the specification and where in the distribution system the specification for particle counting should apply. ASTM D7619, Standard Test Method for Sizing and Counting Particles in Light and Middle Distillate Fuels by Automatic Particle Counter, is technically equivalent to IP 565; however, the precision statement of ASTM D7619 was derived from fuels other than aviation turbine fuels. Accordingly, jet fuel is not included in the scope of the method at this time. One difficulty with the current methods is that water droplets are also counted as solid particles. Ways to remove water and avoid this problem are being researched and tested. As new precision and interlaboratory studies are conducted, it is expected that jet fuel will be included and ASTM D7619's scope will be changed. Discussion would then take place on the merits of including a particulate specification in ASTM D1655.

8.1.9 ASTM D1655, TABLE 2, DETAILED INFORMATION FOR ADDITIVES FOR AVIATION TURBINE FUELS

As stated in Paragraph 6.1.2 of ASTM **D1655**, additives that are used in aircraft fuel systems must be approved by the airframe and engine manufacturers. The use of additives is then further explained in Paragraph 6.2. Additives may be added within the

FIG. 8.20 Microseparometer (MSEP) apparatus. (For details on running the test, see ASTM D3948, Standard Test Method for Determining Water Separation Characteristics of Aviation Turbine Fuels by Portable Separometer.)


concentration limits shown in Table 2 and are subject to any restrictions described in the footnotes of that table. Fuel manufacturers and mid-stream storage operators should not just go ahead and use additives-there is a need to be aware of the pros and cons. Most additives have a "dark side" when not used appropriately. Because of the need to understand the possible unintended consequences associated with additive usage, there is a protocol for approval. This is ASTM D4054, Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives. This is a rigorous set of requirements that is currently being studied to see if a more simplified process can be used to shortcut the full approval process for chemistries with a known history. ASTM D4054 was developed by the original equipment manufacturers (OEMs) through the ASTM process. The OEMs are solely responsible for approval of a fuel or additive in their respective engines and airframes. It is important to realize that the word "approval" in this context means "permission to use" and is not an endorsement of the additive. These "approvals" are listed in OEM fuel specifications such as:

- Pratt and Whitney (P&W) Service Bulletin No.2016
- General Electric (GE) Specification No.D50TF2
- Rolls Royce (RR) engine manuals

Subsequent to OEM "approval" and industry and military review, the fuel additives may then be listed in ASTM **D1655**'s Table 2, Def Stan 91-91, or in military specifications.

The additives that are allowed in civil jet fuel are detailed in Table 2 of ASTM **D1655**. The table is split into two sections—"Fuel Performance Additives" and "Fuel Handling and Maintenance Additives." In the first part of the table, the additives listed are:

- Antioxidants
- Metal deactivator
- · Fuel system icing inhibitor

And in the second part, the additives listed are:

- · Electrical conductivity improver
- Leak detection additive
- Biocidal additives
- · Corrosion inhibitors/lubricity improvers

The antioxidants that are hindered phenols and mixtures of hindered phenols are added to jet fuel to improve storage life, inhibit gum formation, and to counteract peroxides if they are present. Hydrocracking and severe hydrotreating will, in the process of removing sulfur, also remove the natural oxidation inhibitors found in straight run jet fuel. Jet fuel without the natural inhibitors can undergo oxygen attack, producing peroxides. And peroxides that may be formed can attack the elastomer seals and nitrile rubber seals. There is a requirement in Def Stan 91-91 that all severely hydrotreated jet fuel have an oxidation inhibitor additive added to the fuel. In order for the additive to be effective against peroxide formation, it must be added to scavenge the free radicals that are the first step in the chain reactions. And convention suggests, to be effective against that first step, the antioxidant must be injected into the fuel as soon as possible-preferably on the run down exit from the hydrotreater/hydrocracker and before

going to tankage. Although there is a mandatory requirement to add the antioxidant to severely hydrotreated fuels in order to meet Def Stan 91-91, the use of antioxidants in ASTM **D1655** is optional (although many refiners with severe hydrocracking do add antioxidants). Approved hindered phenol antioxidants can be added at a dosage of 24 mg/l maximum of the active ingredient.

The usage of a metal deactivator additive has been very controversial over the last ten years. The metal deactivator additive (MDA) N,N-disalicylidene-1,2-propane diamine acts as a chelating agent and will "wrap up" metal ions, preventing them from catalyzing detrimental reactions usually associated with copper catalysis oxidation reactions and degradation of jet fuel. MDA can be added to fuel on initial blending at a rate of 2.0 mg/l maximum. If, subsequent to initial manufacture, a problem develops with meeting thermal stability tests, then the use of an MDA may help. And it can be further added to the fuel up to a cumulative concentration of 5.7 mg/l maximum. There has been considerable debate over the use of this additive. The engine OEMs do not want to see the additive used at refineries on a regular basis to correct poor practices and the manufacture of poor thermal stability products. A Coordinating Research Council (CRC) program was set up to evaluate MDA's "antifouling properties" and the prevention of deposition in the thermal stability test. In other words, the test program was supposed to find out if the MDA allowed the thermal stability test to be "fooled." Three major points emerged from this CRC program. It was difficult to find a fuel that had marginal thermal stability with non-detectable levels of copper. The MDA does have antifouling properties where it will coat the metal tube surfaces and prevent deposit formation, and this is in addition to its known properties of complexing (chelating) metals. And finally, when 2 mg/l of MDA was added to fuels in a heated nozzle test rig, reduced fouling rates were observed just as when MDA was added to fuels tested for thermal stability by ASTM D3241. The CRC work confirmed that MDA does provide a real and measurable thermal stability benefit in actual engine hardware whether the fuel contains significant copper contamination or not. At this time, the wording restricting the usage of MDA in Note D of Table 2 is as follows:

MDA may be added to fuel to counteract the effects of metals known to be deleterious to thermal stability, such as copper, cadmium, iron, cobalt, and zinc, provided that the nature of the contamination is reported. Where metallic contamination is unproven, an MDA may be used to recover thermal stability provided that the Thermal Stability test (in accordance with Table 2) is determined before and after MDA addition and reported on the test certificate. Initial addition of more than 2.0mg/l MDA is permitted when the fuel will be transported in supply chains where copper contamination may occur; the maximum cumulative addition in Table 2 still applies. Note that fuel containing MDA has been shown to promote the dissolution of copper and may therefore exacerbate thermal stability problems.

There are some that feel this whole situation needs better definition and clarity of meaning and so this wording may change. Both ASTM Sub Committee J and the Aviation Fuels Committee that oversees the Def Stan 91-91 specification would like to have similar wording in their respective specification on how to handle MDA, and this is being studied.

The last additive in the top part of the table is a fuel system icing inhibitor (FSII). The allowed additive is diethylene glycol monomethyl ether (Di EGME) as defined by Type III in ASTM **D4171**, *Standard Specification for Fuel System Icing Inhibitor*. As the name implies, the additive inhibits ice formation. Di EGME can be included in jet fuel provided it is put in at 0.10 vol. % minimum and does not exceed 0.15 vol. % maximum. The FSII is not a biocide per se but does have biostatic properties that help retard microbiological growth. In regard to ice formation, the FSII works by being preferentially absorbed into the water that comes out of solution from the fuel as the aircraft climbs and the temperature drops. The FSII depresses the freezing point to -43° C and thus helps to prevent ice crystals from forming.

The FSII can have deleterious effects on tank coatings and the coatings of filter water separator housings. The FSII in water bottoms will act as a "paint stripper" and will soften epoxy coatings, causing the coatings to lose integrity and even leading to peeling of the coating. When the U.S. Navy was using FSII, they installed stainless steel housings in their filter water separators.

Storage of bulk FSII in hot climates is also problematic because it tends to degrade. Storage should be in stainless steel tanks, preferably with nitrogen blanketing.

In the second half of Table 2 ("Fuel Handling and Maintenance Additives"), the first additive is the electrical conductivity improver-a proprietary additive sold by Innospec, Inc., under the name Stadis 450. Stadis 450 can be added to jet fuel on initial blending at the rate of 3 mg/l maximum. And because it contains a dispersant, it is surface active and will tend to plate out over time during handling. The jet fuel conductivity can be restored by re-blending such that the cumulative concentration does not exceed 5 mg/l maximum. If the additive concentration is unknown at the time of retreatment, then addition of the additive is restricted further to a 2 mg/l maximum. Stadis 450 contains dinonylnaphthylsulfonic acid (DINNSA). The Stadis 450 content can be determined by ASTM D7524, Standard Test Method for Determination of Static Dissipater Additive (SDA) in Aviation Turbine Fuel and Middle Distillate Fuels-High Performance Liquid Chromatograph (HPLC) Method. The conductivity additive will increase electrical conductivity, allowing for the more rapid dissipation of static charges. Additional information on conductivity and the measurement requirements of conductivity once the additive is used were given in the previous section on static electricity.

Other additives in this section are leak detectors. These too are proprietary additives and are used to find underground pipe leaks—not an inconsiderable problem when looking at underground piping in airfields where large expanses of thick concrete are used. Fuel leaks have been known to impinge on underground baggage handling facilities. To facilitate finding these leaks, Tracer A (LDTA-A) can be added to fuel at an amount of 1 mg/l maximum. This additive is a very volatile halo carbon that will find its way from the leak point to the surface, and from there it can then be traced back to the point of the leakage. When using this additive, it is important to follow the manufacturer's instructions and to liaise closely with the pipeline owner and operator—especially in regard to disposal of the treated fuel in the pipeline.

Biocidal additives are allowed under strictly controlled applications and can help in limiting microbial growth. Two proprietary additives are included in Table 2, Biobor JF and Kathon FP 1.5. Neither of these additives are intended for continuous use but for spot treatments. If microbiological growth is found in storage tanks or low points in lines or in aircraft wing tanks, then spot treatment is possible. Where such additives are used in jet fuel that will be consumed by aircraft, then the approval status of the additive and associated conditions of use must be checked for the specific aircraft and engines in which it will be used. One point of reference for determining if either biocide is acceptable is the aircraft maintenance manual (AMM). Because it contains boron, Biobor JF can cause metallic ash to develop in the engine and can only be tolerated in controlled amounts. Kathon FP 1.5 will migrate into the water bottoms and care must be exercised on their discharge. The water bottoms must be treated to remove/deactivate the Kathon FP 1.5 before further discharge to sewers or to water treatment facilities that use microbes to digest hydrocarbons in the water.

The best practice against microbiological contamination (MBC) is to prevent microbial growth in the first place. The main microbial growth in jet fuel, but by no means the only one, is a fungus called *Hormoconis resinae*. (It was originally called *Cladosporium resinae* and is still sometimes referred to by that name [12].) All microbiological growth requires free water, and growth occurs at the interface between water and jet fuel. See Fig. 8.21. Consequently MBC is found where there are water

FIG. 8.21 Microbial growth at the interface between water (brownish-colored bottom layer) and jet fuel (upper layer with some microbial growth clinging to the glass in the upper jet fuel layer).



bottoms in tanks, in vessels, and in low spots on lines, and even in aircraft wing tanks. The best way to prevent MBC is to not have water accumulation and water bottoms in tanks. It is recommended that facilities should be designed to allow water to move into sumps from where it can be drained and removed on a regular and frequent basis. There should be no water bottoms with jet fuel. If water bottoms are not present, MBC does not become a problem. For detailed information on microorganisms in petroleum products, the reader is referred to ASTM **D6469**, *Standard Guide for Contamination in Fuels and Fuel Systems*.

The last class of additive in Table 2 is a dual action group. Corrosion inhibitors also have lubricity improvement capabilities. They will help prevent rusting of mild steel and will improve boundary lubrication. The approved corrosion inhibitor/lubricity improvers are listed in Mil-I-25017 and Def Stan 68-251 as well as in ASTM D1655, Table 2. All the corrosion inhibitors approved for jet fuel will also act as lubricity agents, but users should take note of the specification requirements spelled out in Paragraph 5.2.1 of ASTM D1655. Additive usage must be agreed to by the purchaser. In large airports, it is difficult to obtain agreement to add them at the skin of the aircraft for a single airline user and even more difficult to get approvals to inject the additive upstream where approval would be required from all airlines uplifting fuel at the airport. These additives are highly surface active. They are often derived from di-linoleic acids and work by having a strong bonding end to a metal or other surface with the hydrocarbon tail sticking out into the fuel. This high surface activity means that the additives will disarm and render coalescing filters ineffective for removing water and dirt.

The three corrosion inhibitor/lubricity improvers currently listed in Table 2 are:

•	Hitec 580	23 mg/l maximum
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- Innospec DCI-4A 23 mg/l maximum
- Nalco 5403 23 mg/l maximum

More information on corrosion inhibitor/lubricity improver additives is given in ASTM **D1655**, Appendix X 1.10.

One other additive not approved but that is being considered is referred to as a drag reducer additive (DRA). This class of additives is a very high molecular weight material that will align horizontally in the fuel and help to reduce energy losses in pipelines by reducing turbulence. The driver for considering these additives is that several U.S. airports have restricted growth in the number of flights because the pipelines supplying the airport are at maximum capacity and cannot get enough fuel to the airport for expanded operations. The use of the additive would allow greater volumes of fuel to be delivered down the pipeline. However, past research has shown that traces of the additive will affect atomization of the fuel in engines, especially at low temperatures. Much more work will be needed to attain approval for the DRAs to be used.

Finally, before leaving this section on additives, there are some general words of caution. The allowable maximum dosages are stated in the text of specifications and must be followed. Overdosing can lead to problems. Always follow the recommendations and specific requirements in the specifications and in the AMMs. If there is any doubt about how to use an additive and how and where to inject it, then contact the additive manufacturer. Generally, mixing different additives for injection is not recommended; rather, adding them separately to jet fuel is preferred.

8.1.10 TABLE 3, INCIDENTAL MATERIALS

In ASTM D1655, Paragraph 6.3, there is an explanation that "incidental materials" are chemicals or other components that can sometimes occur in turbine fuels in trace levels that are hard to define. These trace-level incidental materials can be there as a result of crude oil production, processing within the refinery, or they can be from subsequent distribution and storage. These chemicals are unwanted in jet fuel but are considered unavoidable from a practical viewpoint. Table 3 in ASTM D1655 serves as a list of these incidental materials. However, at this time, just one material is listed-fatty acid methyl ester (FAME). FAMEs are usually added to diesel at 5 to 7 volume % to create biodiesel, although sometimes higher levels may be used. In the United States, using FAME at 5 volume % does not need to be declared, and diesel meeting ASTM D975, Standard Specification for Diesel Fuel Oils, can contain FAME when sold. FAMEs are surface active; if diesel containing FAME is passed down a multi-product pipeline, some FAME will adhere to the walls and therefore could be transferred to jet fuel subsequently traveling down the same pipeline. FAME is detrimental to gas turbines, and there is a history of FAME usage causing problems in industrial and marine gas turbines.

Although the OEMs would prefer that the specification note zero FAME inclusion, philosophically, that would not be correct because a limit at zero cannot be defined. Zero is a concept and not a number. Accordingly, after debate at ASTM meetings, a decision was made to include FAME in Table 3 and set a limit at the lowest level of detection by the best available test apparatus and technique. The specification was initially set at 5 mg/kg maximum and, as stated in part in the original Note B, "FAME is not approved as an additive for jet fuel. This level (5 mg/kg max.) is accepted by approval authorities as the functional definition of 'nil addition.'" The original requirement was that the amount of FAME be tested by a double gas chromatography technique usually referred to as a GC-GC method. This requirement was later expanded, and now IP 585 or IP 590 and other methods for testing FAMEs are included in Table 3.

Those in the pipeline industry as well as others have stated that, with the maximum level for FAME at 5 mg/kg, it would not be possible to handle biodiesel and jet fuel in the same pipeline. With restrictions and care in sequencing and extra volumes of transmixes, it might be possible to handle diesel containing FAME if the allowed level was 100 mg/kg maximum. An extensive program was conducted to ascertain the effect of FAME on aircraft turbine engine operations using a rate four times that of the anticipated specification level of 100 mg/kg maximum. Although considerable effort was put into the test program and the 400 mg/kg FAME mixture did not appear to be detrimental, the testing was not absolutely conclusive that there would not be problems in some aircraft with increased deposition under high temperatures. However, a compromise is currently in place to allow the usage of 50 mg/kg maximum FAME for two years to see if any field problems arise. After that time, consideration will be given to the possibility of allowing the level in Table 3 to be increased to 100 mg/kg maximum.

8.1.11 SAMPLING

ASTM **D1655**, Paragraph 9, covers sampling. Every test result is only as good as the sample. Sampling of aviation fuel is very important. ASTM **D4057**, *Standard Practice for Manual Sampling of Petroleum and Petroleum Products*, provides information on sampling and sampling techniques. The sample container also is important. A number of jet fuel properties including thermal stability, electrical conductivity, lubricity, and MSEP are very sensitive to trace contamination and—in the case of electrical conductivity—to light. For recommended sample containers, refer to ASTM **D4306**, *Standard Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination*.

In the case of handling high volatility fuels such as JP-4, Jet B, and aviation gasoline (avgas), the samples must be kept cool (in an ice bath or refrigerated) and it is advisable to follow the suggested sample handling procedures outlined in ASTM **D5842**, *Standard Practice for Sampling and Handling of Fuels for Volatility Measurement*.

8.1.12 REPORTING

Paragraph 109 of ASTM D1655 advises that when the Table 1 test results and Table 2 additive additions are to be reported at the point of manufacture and batch origination, the details should be recorded on a formally identified document-either a certificate of quality (COQ) or a certificate of analysis (COA). Both terms are commonly used. Another important part of the specification that is sometimes overlooked is the requirement noted in Paragraph 10.3.3 that the quality system used by the reporting laboratory must be designated. If no quality system is used, then this should be reported as "none." Suitable laboratory quality reporting systems would be in compliance with ASTM D6792, Standard System in Petroleum Products and Lubricants Testing Laboratories, or ISO 17025, General Requirements for Competence of Testing and Calibration Laboratories. Auditing by an outside agency using either ASTM D6792 or ISO 17025 is recommended and enables the appropriate quality system to be included and reported on the COA/COQ.

Paragraph 10 also makes reference to Appendix X3, which is the recommended but non-mandatory reporting form for the inspection data in the COQ/COA. In particular, it is recommended that whatever form is used, it should also have on it the actual maximum or minimum specification value for each property so it is possible to see if the testing shows the product to be on spec. (There is more on this subject in the next section.)

8.1.13 HOW TO DECIDE IF THE TEST RESULTS MEET THE SPECIFICATION

As explained in Paragraph 7.2 of ASTM **D1655**, the test results shall not exceed the maximum or minimum values in Table 1. No allowance is to be made for the precision (repeatability/reproducibility) of the test method. To determine conformance to the specification, a test result may be rounded to the same number of significant figures as in Table 1 using ASTM **E29**, *Practice for Using Significant* Digits in Test Data to Determine Conformance with Specifications. There is a very deliberate selection and reasoning behind the number of significant figures in the Table 1 specification limits. The number of significant figures is based on the cost to manufacture the product and availability versus the specification test limit's technical justification of need for the operation of an aircraft. In several cases, the test method reporting has a greater number of significant figures than in Table 1 of ASTM **D1655**, and these should be recorded appropriately in laboratory notebooks and records. The laboratory test results should then be reduced to the number of significant figures as indicated in the specification and recorded as such on the COQ/COA.

Single values or averaged test values must meet the specification limit. Failed values cannot be discarded. If a result does not meet the test, it is permissible to repeat the test—in which case, an average result must be recorded, including the failed result. And the averaged result must meet the specification. Most refineries have a decision tree for looking at "unusual" results. Did the operator perform the test correctly? Is the apparatus working correctly and is it accurately calibrated? Was the sample taken correctly? Results should be discarded if there is a known and valid reason to do so; otherwise, failed results should be included in the averaging. EI 1530, *Quality Assurance Requirement for the Manufacture, Storage and Distribution of Aviation Fuels to Airports*, Annex E, "Criteria for Rejecting Laboratory Test Data or Resampling," has some good examples of decision analysis charts [13].

8.1.14 QUALITY CONTROL PROCEDURES

Although not strictly part of ASTM **D1655**, it would be remiss to leave this chapter without commenting on the quality control of aviation fuels. As stated previously, the mantra for aviation fuel movements is "keep it clean and keep it dry." This is accomplished by the use of clay filters, micronic filters, filter water separators, and filter monitors—all of which are a subject outside the scope of this work. (Refer to EI 1550, *Handbook on Equipment Used for the Maintenance and Delivery of Clean Aviation Fuel* [11].) To help judge the acceptability of the cleanliness of jet fuel, there are a number of field tests that are regularly used to measure and detect the presence of:

- Free water
- Particulates/dirt
- Microorganisms

The quality control tests used in the field can be found in *ASTM MNL 5, Aviation Fuel Quality Control Procedure* [14]. This book also has information on maintaining filtration equipment.

The actual quality control procedures are laid out in detailed documents such as Air Transport Association (ATA) Specification 103, *Standards for Jet Fuel Quality Control* [15], which is used extensively in the United States, and the Joint Inspection Group (JIG) manuals, JIG 2, *Aviation Fuel Quality Control and Operating Standards for Airport Depots and Hydrants* [16], and JIG 3, *Aviation Fuel Quality Control and Operating Standards for Supply and Distribution Facilities* [17], which are used outside of the United States. There are also many company-specific operating manuals on quality control procedures.

8.1.15 OVERVIEW AND CONCLUDING REMARKS

For safety reasons, specifications and handling procedures for aviation fuels are more tightly controlled than for other products. The current aviation manufacturing, fuel supply, and delivery systems are based on accumulated experience that has evolved over a long period of time and that continues to evolve today, forming the basis of ASTM D1655, Standard Specification for Aviation Turbine Fuels. The complexities of the interactions among the technical, legal, and financial aspects associated with aviation fuels can make it difficult at times to resolve problems but the processes employed by ASTM can pull these different perspectives together. ASTM is unique in its ability to bring together the world's leading technical experts and to empower them to work together to achieve the common goals of developing first-class aviation standards that the world can use. ASTM's focus is on the development and delivery of high-quality, market-relevant standards providing safety in the skies.

8.2 Aviation Fuels: Aviation Gasoline

There are more than 200,000 piston-engine aircraft worldwide that rely on ASTM **D910**, *Standard Specification for Aviation Gasoline* [1], for safe operation. This part of the chapter is about ASTM **D910**, which defines a lead-containing aviation gasoline. The lead is considered essential for the safe operation of many aircraft. There are two other specifications covering unleaded aviation gasolines, ASTM **D6227** and ASTM **D7547**, and these are mentioned but not covered in detail in section 8.2.18 of this chapter, "Other ASTM Aviation Fuel Specifications."

8.2.1 INTRODUCTION AND BRIEF HISTORY OF MAIN GRADES

The primary requisites of an aviation gasoline property and accompanying specification limit are to ensure satisfactory and acceptable performance without compromising flight safety. Aviation gasoline is used in spark-ignited internal combustion engines to propel aircraft. Aviation gasoline which is often abbreviated as avgas, is not the same as motor gasoline (mogas). The ASTM D910 avgas specification is very tight and specific, detailing special components-some manufactured in the refinery and some possibly brought into the refinery from outside-that are blended together to make the finished product. The lead and dye components are always brought into the refinery, and sometimes toluene is purchased and also brought in. Unlike Mogas, which is unleaded worldwide (at least these days), avgas still contains lead-although there is considerable work being undertaken to find a suitable unleaded fuel with the attributes of the most common grade of avgas (Aviation Gasoline Grade 100LL; the LL standing for low lead).

The first powered flights used automotive gasoline engines, and a replica of the Wright Brothers' Aero engine that flew in 1903 can be seen at the New England Air Museum near Hartford, Connecticut (see Fig. 8.22). World War I saw a huge increase in flying as the tactical advantages of aircraft in mapping and in following ground troop movements became obvious. This FIG. 8.22 A restored working model of a Wright Brother's gasoline engine similar to that which powered the first flight in 1903.



jump-started the military interest in aviation in the United States and in Europe. By the start of the World War II, aircraft were armed and very much in demand as tactical weapons. The growth of aviation after World War I and before World War II makes for fascinating reading in print and online (for example, see https:// oldmachinepress.wordpress.com).

In 1930, the U.S. Army Air Corps specified a fighting grade gasoline with a minimum octane number of 87. And by the start of World War II, fuels very similar to today's Grade 100 were in use. In 1944, the U.S. military issued a specification for Grade 115/145. This fuel, which had the highest antiknock rating of any avgas in large-scale production, was used to obtain maximum output from high-performance engines. There were then five grades of avgas ranging from 80/87 to 115/145. ASTM recognized the need for standardization and, after the war, put these grades into a civil specification. In 1947, ASTM D910, *Standard Specification for Aviation Gasoline*, was issued, and this still is the primary worldwide aviation gasoline standard in use today.

Over time, aviation gasoline was reduced to just two grades, a low lead content 80 octane and a high lead 100 grade. Then, during the mid-1970s, the announcement of a single-grade aviation fuel for all reciprocating aircraft engines created a furor that gradually faded away as pilots and mechanics became more knowledgeable about the actual effects of using the new Grade 100LL. Grade 100LL allows a maximum of 0.53 mL of tetraethyl lead (TEL) per litre (which is equivalent to 2 mL of lead per gallon, or 0.56 gPb/L) and is rated at 100 octane, when the engine is leaned for cruise, and at 130 octane, when the mixture is set rich. The fuel is designated as "low lead" because the previous fuel with a 100/130 octane contained twice as much lead, 4 mL per gallon.

For all practical purposes, Grade 80 fuel, which allows a maximum of 0.13 mL of TEL per litre (one-half millilitre per gallon), has been phased out and is no longer available. Grades of avgas are identified by their nominal minimum lean-mixture antiknock rating. Previously, both the lean and rich ratings were used; now, only the lean-mixture rating is used for grade identification.

Today, avgas is used mainly by small/mid-sized airplanes, made up of personal recreational aircraft, air taxi services, small air charter aircraft, crop dusters, and so on, that are included in what is called the general aviation (GA) market. The GA market is primarily made up of spark-ignited internal combustion engine aircraft, but FAA Part 91, describing the GA market, also includes business jets and rental jet services. Avgas grades are also used in helicopters and in military and civilian transports powered by large piston engines. Additionally and of special note, the Predator drone runs on aviation gasoline, proving that even very sophisticated aircraft run on avgas. See Fig. 8.23.

There are two main specifications that cover avgas, ASTM D910 and Def Stan 91-90 [18]. Of these, ASTM D910 is used more on a worldwide basis. These specifications basically describe the same grades of avgas, although there are minor differences between the specifications for the same grade. They differ over antioxidant content, oxidation stability requirements, and maximum lead content.

In ASTM **D910**, Grade 100LL is the most popular grade by far. But there are other grades within the ASTM D910 specification such as Grade 100, which is still available in certain countries and in Hawaii. Some refineries find it difficult, on a continuous basis, to always meet the 100 octane with only the 0.53 mL of TEL per litre (0.56 gPb/L) maximum allowed by the 100LL specification. In order to be able to continue selling an avgas product on a consistent basis, refineries label it as 100 and dye it green—even though most of the time it meets the lower lead requirements for the 100LL grade. Occasionally, they nudge the lead up above the 0.53 mL TEL per litre and into the range allowed by the 100 Grade, which is 1.06 mL of TEL per litre

FIG. 8.23 Predator drone—it uses aviation gasoline and is powered by a Rotax piston engine.



(1.12 gPb/L) maximum. Not knowing exactly when they will need to nudge the lead levels up, refineries consistently sell the product under the name Grade 100. ASTM recently reintroduced Grade 91 (leaded) into ASTM D910 to facilitate its use in certification testing, but it is not intended as a commercial product. There is one other grade in ASTM D910 (100VLL) that allows for a maximum lead content of 0.45 gPb/L. Rather like the 100 and 100LL cases, there are refiners who can make the 100VLL, but then find that they are sometimes low on octane. They then boost the 100VLL with lead, and the product moves back into the 100LL grade lead level. Both grades are dyed blue. Not unlike the 100 grade example noted earlier, the lead level may be nudged above the 0.045 gPb/L and consistently sold under the name 100LL even though some of the time it will meet the lead limit set in Grade 100VLL. Most airports and fixed base operations serving general aviation will only have the single Grade 100LL available. All of the five grades in ASTM D910 contain lead. Table 8.2 lists the five grades, their lead levels and their colors, and their octanes. Each grade has a dye or dyes added to give it a different color to aid in identification and to help prevent misfueling. The lead level must be measured and reported for each batch made. Measurement of lead content is by either ASTM D3341, Standard Test Method for Lead in Gasoline—Iodine Monochloride Method, or ASTM D5059, Standard Test Method for Lead in Gasoline by X-Ray Spectroscopy.

Under pressure from OEMs, and to ward off the use of unleaded motor gasoline in aircraft, a lower octane grade specification was issued to try to come up with a lower cost product. Grade UL82 was given its own specification, ASTM **D6227**, *Standard Specification for Grade 82 Unleaded Aviation Gasoline*. A Grade UL87 was subsequently added to this specification, and the specification was renamed *Standard Specification for Unleaded Aviation Gasoline Containing a Non-Hydrocarbon Component* (see section 8.2.18, "Other ASTM Aviation Specifications," for further information on ASTM **D6227**). This specification was also put in place to ensure oversight by the aviation industry. This is a low octane grade suitable only for low compression engines. It has a higher vapor pressure and can be manufactured utilizing some motor gasoline components. It is particularly applicable to those aircraft that have supplemental type certificates (STCs) authorizing them to use

 TABLE 8.2
 Simplified table of the five grades of leaded aviation gasoline in ASTM D910.

	Grade 80	Grade 91	Grade 100VLL	Grade 100LL	Grade 100
Octane MON min	80.7	90.8	99.6	99.6	99.6
Octane Aviation Rich Mixture min	87	98			
Performance Number min			130.0	130.0	130.0
Tetraethyl Lead mL					
TEL/L max	0.13	0.53	0.43	0.53	1.06
gPb/L max	0.14	0.53	0.45	0.56	1.12
Color	Red	Brown	Blue	Blue	Green

"automotive type gasolines." Commercialization of this fuel has not proceeded because the development of new engines specifically designed to run on this fuel has been slow to nonexistent. Additionally, the oil company and engine manufacturer have concerns regarding liability. The 30 % of the fleet that cannot operate on an automotive type gasoline but must use avgas consumes 70 % of the fuel. That is because those planes are more highly utilized and typically are larger, more powerful, mid-sized aircraft whose engines take advantage of the higher octane to produce more power. With the limited ability to distribute only one grade, this has meant that 100LL is the major, and often the only, grade sold at airfields.

Finally, there is ASTM D7547, Standard Specification for Hydrocarbon Unleaded Aviation Gasoline. This specification was introduced at the behest of the military to help enable them to purchase an unleaded gasoline of suitable octane for use in the Rotax engines that power the Predator drones. See Fig. 8.23. The drones are a special case because they travel on what is called loitering missions at relatively low speeds; as a consequence, there can be incomplete combustion, which tends to build up spark plug deposits that can be severe. When operating on leaded avgas, the combustion deposits contain lead oxides that make the deposit conductive. Then, when the spark plug gap is bridged, there is no spark and combustion is compromised, making for an insidious problem. (See Fig. 8.24 for a severe case of lead deposits on a spark plug.) The Rotax engines in drone loitering operations require an unleaded gasoline. (It should be noted that some of the more modern history of aviation gasoline is covered in section 8.2.19 of this chapter, "The Ongoing Conundrum of Taking the Lead Out of Aviation Gasoline.")

FIG. 8.24 Spark plugs that have been bridged and have become inoperative.



8.2.2 HOW TO FIND WHERE THE PROPERTIES AND TESTS IN ASTM D910 ARE DISCUSSED WITHIN THIS CHAPTER

In **Table 8.3**, the left column gives the individual properties that are specified in ASTM **D910** and the right column lists the chapter section in which the property is discussed. Hopefully, this will ease the way of finding information associated with the test property.

8.2.3 AVIATION PISTON AIRCRAFT ENGINE PERFORMANCE AND KNOCKING

The importance of fuel knock resistance through adequate octane cannot be overemphasized. Therefore, before a review of the aviation properties and the ASTM **D910** specification, this section of the chapter will review the how and the why of detonation and knocking. There are significant differences in operations and designs between an automobile engine and an aviation engine, and this section will address some of these differences.

Engine knocking is the sound of abnormal combustion. It is also known as spark knock. Normal combustion in a sparkignition internal combustion engine is initiated by a spark. Within a combustion chamber, with normal "good" combustion after the spark, the flame front fans out from the spark plug and travels across the chamber rapidly and smoothly, with emphasis here on the smoothness of the combustion, until all fuel residing in the chamber is consumed. In the most common form of aviation piston aircraft, the engine is a flat four or flat six. See Fig. 8.25. And there are normally two spark plugs per cylinder. See Fig. 8.26 for a typical wiring diagram. So, in an aircraft engine of this type, the flame fronts within the cylinder travel in opposite directions toward each other.

When combustion is abnormal, it generally starts well, but then irregularities occur and the last part of the unburned airfuel mixture ignites spontaneously (auto ignition) and burns very rapidly, like an explosion, causing the pressure in the cylinder to rise rapidly. This creates the characteristic knocking or pinging sound. Conditions that create heavy or prolonged knocking can result in:

- · Loss of power
- Overheating of engine parts
- Knock-induced surface ignition
- Engine damage

Spark-ignition aircraft engines are more susceptible to catastrophic problems related to the overheating of engine parts because of the extensive use of aluminum alloys and other lowmelting-point metals to keep weight down and to allow for good conductance of heat in these air-cooled engines. It is also easier and cheaper to manufacture the complicated fins surrounding the cylinders from aluminum alloys. These air-cooled fins are the main way of conducting heat from the cylinder to the cooling air, thereby keeping the engine cylinder operating within controlled temperature limits.

Knock occurs because the burning of the aviation gasoline is not smooth under the conditions pertaining at the time in

TABLE 8.3 Location guide.

Detailed Requirements of Aviation Gasoline Fuel	Test Method	Chapter Section Where the Requirement is Discussed
Workmanship, Finish, and Appearance	See Para. 8 of ASTM D910	8.2.4 The Set-up of ASTM D910 -Table 1 and Appendix 1
		8.2.11 Fuel Cleanliness, Handling, and Storage Stability
		8.2.17 Quality Control Procedures
ASTM D910 Table 1 Specification Requirements		
Octane Ratings		8.1.1 Introduction and Brief History of Main Grades
Motor Octane Number	ASTM D2700	8.2.3 Aviation Piston Aircraft Engine Performance and Knocking
Aviation Lean Rating	ASTM D2700	8.2.6 Compusition Characteristics and Knock Resistance
Knock Value—Rich Mixture		
Octane Number	ASTM D909	
Performance Number	ASTM D909	
Tetra Ethyl Lead	ASTM D3341	8.1.1 Introduction and Brief History of Main Grades
ml of TEL/L	or	8.2.3 Aviation Piston Aircraft Engine Performance and Knocking
ml of gPb/L	ASTM D5059	8.2.6 Combustion Characteristics and Knock Resistance
Color	ASTM D2392	8.2.13 Additives
Dye Content		
Density at 15°C kg/m³ Report	ASTM D1298 or ASTM D4052	8.2.8 Fuel Metering and Aircraft Range
Distillation Temperatures Initial Boiling Point—Report °C 10 % Evaporated 75°C max. 40 % Evaporated 75°C min. 50 % Evaporated 105°C max. 90 % Evaporated 135°C max. Final Boiling Point 170°C max. Sum of 10 % and 50 % 135°C min. Recovery vol. %, 97 min. Residue % 1.5 max. Loss % 1.5 max.	ASTM D2887	8.2.7 Volatility, Carburetion, and Vaporization
Vapor Pressure at 38°C 38.0 min. 49.0 max.	ASTM D323 or ASTM D5191	8.2.7 Volatility, Carburetion, and Vaporization
Freezing Point –58°C max.	ASTM D2386	8.2.9 Fluidity at Low Temperatures
Sulfur 0.05 mass % max.	ASTM D1266 or ASTM D2622	8.2.10 Non-Corrosivity and Compatibility
Net Heat of Combustion 43.5 MJ/kg min.	ASTM D4529 ASTM D3338 ASTM D4809	8.2.8 Fuel Metering and Aircraft Range
Copper Strip Corrosion, 2 h at 100°C, No. 1 max.	ASTM D130	8.2.10 Non-Corrosivity and Compatibility
Oxidation Stability 5 h Aging Potential Gum 6 mg/100 ml max. Lead Precipitate 3 mg/100 ml max.	ASTM D873	8.2.11 Fuel Cleanliness, Handling, and Storage Stability 8.2.13 Additives
Water Reaction	ASTM D1094	8.2.11 Fuel Cleanliness, Handling, and Storage Stability
Volume Change No More Than + or −2 ml		
Additives Electrical Conductivity (If Additive is Used) 50–450 pS/m under the Conditions at Point of Use	ASTM D2624	8.2.12 Static Electricity 8.2.13 Additives

FIG. 8.25 UL Power UL260i horizontally opposed four-cylinder, air-cooled aero engine.



the engine. The antiknock rating (octane number) is below the antiknock requirements of the engine at that particular moment of operation. Generally, the situation involves high-load conditions, such as hard acceleration and climb during takeoff, but knocking also can occur in lean cruise operation. Knocking in an aircraft engine may not be audible, either on the ground or during flight, because of propeller noise, wind, engine cowling rubber closures, and cabin insulation.

Other abnormal combustion phenomena can occur in addition to knocking. Surface ignition involves ignition of the air-fuel mixture by a hot spot rather than a spark. Potential ignition sources include glowing combustion chamber deposits and overheated spark plug electrodes.

Heavy, prolonged spark knocking can generate hot spots that produce surface ignition. A hot spot can ignite a portion of the airfuel mixture before the mixture would normally start to burn. This may occur either before or after the spark ignition. Surface ignition before a spark is called pre-ignition. Surface ignition after the spark is called post-ignition. When pre-ignition occurs, ignition timing is lost and upward movement of the piston is opposed by the high pressure generated by the early combustion. This results in engine roughness, power loss, and severe localized heating of the piston crown. If it is prolonged, the localized heating can burn a hole in the piston.

When pre-ignition is caused by a hot spot generated by prolonged, heavy spark knock, it is known as knock-induced pre-ignition. It has the same adverse effect on engine operations as pre-ignition from other sources. Knock-induced pre-ignition is the most damaging side effect of spark knock.

Post-ignition reduces combustion time, and loss of combustion control can cause knock, engine roughness, and reduced power output. The extent of the effect of post-ignition depends on its location in a combustion chamber and the time in the combustion cycle at which it occurs.

In modern automotive engines, there is electronic spark timing linked to knock sensors that will retard the timing of the spark and limit the damage caused by knocking. In fact, it is not uncommon for auto manufacturers to claim that "light knock is the sound of fuel economy" and not something to worry about. In automotive engines, the timing changes with speed and load by the computer-controlled ignition system. Because of the need for absolute reliability of the systems over significant temperature changes, +30°C on the ground to -10°C at 15,000 ft, many aircraft engines do not rely on computers and timing changes; instead they use magnetos with fixed spark timing. (This non-reliance on computers for GA aircraft components is changing with the advent of full authority digital engine control [FACE].) Almost all aviation engines have very reliable fixed timing engines. The magnetos, required to produce robust sparks in the less dense air at altitude, always fire the plugs 25° or 20° (or however the engine was set up) before top dead center of the piston. That does not vary with engine

FIG. 8.26 Four-cylinder, horizontally opposed engine-ignition system components.



FIG. 8.27 Electronic ignition coils (a) and left and right magnetos in a Continental flat six engine (b).



(a)

(b)

speed or engine load. With fixed timing, there are some engine conditions where the timing is not optimal, and that off-ideal operation is where the need for an aviation gasoline with high octane to avoid suboptimal detonation is paramount. Aviation engines need high octane gasoline with lead in it to help create that smooth combustion and to stay away from destructive abnormal detonations. (More on the lead factors is discussed later in the chapter; the industry is striving to move away from the use of lead because of toxicity concerns.) See Fig. 8.26 for a diagram of the ignition system and the magnetos, Fig. 8.27a for a photograph of the electronic ignition control in a Van Kit plane, and Fig. 8.27b, which shows the left and right magnetos in a flat six cylinder Continental engine.

Another difference in aviation engines versus automotive engines is the lack of a water cooling system in aviation engines. Most aviation gasoline engines rely on air cooling. The horizontally opposed engines have finned castings around the outside of the cylinders and rely on the passage of air across these fins to keep the engines cool. Heat is the enemy of smooth combustion, and a lack of good heat dissipation from the cylinders can set up trouble and the onset of knock. Air is carefully channeled into the engine compartment and diverted to flow evenly around the engine cylinders. On an automotive engine, the liquid coolant system takes heat away relatively easily and ejects it through the radiator. By having an air-cooled system, the aviation engine avoids a substantial weight penalty. A good way to keep the heat level down inside the cylinder is to run rich, with extra gasoline present. As the gasoline liquid evaporates in the manifold, it helps to take heat out of the air and vapor entering the engine's cylinders. Running rich is also a natural occurrence in aviation engines. Due to the drop in atmospheric pressure as altitude is increased, the density of the air also decreases. A normally aspirated engine has a fixed amount or volume of air that it can draw into each cylinder during the intake stroke; therefore, less air is drawn into the engine as altitude increases. Less air makes carburetors run richer at altitude than at ground level because of the decreased density of the airflow through the carburetor throat for a given volume of air. Thus, it is necessary that a mixture control be provided to lean the mixture and to compensate for this natural enrichment. Some aircraft use

carburetors in which the mixture control is operated manually. Other aircraft employ carburetors that automatically lean the carburetor mixture at altitude to maintain the proper fuel/air mixture. An engine running at full power requires a rich mixture to prevent overheating and detonation. There is a delicate balance on takeoff and climb between the need to lean out the mixture because of air density changes and the need to stay rich to prevent detonation; but once cruise at altitude is reached, the engine can be leaned slightly. Because aviation is weight and reliability sensitive, this places greater emphasis on fuel octane and prevention of detonation. Prevention of knocking detonation is much more critical to achieving aircraft performance efficiency than it is to automobiles.

The role of lead in preventing knocking detonation is not fully understood but a layman's view of what happens inside an aircraft cylinder may help the reader in appreciating the value of lead in aviation operations. Using your imagination and an approach used by Sir Harry Ricardo in explaining the operation of a diesel engine, Alisdair Clark of BP has suggested the following:

How does the octane enhancement additive TEL work in an aviation spark-ignition piston engine?

Imagine you are standing on top of the piston in the very heart of the engine. You feel yourself falling, faster than any elevator you have ever known, as the piston races downward. Above you, in the darkness, the inlet valve opens. There is a howl of wind as turbulent air already mixed with fuel vapor races into the chamber, sucked in by the downward pull of the piston. The inlet valve closes precisely on time and tightly. The piston stops at the bottom of the revolution, all is quiet. Next moment, you are hurtling upwards, as the piston accelerates in the compression stroke. It's becoming hot as the air/fuel mixture is compressed, really hot, up to 490°C (over 900°F), and the pressure climbs to between 150 psig to 300 psig (10 to 20 atmospheres). In the blackness above your head two flashes leap from the darkness like lightning bolts-the spark plugs, again precisely on time, have lit the fuel. Two balls of fire now steadily proceed out from each plug across the chamber. The temperature soars to over 1650°C (3000 °F) and pressure is immense at over 1050 psig (70 atmospheres). The piston changes direction again and you are now falling, pushed back by the immense force of this, the power stroke.

Heat is radiated from the flame fronts across the engine chamber. You look to one side, across the piston, at the fuel which is yet to burn. The air and fuel molecules rattle, they are keen to get going with the oxygen, and they are getting over excited, and busting to react in the immense heat and pressure. No, they must not explode—if they do the shockwave will blast metal from the piston and damage the engine. They must wait, wait for the flame. But can they cope? Suddenly you see another reaction, accelerating forward to match the severity of the conditions—a mist of lead oxide forming as the additive tetraethyl lead decomposes. This races ahead of the flame, reaching across the combustion chamber and calming the fuel and air and reassuring it, "Don't get excited and all will be well." Now they will burn smoothly, and all is well. No explosion, no knock, and no burnt piston.

Severe engine conditions promote detonation but also accelerate the decomposition of tetraethyl lead to control detonation. The additive is like a fire engine—the more severe the fire, the more quickly it drives to the rescue. This effect offers an explanation for the 2–3 octane numbers difference often seen in the full size engine anti-detonation performance of leaded versus unleaded aviation gasolines.

(For the structure of tetra ethyl lead see section 8.2.13, "Additives," in this chapter.)

8.2.4 THE SET-UP OF ASTM D910—TABLE 1 AND APPENDIX 1

In ASTM **D910**, *Specification for Aviation Gasolines*, there is the all-important Table 1. Table 1, Detailed Requirements for Aviation Gasoline, is the main part of the specification, giving the properties and limits for all five of the grades. Along with each property, there is an assigned ASTM test method or methods detailing how the property is to be measured. And of course, there is a limit (a maximum or minimum or range) associated with the property.

Table 1 of ASTM **D910** is not the only place where the quality level is stated in order for the product to be labelled as Aviation Gasoline meeting ASTM **D910**. Paragraph 8 ("Workmanship, Finish, and Appearance") is as equally important as the requirements in Table 1. There is a critical statement in Paragraph 8 that, "The aviation gasoline specified in this specification shall be visually free of undissolved water, sediment, and suspended matter. The odor of the fuel shall not be nauseating or irritating. No substance of known dangerous toxicity under usual conditions of handling and use shall be present, except as permitted in this specification." Unlike many other fuel specifications, there is no actual measurement of water and sediment required for aviation gasoline or jet fuel; instead, ASTM **D910**, *Specification for Aviation Gasolines*, relies on the wording in Paragraph 8. The requirements of Paragraph 8 must not be ignored.

Appendix X1 ("Performance Characteristics of Aviation Gasoline") contains non-mandatory useful information about

the specification and the performance characteristics of aviation gasolines. It is worthwhile to read and understand Appendix X1.

8.2.5 PERFORMANCE REQUIREMENTS OF AVIATION GASOLINES

Aviation gasolines primarily are based on performance testing rather than on closely defined product composition. That being said, the limits set by the performance tests do tend to dictate the compositional requirements, and that will be explained in later sections of this chapter.

8.2.6 COMBUSTION CHARACTERISTICS AND KNOCK RESISTANCE

Knock-free engine performance is essential to smooth, reliable engine operations (see section 8.2.3, "Aviation Piston Aircraft Engine Performance and Knocking"). Octane number and performance numbers are measures of the ability of avgas to resist knocking as it burns in the combustion chamber. Two laboratory engine test methods are used to measure the antiknock performance of avgas. One measures performance at a lower fuel-air ratio (lean mixture conditions) that simulates cruising and the other at a higher fuel-air ratio (rich mixture conditions) that simulates take-off, where extra power is needed. Two tests are required because knock-free performance in the lean fuel-air regime does not guarantee knock-free performance in the rich regime in some engines. Using the motor octane number (MON) of a fuel solely to predict full-scale engine knock performance for leaded fuels is inadequate.

Aviation gasoline knock resistance is measured by the lean and rich engine tests. In the lean mixture method, ASTM D2700, Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel, the test variable is compression ratio, which is the ratio of the total volume displaced by the piston to the volume above the piston at the top of the compression stroke. When testing an unknown fuel, a single-cylinder engine conforming to the requirements in ASTM D2700 has the ability to change the compression ratio, and the ratio is increased until knock is detected. Blends of n-heptane and isooctane are then made and adjusted such that the ratio of the components changes. For example, a 10 % blend of n-heptane and 90 % isooctane would be called a 90 octane blend. Different blends are tested in the ASTM D2700 engine until a match is found with the test fuel. The percent isooctane in the matching blend is then taken as the test fuel's octane number. If the fuel octane exceeds 100, the match is made using pure isooctane and different amounts of tetraethyl lead (TEL) added to the isooctane. The quantities of TEL added to isooctane that the gasoline matches in knock characteristics when compared by the procedure specified may be converted to performance numbers by use of a chart in Table 8 ("Conversion of Motor ON to Aviation Method Rating") in ASTM D2700. The specification in ASTM D910 requires ratings by the old aviation octane method— ASTM D614, Standard Test Method for Knock Characteristics of Aviation Fuels by the Aviation Method-but this test was withdrawn in 1971 and replaced by the ASTM D2700 method. Currently "aviation lean" ratings are determined from the MON conversion tables in ASTM D2700. The equivalent aviation lean rating is

maintained in ASTM **D910** Table 1 as a specified parameter to ensure aircraft compliance with historical type certification.

The rich rating method ASTM D909, Standard Test Method for Supercharge Rating of Spark Ignition Aviation Gasoline, is more complex. Engine output is measured and controlled by a dynamometer. Air into the engine is compressed and cooled. Both fuel and air flow to the engine are metered. Engine loading by the dynamometer is increased at a constant fuel-air ratio until knock occurs. The same process is repeated at increasing fuel-air ratios to develop a curve of knock-limited engine output against fuel-air ratio. This curve is bracketed by similar curves using isooctane with varying concentrations of TEL. The test fuel rating is established by interpolation among the bracketing fuel curves and is expressed in terms of performance numbers that are directly proportional to engine power output. Thus, with a fuel having a performance number of 130, the engine developed 30 % more power than straight isooctane. (The octane number of the five grades in ASTM D910 are given in Table 8.2 of this chapter.)

8.2.7 VOLATILITY, CARBURETION, AND VAPORIZATION

Volatility is a fuel's tendency to vaporize, or move from a liquid to a vapor state. Aviation gasoline volatility is a major factor in engine operations and has to be carefully balanced between volatility that is high enough to start under cold conditions and yet low enough to avoid vapor formation in lines and pump suctions during rapid rates of climb.

Two physical properties are specified and tested to characterize avgas volatility. These are vapor pressure and distillation. A more volatile fuel has a higher vapor pressure and distills at lower temperatures. The strictly controlled distillation temperatures are shown in ASTM **D910** Table 1 and reproduced in **Table 8.4** of this chapter. The distillation temperatures are determined using ASTM **D86**, *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure*.

Aircraft engines use one of two basic systems to deliver fuel to the cylinders-either carburetion or fuel injection. In a carburetor, the fuel is drawn through by the suction created by the downward stroke of the piston with the inlet valve open. At the same time, air is drawn through the carburetor and the fuel and air are mixed in the throat area of the carburetor. This air and fuel mixture is then drawn through the inlet manifold where complete mixing occurs and the fine liquid fuel droplets evaporate to form a vapor. That vapor is then drawn into each of the cylinders in turn as they go through their downward strokes. In a fuel injection system, fuel is injected under pressure into the inlet manifold just above the intake ports. The injection of fuel is through very fine orifices, and the fuel is atomized to very fine droplets that help to speed up the evaporation and mixing. Mixing then continues in the cylinder during the compression stroke. The complete evaporation of the fuel is important and, in some carburetor engines, the greater length of time in the inlet manifold provides for more complete evaporation leading to smoother burning and operation than obtained with fuel injection. Remember, the air intake can be cold at altitude and injecting into very cold air may not give the atomized droplets sufficient time for full evaporation. Of course, for fuel injection, heating of the air inlet manifold is important.

Carburetion was used exclusively in early aviation engines and still is used today—although many planes manufactured in the last 20 years have fuel injection. Because the early planes were all carbureted, the avgas volatility specifications were developed for them and have remained unchanged. The same volatility specifications are suitable for fuel-injected engines.

A more volatile fuel decreases the likelihood of starting and running problems but increases the likelihood of vapor lock and boil-off problems. Additionally, icing problems increase slightly with higher volatility fuel. As stated at the outset, the distillation properties of avgas are a balancing act. **Fig. 8.28** shows a typical boiling curve for avgas; the specification limits are also marked in the figure. The distillation limits, along with vapor pressure limits, are shown in **Table 8.4**.

As can be seen from the curves in **Fig. 8.28**, the volatility of avgas is very carefully controlled. The boiling range is about 30°C to 150°C, which confines the hydrocarbons that can be present to the C_5 to C_{10} range predominated by molecule that are C_7 , C_8 , and C_9 . The constraints imposed by the distillation range, freezing point, vapor pressure, and the antiknock properties significantly limit the hydrocarbon molecules that can make up avgas, and it becomes a specialized material blended from individual components. The primary components are alkylate, toluene, iso-pentane, tetraethyl lead, and a dye or dyes.

Liquids do not burn-only vapors burn. In the vapor state, a fuel's molecules are spread far enough apart to allow for the oxygen from the air to react with the carbon and hydrogen atoms contained in the molecules of the fuel in the process of what we call combustion. So, starting a cold engine either on the ground or restarting it at altitude requires a fuel with a high enough volatility to form a vapor and air mixture in the flammable range. The lower the ambient temperatures, the higher the volatility of the fuel must be in a cold engine. Once the mixture of fuel and air has been formed on exit from the carburetor, it must be distributed evenly among all the cylinders. In a carbureted engine, the fuel must mix with the air-typically within one-sixteenth of a second, which is the time the fuel spends in the carburetor and manifold before entering the cylinder. If the fuel is only partially vaporized, some cylinders will receive a mixture of liquid fuel along with some fuel vapor and air. This will be a richer mixture. Other cylinders will receive a mixture of fuel vapor and air that is on the lean side. Also, because tetraethyl lead is less volatile than the fuel, the antiknock additive will tend to be concentrated in the liquid fuel. Tetraethyl lead breaks up before it boils because its decomposition temperature is 198°C. All of this leads to maldistribution of the fuel, along with differing lead contents among the cylinders and will create rough running conditions and poor fuel economy.

Vapor lock is a phenomenon that occurs when excessive heat from the engine enters the line and causes the gasoline to vaporize in the line or the pump. This reduces the fuel flow to the engine and causes it to run lean; loss of power and sometimes knocking occurs. In the worst case, the engine can stop and may be difficult to restart until the fuel system has cooled and the vapor either moves through the line or condenses back to a liquid. The altitude at which the





TABLE 8.4	ASTM D910 volatility limits of distillation and vapor
	pressure.

Property	Test Method	Value
Distillation	ASTM D86	75 max.
10 volume % at °C		75 min.
40 volume % at °C		105 max.
50 volume % at °C		135 max.
90 volume % at °C		170 max.
Final boiling point °C		135 min.
Sum of 10 % + 50 % evaporated		97 min.
temperatures °C		1.5 max.
Recovery vol %		1.5 max.
Residue vol %		
Loss vol %		
Vapor Pressure 38 °C, kPA	ASTM D323 or ASTM D5191	38.0 min. and 49.0 max.

engine is operating has opposing influences in regard to both vapor lock and boil-off (see next paragraph for discussion on boil-off). Ambient temperatures are lower at higher altitudes, which helps to improve fuel system cooling, but ambient pressure is also lower, making vaporization easier. Vapor lock is also augmented by the air that comes out of solution as the aircraft climbs. If the fuel becomes supersaturated, then air can be evolved very quickly and cause frothing of the fuel. The fuel tanks, pump pickups, and total fuel system are designed to handle these problems but only on the basis of the known volatility properties of the avgas specifications. And maintaining those properties during handling is very important for safe operations.

Another volatility phenomenon closely related to fuel vaporization is fuel boil-off. The boiling point of a liquid is the temperature at which its vapor pressure is equal to the local atmospheric pressure. Atmospheric pressure decreases with increasing altitude. At 10,000 ft, atmospheric pressure is only about 70 % as much as it is at sea level. Liquids will boil at a lower temperature at higher altitudes. Of course, atmospheric temperature decreases as altitude increases, at least within the troposphere. The problem is that aircraft on the ground can be filled with relatively warm or hot fuel, and it takes time for the avgas in the wing tanks to cool down. But the pressure in the tank ullage space above the fuel changes almost instantaneously to match the outside air pressure, and as the aircraft climbs the pressure above the fuel can drop below the vapor pressure of the avgas causing the fuel to boil in the tanks. Some of the vapor coming out of solution may form at the pump suction and be pulled into the lines leading to vapor lock, as described previously.

Boil-off occurs in tanks, which means that the lightest components will boil and then the vapor can escape out through the vent system. The composition of the fuel in the tank is then made up of less volatile material with a lower vapor pressure and eventually the boiling will stop. But without the front end volatility, this fuel may make restarting an engine much more difficult in the event of lost power and a cold engine at altitude.

Finally, there is one other operational phenomenon associated with volatility—that is carburetor icing. As avgas evaporates in the carburetor, it will cool the incoming air. If that air has water vapor in it, the cooling effect can lower the temperature sufficiently enough to form ice. The ice will cling to the surface of the cold carburetor and can lead to a partial blockage of the Venturi throat and throttle plate. Carburetor icing occurs under certain conditions where there is an air intake temperature from about -4° C to $+10^{\circ}$ C and high humidity levels. The lower amounts of air and fuel coming past the partially blocked Venturi and throttle plate can cause the aircraft engine to stall. Very high volatility gasolines, such as some automotive gasolines (if they were allowed), will have a higher tendency to create ice formation because they will have a greater fraction of fuel that will evaporate in the carburetor before entering the fuel manifold.

The strict controls placed on distillation have been covered earlier in this chapter, but there is one other test besides distillation that controls volatility-the vapor pressure test. In ASTM D910, the vapor pressure is measured by ASTM D323, Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method), or by ASTM D5191, Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method). Both methods give the vapor pressure at 38°C (Reid Vapor Pressure), and the limits for all avgas grades is set with a minimum of 38.0 kPa and a maximum of 49.0 kPa. It is instructive to note that in the automotive gasoline specification ASTM D4814, Standard Specification for Automotive Spark-Ignition Engine Fuel, there is no minimum vapor pressure requirement; in addition, the maximum can vary from 54 kPa to 105 kPa depending on location and time of year the motor gasoline is purchased. The volatility of automotive Mogas does not in any way correspond to the requirements for acceptable safe aviation operations.

8.2.8 FUEL METERING AND AIRCRAFT RANGE

The measurement of fuel quantity and fuel flow is important for ground as well as flight operations. On the ground, avgas is bought, sold, and transferred on a volume basis. Fuel volume changes with temperature, so the volume is usually corrected to a standard temperature using the equations and subroutines that are in a tabulated format in ASTM **D1250**, *Standard Guide for Use of the Petroleum Measurement Tables*. In the United States, the standard temperature is 60°F (15.5°C); in other countries, the standard is usually 15°C. Although there are some countries with higher year-round ambient temperatures that standardize to 20°C. Density measurements include kg/m³ at 15°C, relative density (which is the ratio of the density of the fuel to the density of water at 15°C), and API gravity (which is an arbitrary scale and standardized at a temperature of 60°F). The ASTM **D910** specification for density is required to be reported in kg/m³ at 15°C, although it is still not uncommon in the United States to see the API gravity being reported at 60°F.

Aircraft range is controlled by the total heat content of the fuel along with the fuel economy and operation of the aircraft, which is highly dependent on the weight of the aircraft and on the conditions of the flight (e.g., wind and altitude). Aircraft operations have to take these external factors into account along with heat content when deciding on flight routes/plans and duration of flight. In ASTM D910, the net heat of combustion is set at a minimum of 43.5 MJ/kg. The net heat of combustion of a fuel can be measured by ASTM D4809, Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method), but this test involves very precise thermometry and calorimetry and is not used very much. However, in ASTM D910, it is the method used in cases of dispute. Generally, the heat of combustion is nearly always estimated based on equations using other pertinent fuel characteristics. ASTM D3338, Standard Test Method for Estimation of Net Heat of Combustion of Aviation Fuels, is the most common method. ASTM D3338 uses values for density, distillation temperatures, and aromatic content, along with a sulfur correction and because all of these properties have to be measured anyway in certifying avgas against ASTM D910, ASTM D3338 is the method most often used to determine the heat of combustion. The second estimation method allowed is ASTM D4529, Standard Test Method for Estimation of the Net Heat of Combustion of Aviation Fuel, which uses the density, aniline point, and sulfur as variables; but because of the toxicity concerns associated with aniline, this method has dropped out of favor.

The energy content of avgas does not vary much because the avgas specification tightly constrains chemical composition. The typical density is about 715 kg/m³, and the typical energy content is 43.71 MJ/kg.

8.2.9 FLUIDITY AT LOW TEMPERATURES

Avgas begins to freeze when cooled to a low enough temperature. Because it is a mixture of many individual hydrocarbons, each with its own freezing point, avgas does not become solid at one temperature. As the avgas is cooled, the higher molecular weight straight chain paraffins that are present can form "crystals." Avgas, unlike jet fuel, does not tend to become slushy but rather forms distinct "crystals" relatively rapidly at around -75 to -80° C and can become solid. Avgas can be subject to low temperatures both at altitude and on the ground but, fortunately, avgas usually is not subjected to low enough temperatures to form "crystals." Nevertheless, it is important that the fuel retain fluidity at low temperatures to enable the correct flows of fuel to the engine to be maintained. Air temperatures at altitude vary

seasonally and with latitude. The lowest average temperature at 10,000 ft is about -25° C, and at 20,000 ft, it is about -40° C (although there can be extremes substantially below these norms). Although most avgas hydrocarbons will not crystalize at these temperatures, it is conceivable that the highest molecular weight materials, C₁₀ paraffins, could; therefore, the ASTM **D910** specification is set at -58° C maximum. Most laboratories report the result as "less than -58° C" because no crystals have formed to allow for the determination of the disappearance of crystals as required by the freeze point test method ASTM **D2386**. The method used to determine the freeze point is ASTM **D2386**, *Standard Test Method for Freezing Point of Aviation Fuels*.

8.2.10 NON-CORROSIVITY AND COMPATIBILITY

Avgas is in contact with a variety of materials during distribution and use. It is essential that the fuel not corrode or react with these materials, especially those in aircraft fuel systems. The need for "managing" the compatibility of fuel and system components has been recognized as a result of new and different fuels being proposed for aircraft use. Accordingly, a new standard has recently been issued: ASTM **D7826**, *Standard Guide for Evaluation of New Aviation Gasoline and New Aviation Gasoline Additives* [9]. In this new guide, Annex A2 ("Evaluating Compatibility of Additives or Fuels with Fuel System Materials") will provide the reader with the vast array of materials, including metals with which avgas comes into contact.

Sulfur is the main potentially corrosive element in avgas and is limited in ASTM D910 to 0.05 mass % maximum. Sulfur may be present as thiophenols, mercaptans, sulfides, disulfides, thiophenes, thiophanes, and even as traces of free sulfur. The method that seems to have the most usage is the Horiba sulfur analyzer used in ASTM D2622, Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry. Other manufacturers' equipment can be used with this method. The other method allowed by the specification is ASTM D1266, Standard Test Method for Sulfur in Petroleum Products (Lamp Method), which is the so-called "lamp method" that uses wet chemistry and is very much out of favor. The sulfur limit of 0.05 mass % is high by motor gasoline standards; many countries limit the sulfur content to 0.0080 mass % or even lower. Sulfur compounds are also limited in avgas by the copper strip corrosion test, ASTM D130, Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test. The ASTM D910 specification limit is set at a No. 1 strip maximum after the copper strip has been immersed in the avgas for 2 h at 100°C. For more information on the copper strip test and its significance, refer to section 8.1.8.7, "Corrosivity," in this chapter.

8.2.11 FUEL CLEANLINESS, HANDLING, AND STORAGE STABILITY

Aviation gasoline is subject to oxidation, and this propensity is evaluated by the oxidation stability test, ASTM **D873**, *Standard Test Method for Oxidation Stability of Aviation Fuels (Potential Residue Method)*, in which the fuel is exposed to pure oxygen under pressure at 100°C for 5 or 16 h. The fuel is then evaporated, and the residue (or gum), together with any lead precipitate, is weighed. The ASTM **D910** specification limit is set at:

- Potential gum 6 mg/100 ml maximum
- Lead precipitate 3 mg/100 ml maximum

These limits were set based on storage tests conducted during World War II. By meeting these test requirements, the fuel is considered to be acceptable for storage of up to one year under relatively high temperature desert storage conditions.

Fuel cleanliness for avgas is set in ASTM **D910**'s Paragraph 8 ("Workmanship, Finish, and Appearance"), which has previously been covered in Section 8.2.4 of this chapter ("The Set-Up of ASTM **D910**—Table 1 and Appendix 1"). As emphasized in that section, it is imperative to keep free water out of the fuel. During high altitude flights, any water in the fuel system prior to the engine compartment is subject to freezing and can potentially impede flow. During other periods of warming, such as during descent, ice released from pipes may plug filters and impede fuel flow.

With the advent of supplemental type certificates allowing the use of motor gasoline in specific aircraft, concerns were raised about ethanol used in motor fuels. In ASTM D910, there is a water reaction test, ASTM D1094, Standard Test Method for Water Reaction of Aviation Fuels. The requirement in ASTM D910 is that the volume change in millilitres be no more than plus or minus 2 mL. This test was originally intended to be used as a very simple test to look for surfactant materials. It was about to be removed from specifications because its usefulness was considered minimal. However, the possibility of a mix-up between motor gasoline with ethanol and avgas caused this test to be kept on in aviation gasoline. With the Renewable Fuel Standards, it is mandatory in the United States to use a given volume of biomass-origin blending component in the motor gasoline pool. And the biomass material of choice is ethanol. Up to 10 % ethanol can be used in any gasoline without recourse to any form of notification that ethanol is in the fuel. Hence, most pumps at service stations merely are labeled, "This fuel may contain ethanol" because it is not known whether the fuel does or does not contain ethanol. Ethanol is an economic alternative because of the tax subsidies associated with its use and its high-octane blending value. But there is a problem with aviation fuels. Ethanol is water friendly and will absorb, up to a point, the water from tank bottoms, pulling it into the fuel. (At a high level of free water content, the ethanol will be pulled into the water phase and form a water bottom.) Fuel in aircraft tanks is saturated at ground temperatures and humidity levels with dissolved water. As an aircraft climbs to altitude, the temperatures drop and any water-ethanol mixture in the Mogas fuel cools. The solubility of the water in ethanol also drops, and water comes out in the fuel tank. If the temperatures are below freezing, there is the possibility of ice formation. In addition, the removal of the ethanol will change and lower the octane rating. Additionally, there are material incompatibilities with ethanol and aviation fuel systems. Aluminum corrosion rates are significantly accelerated, and hoses, gaskets, and elastomeric seals can swell and adversely affect aircraft operations. Aluminum corrosion remains a significant issue for "wet wing" aircraft where the aircraft wing structure is sealed and functions as the fuel tank. The FAA decided that significant

certification work would be needed to approve the use of gasolines containing ethanol; therefore, as of this time, ethanol is not permitted in avgas. If there was any ethanol in an avgas sample, it would show up in the ASTM **D1094** test because water is added to the avgas in sufficient quantity to pull the ethanol out of the fuel, into the water phase, and to produce a volume change.

8.2.12 STATIC ELECTRICITY

ASTM **D910** allows for the use of a static dissipater additive, Stadis 450. If the additive is used, then the electrical conductivity requirement, which is set as 50 pS/m minimum and 450 pS/m maximum at the point of use, must be met. (For more information, also see Section 8.1.8.10.) Like in jet fuel, if the static dissipater additive Stadis 450 is used, it can only be added up to 3 mg/l initially and then, if conductivity is lost during distribution, it can be re-additized up to a maximum cumulative amount of 5 mg/l. If Stadis 450 is used, it also must be reported on the COA. Further information on static electricity and its dissipation can be found in ASTM **D4865**, *Standard Guide for Dissipation of Static Electricity in Petroleum Fuel Systems* [8].

8.2.13 ADDITIVES

Section 6 of ASTM **D910** ("Materials and Manufacture") details the additives that are mandatory for addition to all grades in the specification in accordance with the amount and composition as stated for each additive. Mandatory additives are tetraethyl lead and the color dyes used to identify the various grades. Antioxidant, anti-icing, corrosion inhibitors, and electrical conductivity additives are optional. New additives proposed for use in aviation gasoline have to go through a rigorous protocol before they are accepted by engine and aircraft system OEMs and then, subsequently, the additive can be listed in the ASTM **D910** specification. This protocol is given in ASTM **D7826**, *Standard Guide for the Evaluation of New Fuels and New Fuel Additives for Use in Aviation Spark-Ignition Engines and Associated Aircraft Installations*.

Tetraethyl lead has to be added in the form of what is normally called "aviation mix." It is added to all grades in the amounts to meet the lead levels specified (Table 8.1). This additive not only has tetraethyl lead in it but also a bromine scavenger, ethylene dibromide, to help remove lead oxides from the combustion chamber. Ethylene dibromide reacts with the lead oxide and converts it to a mixture of lead bromide and lead oxybromide; both of these compounds are volatile and will exit with the exhaust instead of building up as lead oxide deposits in the engine. The ethylene dibromide is present in the aviation mix at a 1:1 molar ratio, resulting in two atoms of bromine being available per atom of lead, which is just sufficient to react with all the lead. Excessive amounts of ethylene dibromide would create an aggressively acidic exhaust that would corrode exhaust systems. Even though the stoichiometric amount of ethylene dibromide is in the aviation mix, some of the more volatile compounds do not react with the lead, and it remains as lead oxide in the engine and can potentially coat the valves and spark plugs. Coating the spark plugs leads to conductance of the electrical charge without the formation of a spark across the plug gap to initiate combustion in the cylinder. Excessive lead oxide deposits on valves are a problem, but small amounts may be

FIG. 8.29 Tetraethyl lead.

$$\begin{array}{c} \mathsf{CH}_{3} \\ | \\ \mathsf{CH}_{2} \\ \mathsf{CH}_{3} - \mathsf{CH}_{2} - \mathsf{Pb} - \mathsf{CH}_{2} - \mathsf{CH}_{3} \\ \mathsf{CH}_{2} \\ \mathsf{CH}_{2} \\ \mathsf{CH}_{3} \end{array}$$

FIG. 8.30 Ethylene dibromide.

advantageous in preventing valve seat wear in older-type valve metallurgy. In modern engines, the lead oxide probably has no advantages in regard to valve seat wear. There is also a small amount of blue dye in the tetraethyl lead aviation mix to help identify it (because it is poisonous); otherwise, the aviation mix would be a clear liquid. See Fig. 8.29 and Fig. 8.30 for the chemical structure of tetraethyl lead and ethylene bromide.

When the aviation mix is added to the base aviation gasoline, the dye in the aviation mix is so diluted as not to be noticeable. Accordingly, the actual product must then be dyed to the prescribed color—red, brown, blue, or green—using specific chemical dyes and at the levels required in the specification (see **Table 8.2** and **Table 8.5**). The color is part of the specification and must be measured using ASTM **D2392**, *Standard Test Method for Color of Dyed Aviation Gasolines*.

The specific dyes used are given in ASTM **D910** (Paragraph 6.2.2, Dyes). Blue is 1,4-dialkylaminoanthraquinone; yellow can be either p-diethylaminoazobenzene or 1,3-benzenediol 2,4-bis {(alkylphenyl) azo-}; the red dye is an alkyl derivative of azobenzene-4-azo-2-napthol; and the orange dye is bezene-azo-2-napthol.

The allowed antioxidants are hindered phenols and mixtures of hindered phenols. The amounts of each approved antioxidant can be varied, but the total cannot exceed 12 mg of active inhibitor. The approved additives are listed in Paragraphs 6.3.1.1 through 6.3.1.8 in ASTM **D910**. As with jet fuel, these antioxidants interrupt the oxidation chain reactions and help to prevent the formation of peroxides and hydroperoxides as well as suppressing gum formation. Aviation gasolines have the potential to contain olefins, which are much more readily susceptible to forming polymerized products and gums because their double bond will react more easily with oxygen.

Two types of fuel system icing inhibitors (FSIIs) are permitted for use in aviation gasoline. One of these is di-ethylene glycol monomethyl ether (Di-EGME) Type III, which meets ASTM **D4171**, *Standard Specification for Fuel System Icing Inhibitor*. More information is given in Section 8.1.9 of this chapter (and also in "ASTM **D1655**, Table 2, Detailed Information for Additives for Aviation Turbine Fuels"). The other FSII allowed in aviation gasoline is isopropyl alcohol (propan-2-ol). Isopropyl alcohol (IPA) is not allowed in jet fuel. The isopropyl alcohol must meet the

Dye Content	Grade 80 Red	Grade 91 Brown	Grade 100VLL Blue	Grade 100LL Blue	Grade 100 Green
Blue dye mg/l	0.2	3.1	2.7	2.7	2.7
Yellow dye mg/l	none	none	none	none	2.8
Red dye mg/l	2.3	2.7	none	none	none
Orange dye mg/l	none	6.0	none	none	none

TABLE 8.5 Color and dye amounts in each grade of aviation gasoline.

requirements in ASTM **D4171** Type II. There is a Note 3 in ASTM **D910** stating that addition of isopropyl alcohol may reduce the knock rating below the specification minimums. Generally, icing inhibitors are not added to avgas at the time of manufacture but are sold as an after-market additive and used at the discretion of the aircraft owner/operator. Di-EGME is more often used than isopropyl alcohol and works by partitioning into free water and suppressing its freeze point.

Corrosion inhibitors are permitted and listed in Paragraph 6.3.4 of ASTM D910 along with their maximum allowable concentration (MAC). In the early days, corrosion inhibitors were approved for use in the military avgas specifications to overcome refining deficiencies that sometimes left corrosive materials in the fuel. As refining processes improved, they were dropped from the specification but have now been reintroduced to help control corrosion in the distribution system. Aviation gasoline is often distributed and stored in drums. In humid conditions, leakage past drum seals can lead to condensation and corrosion (rust) formation in the drums; the corrosion inhibitor will help to ameliorate this situation but in no way does it make up for incorrect drum storage and handling. Drums should be internally lined and, before filling, they should be inspected for rust. However, the linings can break down, and internal inspection is not easy to perform. All it takes is for one speck of rust to clog the carburetor jets or to block the fuel injector and prevent fuel flow, so any insurance, such as using a corrosion inhibitor in drummed aviation gasoline, is a reasonable palliative and worth considering.

The last optional additive is a static dissipater additive. As a safety precaution, Stadis 450 may be added to aviation gasoline. (This is discussed in more detail in section 8.2.12 on static electricity.) Additional information on the use of a static dissipater additive is given in the jet fuel sections of this chapter headed "Static Electricity" (Section 8.1.8.10) and "ASTM **D1655** Table 2 Detailed Information for Additives for Aviation Turbine Fuels" (Section 8.1.9). If a static dissipater is used, ASTM **D910** requires that the electrical conductivity be tested as per ASTM **D2624**, *Standard Test Method for Electrical Conductivity of Aviation and Distillate Fuels*, and it must be between 50 pS/m minimum and 450 pS/m maximum at the point of use.

8.2.14 SAMPLING

As with jet fuel, there are recommended practices for sampling avgas. These are ASTM **D4057**, *Standard Practice for Manual Sampling of Petroleum and Petroleum Products*, and ASTM **D4177**, *Standard Practice for Automatic Sampling of Petroleum and Petroleum Products*. However, for avgas, initial refinery compliance testing must be performed on a sample taken following the procedures given in ASTM **D4057**. Although not mentioned as part of ASTM **D910**, it is recommended that sampling be conducted in accordance with ASTM **D5842**, *Standard Practice for Handling of Fuels for Volatility Measurement*.

Equally important to the sampling are the containers in which samples are placed. The copper corrosion and electrical conductivity tests, as well as others, are sensitive to trace contamination. Samples should be placed in containers as recommended by ASTM **D4306**, *Standard Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination.*

8.2.15 REPORTING

The type and number of reports to ensure conformance with the specification can be mutually agreed between the purchaser and the supplier. However, it should be noted that all additives used must be reported, stating both the type and quantity used. Additives included after the point of manufacture must also be recorded and reported.

8.2.16 HOW TO DECIDE IF THE TEST RESULTS MEET THE SPECIFICATION

For guidance in determining whether or not avgas testing results meet the specification, the reader is referred back to the similarly named section in the preceding jet fuel portion of this chapter. See Section 8.1.12, "How to Decide If the Test Results Meet the Specification."

8.2.17 QUALITY CONTROL PROCEDURES

Fuel cleanliness means keeping the avgas clean and dry. This is an easier task than with jet fuel because the viscosity of the avgas is so much lower that water and dirt tend to separate out faster. In addition to being clean at the point of manufacture, the fuel must be delivered to the aircraft free of contaminants. It is recommended that avgas be filtered as it is fed into drums and also filtered after bulk intermediate storage or pipelining where the avgas could have come into contact with water or rust. One contaminating product that avgas used to come into contact with was motor gasoline, but this is much less of a problem than it used to be. Because the avgas contains lead, it has to be kept separate from motor gasoline, which is all unleaded. Other contaminants that avgas can come into contact with are surfactants and microbes. Microbial contamination, as with jet fuel, is best dealt with by keeping avgas storage dry.

Avgas presents a set of problems separate from that of jet fuel because much of the avgas supply is drummed. Information on the handling and precautions needed are given in EI 1530, Quality Assurance Requirements for the Manufacture, Storage, and Distribution of Aviation Fuels to Airports [13]. Section 10.4 of EI 1530 is entitled "Drum and Intermediate Bulk Container (IBC) Filling and ISO Tank Container Loading" and has recommendations and requirements on drum filling. Before filling, all drums, including those that are new, should be examined internally before filling to ensure their satisfactory condition (i.e., clean and free from rust, water, drum manufacturing oils, and other contaminants, and the drum lining must free of defects). After filling a batch of drums, control checks have to be made on a representative number of drums (as per Table 16 of EI 1530), including the first and last drums filled. The drums should be sealed with suitable avgas-compatible seals immediately after filling, and the consignment of drums should be released under cover of a release certificate. The drums should be stored in a well-ventilated building or covered open-sided storage that provides protection from rain and sunlight. The drums should be stored horizontally with the bung below the liquid level. Drums should be inspected on initial storage and then monthly for leakage. Batches stored in stock after 12 months from the date of manufacture need to be sampled and tested before supplying to aircraft and should be tested every six months after that initial one-year period. Testing should be run for octane (ASTM D2700 to determine MON) and volatility (ASTM D86 Distillation and ASTM D323 RVP/ASTM D5191 RVP Mini-Method).

Storage at high ambient temperatures can present a challenge for avgas whether in drums or bulk storage. The most volatile components can evaporate from the fuel and be lost to the atmosphere, especially if drums are partially used and if they are kept upright. If enough of the high vapor pressure components are lost, the tetraethyl lead can increase to above the specification maximum and the vapor pressure can fall below the specification minimum. The best way to avoid these problems is stock control and to not have avgas stored over long periods.

8.2.18 OTHER ASTM AVIATION GASOLINE FUEL SPECIFICATIONS

ASTM **D910** is not the only ASTM aviation fuel specification covering avgas. There are two other major specifications:

- ASTM D6227, Standard Specification for Unleaded Aviation Gasoline Containing a Non-Hydrocarbon Component
- ASTM **D7547**, Standard Specification for Hydrocarbon Unleaded Aviation Gasoline

Although all five grades in ASTM D910 contain tetraethyl lead, these other two specifications (ASTM D6227 and ASTM D7547) are unleaded.

ASTM **D6227** was originally issued in 1998 with the title *Standard Specification for Grade UL82 Unleaded Aviation Gasoline*. The name was changed in 2012 to better reflect that the fuel could contain ethers. This was one way to meet the specification's octane requirements without the use of lead. Although no deliberate addition of alcohols is allowed (other than isopropyl alcohol used as an FSII), the aliphatic ethers can be added up to an oxygenate limit of 0.3 mass % maximum. The specification was introduced as an

aviation grade replacement for the automotive gasolines specified in many autogas supplemental type certificates issued since the early 1980s. The FAA released Safety Awareness Information Bulletin (SAIB) No. CE-00-19R1 approving the use of ASTM **D6227** UL82 as an alternative for autogas STCs. This SAIB was released to registered owners and operators of airplanes approved for the use of autogas and allows them to use UL82 without requiring changes to the applicable airplane documentation. Additionally, the specification was developed so that an aviation grade fuel from "normal" petroleum gasoline stocks could be made rather than the specifically tailored stocks of iso-pentane, high grade alkylate, toluene, and lead used to blend up 100LL aviation gasoline.

ASTM D7547, Standard Specification for Hydrocarbon Unleaded Aviation Gasoline, was introduced in 2009 at the behest of the U.S. military. ASTM D7547 covers formulating specifications for purchases of aviation gasoline under contract and is intended primarily for use by purchasing agencies-primarily the Defense Energy Support Center (renamed in 2010 as the Defense Logistics Agency-Energy). The need for this specification was brought on by the increasing use of drone aircraft powered by the Rotax engine, which was designed around unleaded gasoline with a MON of 91.0 minimum (see Fig. 8.23 and Fig. 8.24.) Using the normally available 100LL with up to 0.56 gPb/l was causing severe spark plug fouling because many of these drones were not being operated at full power but on long, slow cruise missions in order to obtain high quality surveillance photographs. With the exception of there being no lead and the octane being specified only by the MON value of 91.0 maximum, the other requirements of ASTM D7547 are the same as ASTM D910. There is a lead content specification of 0.013 g/l maximum. This figure is taken from the automotive gasoline specification where, based on extensive testing, that level was considered the highest level of incidental contamination from general lead picked up as the unleaded gasoline passed through the previous infrastructure used for leaded gasolines.

There has been a growth industry in specialized ASTM aviation gasoline specifications as the search for an unleaded fuel as an alternative to ASTM **D910** leaded grades continues. These additional specifications and their intended uses are given in **Table 8.6**. Many of these grades are intended for research purposes and to enable certification for in-flight testing.

8.2.19 THE ONGOING CONUNDRUM OF TAKING THE LEAD OUT OF AVIATION GASOLINE

The 1990 amendments to the U.S. Clean Air Act (CAA) mandated lead phase-out for all "non-road" engines and vehicles. It stated that, after 1992, engines could not be manufactured that required leaded fuels. In addition, in 1996, no leaded fuel was to be sold commercially. These amendments to the CAA were responsible for initiating the effort toward the development of an unleaded fuel to replace avgas 100LL.

After careful review of the legislative record behind the CAA, it was determined that aircraft emissions were regulated under a separate title of the act, and that aircraft were not considered by Congress to be "non-road" vehicles. At the same time, it was recognized that the Environmental Protection Agency (EPA) held the authority to regulate lead emissions from aircraft stemming from TABLE 8.6 Brief outline of ASTM specifications and guides being used or intended for use in looking for alternatives to unleaded aviation gasoline.

ASTM Specification No.	Name	MON	Comments and Possible Future Application*
ASTM D910	Specification for Aviation Gasoline	100 Leaded	Could be phased out but probably only very slowly. Used where refiners cannot meet the octane requirements of the MON 100 aviation lean rating without the use of higher lead levels than allowed in 100LL.
ASTM D7547	Specification for Unleaded Aviation Gasoline	91 Unleaded	Currently, this is used by the military purchasing agency for aircraft designed to operate on 91 MON unleaded fuel. Could have additional grades added. Anticipate that a 94 MON unleaded grade will be added to this specification, and it could become the main aviation gasoline specification.
ASTM D7592	Specification for Grade 94 Unleaded Aviation Gasoline Certification and Test Fuel	94 Unleaded	Currently, this is for certification and testing of an engine and engine components. Could be phased out, and a 94 octane grade added to ASTM D7547 to replace it. Or, it could be made into a specification (rather than a test fuel) and have a 91 MON unleaded grade added to it. (Most likely, ASTM D7547 will become the main aviation fuel specification.)
ASTM D7719	Specification for High Octane Unleaded Test Fuel	102.2 Unleaded	See scope section of ASTM D7719 . This is for the purchasing of a high octane unleaded fuel for testing purposes. Usually thought of as a mix of mesitylene and isopentane. May be used to purchase fuels for submission to the Unleaded Avgas Transition Aviation Rulemaking Committee (UAT ARC) testing process at the FAA William J. Hughes Technical Center. May not survive because of costs that are uncertain at this time. But could, if approved under UAT ARC, be more widely used.
ASTM D6227	Specification for Unleaded Aviation Gasoline Containing a Non- Hydrocarbon Component	82.0 and 87.0 Unleaded	Loosely based on automotive gasoline. (See additional information in Section 8.2.18 of this chapter.) Only for use in engines and associated aircraft that are specifically approved by the engine and aircraft manufacturers and certified by national certifying agencies with supplemental-type certificates. Components containing ethers may be present, but alcohols are specifically excluded.
ASTM D7826	Standard Guide for the Evaluation of New Fuels and New Fuel Additives for Use in Aviation Spark-Ignition Engines and Associated Aircraft Installations	See method for MONs required	Very much a part of the UAT ARC recommendations and requirements to be met by prospective suppliers of new fuels before undertaking actual engine testing. Quite extensive and will require upfront capital to demonstrate meeting all the test requirements.
ASTM D6424	Standard Practice for Octane Rating Naturally Aspirated Spark-Ignition Aircraft Engines	Rates MON for primary reference fuels at specific points in engine operation	Put in place to be able to standardize test procedures for evaluating the octane rating of new fuels (specifically, the ground-based octane rating for naturally aspirated spark-ignition engines using primary reference fuels).
ASTM D6812	Standard Practice for Ground-Based Octane Rating Procedures for Turbocharged/Supercharged Spark-Ignition Aircraft Engines	Collect data on knocking and conditions	Put in place to be able to standardize test procedures for evaluating the octane rating of new fuels. Similar to ASTM D6424 , but this method is for ground-based ratings of turbocharged/supercharged engines.

Brief Outline of ASTM Specifications and Guides Being Used or Intended for Use in Looking for an Unleaded Aviation Gasoline to Replace Avgas 100LL

*Some of these comments should be considered speculative.

the original Clean Air Act in 1970. The aviation industry (i.e., the General Aviation Manufacturers Association [GAMA], Aircraft Owners and Pilots Association [AOPA], Experimental Aircraft Association [EAA], the FAA, etc.) approached the EPA asking for a reprieve from the regulations to allow time for research and development toward finding an unleaded replacement for 100LL.

To that end, an industry group consisting of the FAA, OEMs, and aviation consumer groups visited producers to demonstrate the desire for, and to request the development of, an unleaded 100 octane aviation gasoline (i.e., UL100 avgas). Simple solutions that were thought to hold promise, such as replacing TEL with more toluene (the option adopted in moving from Grade 100/130 normal lead to 100/130 low lead, referred to as 100LL) or attempting the use of other metal additives, failed. Moreover, readily available octane-boosting oxygenated streams used in motor gasoline (Mogas) at the time (e.g., methyl tertiary butyl ether [MTBE], ethyl tertiary butyl ether [ETBE], tertiary amyl methyl ether [TAME], and ethanol) also failed to produce the necessary octane performance. It was then recognized that the problem was more complex than initially anticipated and that a significant effort would be required to remove lead from aviation gasoline and maintain safe octane levels for the existing aircraft fleet.

Parallel to this initial effort, the industry was attempting to determine the aircraft fleet octane requirement. In order to make this determination, two ASTM methods needed to be developed, providing standard practices for octane rating aircraft engines (i.e., ASTM D6424 and ASTM D6812). One method applies to naturally aspirated spark-ignition aircraft engines, while the other applies to octane rating turbocharged engines.

Despite extensive efforts going back to the late 1970s and the acceleration in development after 1990, no unleaded replacement aviation gasoline fuel has been found and approved that provides adequate safety and performance comparable to 100LL. Work on this important issue continues and is now moving forward through the FAA with efforts to study and develop a suitable unleaded alternative to 100LL. The FAA and EPA were very much brought into the research and development effort as a result of a petition from the Friends of the Earth (FOE).

In the previous sections, we have seen that the tetraethyl lead (TEL) added to the avgas, as required by ASTM **D910**, is necessary in order to achieve the required octane for safe operations in many aircraft. The combustion products of TEL are exhausted to the atmosphere, increasing the burden of lead found in the environment. These lead combustion products are serious neurotoxins that have been shown to harm neurological development, especially in children. In 2006, FOE petitioned the EPA to issue an endangerment finding for lead emissions from piston-powered aircraft or, if there was insufficient information to support an endangerment finding, to study the health and environmental impacts of aircraft lead emissions. The FOE stated in its petition that lead emissions from general aviation (GA) cause or contribute to air pollution that reasonably may be anticipated to endanger public health and welfare.

On July 8, 2012, the EPA issued a final decision to the FOE petition basically stating it did not have the data to support an endangerment finding. Then, in March 2013, the U.S. District Court of the District of Columbia granted the EPA a summary judgment to dispose of the suit brought by the FOE, including an understanding that the EPA would continue doing testing of lead levels at airports with significant GA operations.

Entirely separate from the FOE petition but under a federal court order to set a new standard by October 15, 2008, the EPA cut the acceptable limits for atmospheric lead from the previous standard of 1.5 μ g/m³ to 0.15 μ g/m³ (or 150 ng/m³). This was the first change in the standard since 1978 and represents an order of magnitude reduction over previous lead levels. The EPA also identified avgas as one of the most "significant sources of lead." They also committed to a yearlong study of 17 airports with heavy GA traffic. Contrary to their statement that avgas was a significant source of lead, the final results from the EPA's modelling study at the Santa Monica Airport shows that off-airport lead levels are below the current 150 ng/m³ and 15 of the 17 airports monitored during the yearlong study have shown lead emissions well below the current U.S. National Ambient Air Quality Standard (NAAQS) for lead. Only the San Carlos Airport and Carlsbad's McClellan-Palomar Airport showed data exceeding the national standard. Concern was registered over the placement of the lead sensors at these two California airports. The sensors were moved to less directly trafficked areas of these airports, and the new locations have not shown lead levels above the NAAQS.

Nevertheless, there is recognition that lead should be removed from avgas, and in May 2012, the FAA's Unleaded Avgas Transition Aviation Rulemaking Committee (UAT ARC) issued a report. The EPA was a partner to the recommendations in the UAT ARC report, which emphasizes the need for safety. Safety for piston aircraft operations and their owners as well as the far-reaching economic impacts will override any EPA wishes to see lead summarily removed from avgas. After consulting with experts from many parts of the industry, the UAT ARC put a plan together to replace leaded avgas with an unleaded alternative fuel within eleven years. A part of this transition is the creation of the Piston Aviation Fuels Initiative (PAFI) with the goal of facilitating the development and deployment of a suitable and high enough octane fuel that will have the least impact on the GA fleet and distribution system. The evaluation process will focus on a fuel's production and distribution infrastructure and toxicology, and on the overall cost of aircraft operations.

Through PAFI, the FAA has now embarked on the search for the Holy Grail—an unleaded avgas to replace 100LL. On July 1, 2014, the FAA closed its submission for fuels under the PAFI plan. Nine fuels were submitted from five different groups, including the Afton Chemical Co., Avgas LLC, Shell Oil, Swift Fuels, and a consortium made up of BP, TOTAL, and Hjelmco. These fuels are now undergoing preliminary testing at the FAA's William J. Hughes Technical Center. As of this writing, Congress is supporting this program with \$6 million in the current fiscal year (2015) will likely provide similar support in the future. If all goes well, a new unleaded aviation gasoline may be deployed in 2018. Its acceptance as a replacement for 100LL will depend on availability and cost as well as technical feasibility.

Apart from the fuel aspect, there are some excellent parts of the UAT ARC report that may allow for engine modifications and changes-in particular, changing over to modern engines capable of running on UL94 but with performance "similar" to that of current aircraft operating on 100LL. Under this scenario, 100LL gradually will move out of the market as older high-performance aircraft are retired or re-engined. OEMs are working on making engines that can operate on UL 94 with similar performance to engines operating on 100LL and that will be suitable for reengining of some specific aircraft that were originally certified to run on 100LL. The OEMs may follow Continental's lead. Continental has reduced the compression on an engine and fitted it with Full Authority Digital Engine Control (FADEC) systems so it can operate on 94 MON unleaded with performance similar to the original older engine(s) requiring 100LL. However, with this approach, the conundrum of supplying two grades of aviation gasoline, at least for a period of time, still will need to be solved.

8.2.20 OVERVIEW AND CONCLUDING REMARKS

There are approximately 167,000 piston-engine aircraft in the United States and a total of 230,000 worldwide that primarily rely on the currently available avgas 100LL as defined in ASTM D910, *Standard Specification for Aviation Gasoline*. The 100LL specification has been developed iteratively over many years using the ASTM consensus process. The limits for all the critical properties have been vetted and agreed to only after considerable debate and understanding of aircraft and engine operations and always with a view to flight safety. All grades of gasoline in ASTM D910 are currently leaded, but a considerable research effort is being headed up by the FAA through the PAFI program to come up with an unleaded alternative to 100LL. ASTM will continue as the main organization setting the specifications for these new and alternative replacement unleaded fuels based on flight safety.

References

- Annual Book of ASTM Standards, Section 5: Petroleum Products, Lubricants, and Fossil Fuels, Volume 05.01, Petroleum Products and Lubricants (I), ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [2] Annual Book of ASTM Standards, Section 5: Petroleum Products, Lubricants, and Fossil Fuels, Volume 05.03, Petroleum Products and Lubricants (III), ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [3] Defence Standard 91-91, *Turbine Fuel, Kerosine Type, Jet A-1* (NATO Code: F-35, Joint Service Designation: AVTUR) UK Ministry of Defence, London, 2011.
- [4] Datschefski, G., Lewis, C., and Walters, M. B., "Jet Fuel Specification Requirements. Strategic Review," DERA SP-101, Defence Evaluation and Research Agency, Farnborough, UK, 1997.
- [5] Pedley, J. F., Hiley, R. W., and Hancock, R. A., "Storage Stability of Petroleum Derived Diesel Fuel," *Fuel*, Vol. 68, No. 1, 1989, pp. 27–31.
- [6] Energy Institute, "Joint Industry Project: Seeking Original Equipment Manufacturer (OEM) Approvals for 100 mg/kg Fatty Acid Methyl Ester (FAME) in Aviation Turbine Fuel," Energy Institute, London, 2014.
- [7] Langton, R., Clark, C., Hewitt, M., and Richards, L., Aircraft Fuel Systems, Wiley, Hoboken, NJ, 2009.
- [8] Annual Book of ASTM Standards, Section 5, "Petroleum Products, Lubricants, and Fossil Fuels," Volume 05.02, Petroleum Products and Lubricants (II), ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [9] Annual Book of ASTM Standards, Section 5, "Petroleum Products, Lubricants, and Fossil Fuels," Volume 05.04, Petroleum Products and Lubricants (IV), ASTM International, West Conshohocken, PA, 2015, www.astm.org

- [10] Coordinating Research Council, Inc., "Handbook of Aviation Fuel Properties," 4th ed., CRC Report No. 663, CRC, Alpharetta, GA, 2014.
- [11] Energy Institute, "Handbook on Equipment Used for the Maintenance and Delivery of Clean Aviation Fuel," El 1550, Energy Institute, London, 2007.
- [12] Smith, M., Aviation Fuels, Foulis, London, 1970.
- [13] El/JIG Standard 1530, Quality Assurance Requirements for the Manufacture, Storage, and Distribution of Aviation Fuels to Airports, JIG and Energy Institute, London, 2013.
- [14] Gammon, J., Aviation Fuel Quality Control Procedures, MNL5, 4th ed., ASTM International, West Conshohocken, PA, 2009.
- [15] ATA Specification 103, Standard for Jet Fuel Quality Control at Airports, Air Transport Association of America, Washington, DC, 2009.
- [16] Joint Inspection Group, Aviation Fuel Quality Control and Operating Standards for Airport Depots and Hydrants, Jig2, No. 11, 2014, www.jigonline.com
- [17] Joint Inspection Group, Aviation Fuel Quality Control and Operating Standards for Supply and Distribution Facilities, JIG3, No. 11, 2014, www.jigonline.com
- [18] Defence Standard 91-90, Gasoline Aviation: Grades 80/87, 100/130, and 100/130LL, UK Ministry of Defence, London, 2009.
- [19] Chevron Global Aviation, "Aviation Fuels Technical Review," Chevron International, San Ramon, CA, 2007.

Chapter 9 | Discussion on Uses of the Specification for Turbine Fuels Using Synthesized Hydrocarbons (ASTM **D7566**)

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9.1 Introduction

ASTM International (ASTM) **D1655**, *Standard Specification for Aviation Turbine Fuels* (jet fuels) [1], specifies the starting materials that are approved for the manufacture of jet fuel. These are crude oil, natural gas liquid condensates, heavy oil, shale oil, and oil sands. ASTM **D7566** [2] was first introduced in 2009 and allows for the use of blend components in jet fuel that are derived from other starting materials.

ASTM **D1655** was developed around the implicit assumption that jet fuel is manufactured from petroleum in refineries. Listed in Table 1 in ASTM **D1655** are batch quality control requirements that ensure a consistent product that allows for safe and reliable operation of airplanes and engines. However, if new sources of raw material are used for jet fuel manufacture, there is no guarantee that the resulting product will be fit-for-purpose as a jet fuel.

Biomass is increasingly looked to as a new source of fuels mainly because its use reduces carbon emissions. Bio-derived fuels have been widely used in ground transportation. Their introduction has been mandated by various government regulations. But because of the safety-critical nature of aviation fuels, introduction of new fuels or fuel blend components is not a simple matter.

The International Air Transportation Association (IATA) has set goals of carbon neutral growth by 2020 and a 50 % reduction in aviation carbon emissions relative to 2005 by 2050. These aggressive goals will require the use of significant amounts of bio-derived blend components.

In order to meet these goals, the aviation fuel technical community has developed a guideline for evaluation and approval of jet fuel blend components from non-petroleum sources, ASTM D4054, *Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives* [3].

ASTM D7566 describes semisynthetic blends consisting of petroleum-derived aviation fuels (Jet A or Jet A1) with a syntheticblend component from a non-petroleum source. After certification, the semisynthetic blend is considered as ASTM D1655 Jet A/A1. It is not segregated in the distribution system and requires no special handling. It is fully fungible with petroleum-derived

¹ Retired.

Jet A/A1. It is sometimes call a "drop-in" fuel because it is fully compatible with the existing jet fuel distribution system and with use in aircraft and engines. Bio-derived fuels are sometimes called "alternative fuels" but are better described as alternative *sources* of fuel in the case of aviation because the final fuels are essentially identical to petroleum-derived fuels.

ASTM **D1655** is one of two major specifications used worldwide for commercial jet fuel. The other specification is Defence Standard (Def Stan) 91-91 [4] issued by the UK Ministry of Defence (MOD), and it covers Jet A1 used in many regions of the world. The first approval for jet fuel from non-conventional sources was by Def Stan 91-91. The South African company Sasol had been using the Fischer-Tropsch (FT) process for many years and approached the MOD about using synthetic paraffinic kerosine from the Fischer-Tropsch process (FT SPK) in jet fuel. After an extensive review process, FT SPK, produced only by Sasol, was approved as blend component at up to 50 % by volume with conventional jet fuel in 1999. Since then, this synthetic blend has been used routinely at the airport in Johannesburg, South Africa.

Because ASTM D7566 semisynthetic blends are essentially ASTM D1655 fuels, this chapter will not go into detail on jet fuel properties covered by the specification. (These were covered in Chapter 8 on ASTM D1655.) This chapter will discuss the individual approvals and the additional requirements beyond ASTM D1655.

9.2 Approval of Synthesized Hydrocarbons

New blend components are only incorporated into ASTM **D7566** after a thorough review and evaluation by aircraft and engine original equipment manufacturers (OEMs), in accordance with ASTM **D4054**, to ensure that they are fit-for-purpose as a jet fuel. The initial ASTM **D4054** requirements include a section on the composition of the synthesized hydrocarbons including trace materials and testing of a blend of synthesized hydrocarbons with petroleumderived Jet A to the ASTM **D1655** Table 1 requirements. This is followed by testing of the semisynthetic blend for bulk physical and performance properties, electrical properties, ground handling and safety properties, and fuel system materials compatibility. This set of tests is called fit-for-purpose properties.

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A preliminary report covering this testing is prepared and submitted to the OEMs for review. If there are negative effects, the fuel can be rejected. If there are no negative effects, the OEMs can then request additional rig testing, engine testing, or flight testing at their discretion.

A final report covering all testing is submitted to the OEMs for review. Airworthiness authorities, such as the Federal Aviation Administration (FAA) or the European Aviation Safety Agency (EASA), also review the final report. If the OEMs advise the FAA that the fuel pathway is fit for purpose, then the new synthetic blend component will move on to an ASTM ballot for review by the subcommittee on aviation fuels. Successful approval of the ballot by ASTM and subsequent incorporation into ASTM **D7566** provides confirmation that the new fuel pathway fits within the existing aviation fuel operating limitations approved by the airworthiness authorities. The fuel may now be used by the existing fleet of aircraft. At their discretion, the OEMs may also revise their aircraft or engine service documentation to specifically identify the new fuel pathway.

9.3 Organization of ASTM D7566

The main body of ASTM **D7566** currently covers semisynthetic blends (i.e., blends of synthesized hydrocarbons with conventional blending components, or Jet A/A1). Table 1 of ASTM **D7566** specifies criteria that the semisynthetic jet fuel must meet after blending. ASTM **D7566** also includes an annex for each approved synthetic blending component that describes the criteria that must be met before blending with the conventional blending components or Jet A/A1. As of this writing, there are three annexes. Several other synthesized hydrocarbon streams have been proposed for jet fuel

blending, and new annexes will be added as these are approved by the OEMs. Fig. 9.1 provides an overview of ASTM D7566 structure.

ASTM **D7566** was first published in 2009 with Annex A1. Annex A2 was added in 2011. Annex A3 was added in 2014.

Both ASTM **D7566** and ASTM **D1655** include provisions that allow a semisynthetic fuel that meets the criteria of ASTM **D7566** to be recertified as a jet fuel meeting ASTM **D1655**. This enables a seamless transition into the distribution infrastructure without the need for special handling or tracking of these fuels as shown in **Fig. 9.2**.

9.4 Synthetic Blending Components

9.4.1 ANNEX A1 FISCHER-TROPSCH HYDROPROCESSED SYNTHESIZED PARAFFINIC KEROSINE

This annex covers synthesized paraffinic kerosine (SPK) produced via the Fischer-Tropsch (FT) process. The FT process starts with the gasification of coal or biomass, or reforming of natural gas, to produce a mixture of carbon monoxide and hydrogen called synthesis gas, **Fig. 9.3**. This synthesis gas is then converted to a hydrocarbon product in the FT reactor. It can be thought of as a polymerization of carbon monoxide coupled with reduction by hydrogen to form hydrocarbons. This FT product undergoes additional processing to produce a range of fuels and chemicals. The jet fuel product, called FT SPK, is composed mainly of iso-paraffins and does not include aromatics.

Any carbon source, including coal, natural gas, or biomass, is acceptable. The initial conversion of starting material to synthesis





FIG. 9.2 ASTM D7566 enables drop-in fuel.



FIG. 9.3 Fischer-Tropsch conversion to synthesized paraffinic kerosine. Figure courtesy of Sasol.



gas and its purification before FT synthesis breaks any linkage with the starting material. The properties of the FT product are independent of the carbon source (given the same synthesis gas composition). This allows the use of any starting material with the assurance that the product will be essentially 100 % hydrocarbon and that subsequent processing will give a suitable SPK.

The annex allows blending up to 50 % by volume FT SPK with Jet A, subject to density and aromatics content limitations on the blend.

Annex A1 contains two tables that list property requirements of the FT SPK. Table A1.1 specifies the requirements that must be met for each batch of FT SPK before blending with Jet A. **Table 9.1** compares some ASTM **D1655** Table 1 properties for conventional jet fuel with those specified in Table A1.1 for the synthetic blending component. The differences from ASTM **D1655** either reflect fundamental differences between FT SPK and Jet A in the case of density or are more restrictive than in ASTM **D1655** to ensure that any SPK blended into jet fuel has the same characteristics as the FT SPK that was used in the test program that led to approval. This is the case for thermal stability and distillation. The annex table also limits FT SPK flash point and freezing point but at the same limits as for Jet A.

Table A1.2 contains other detailed requirements for FT SPK, including bulk hydrocarbon composition and trace materials.

TABLE 9.1 Differences between ASTM D7566 Annex A1.1 and ASTM D1655 Table 1.

Property	Test Method	ASTM D1655 Jet A	ASTM D7566 Annex A1.1 SPK
Acidity, total mg KOH/g max	ASTM D3242	0.10	0.015
Physical Distillation,°C	ASTM D86		
T90-T10, min		No requirement	22
Simulated Distillation,°C	ASTM D2887	No requirement	Report
Density @ 15°C, kg/m³	ASTM D4052	775-840	730-770
Thermal Stability,°C	ASTM D3241		
Control Temperature, min		260	325

Each batch of FT SPK must meet these requirements; however, testing on each batch is not required. This testing should be done at the start of production, after significant changes to the process, and as required thereafter to ensure consistent, high-quality product.

9.4.2 ANNEX A2 SYNTHESIZED PARAFFINIC KEROSINE FROM HYDROPROCESSED ESTERS AND FATTY ACIDS

This annex covers synthesized paraffinic kerosine from hydroprocessed esters and fatty acids (HEFA). The starting material is typically a triglyceride such as soy oil, but any mono-, di-, and tri-glycerides, free fatty acids, and fatty acid esters are acceptable. The ester is catalytically processed to hydrogenate and deoxygenate the starting material; see **Fig. 9.4**. The catalyst chosen may also isomerize the product to improve the low temperature properties. The synthetic blending component is composed mainly of iso-paraffins and is similar in composition and properties to FT SPK.

FIG. 9.4 Conversion of triglycerides to synthesized paraffinic kerosine. (Courtesy of UOP.)



The annex allows blending up to 50 % by volume HEFA SPK with Jet A, subject to density and aromatics content limitations on the blend.

Annex A2 is very similar to Annex A1. There are two tables that list requirements for the neat synthesized blending component, HEFA, before blending. Table A2.1 contains the same requirements as Table A1.1 for FT SPK plus two additional requirements, fatty acid methyl ester (FAME) and existent gum. The FAME requirement is to ensure there is no unreacted starting material in the final product. The test method was developed for FAME in jet fuel and must be modified to detect the particular starting material used.

Table A2.2 covers hydrocarbon composition and trace materials. The requirements are the same as for FT SPK but, unlike FT SPK, all batches of HEFA SPK must be tested to the requirements.

9.4.3 ANNEX A3 SYNTHESIZED ISO-PARAFFINS (SIP) FROM HYDROPROCESSED FERMENTED SUGARS

The synthetic blending component described in this annex is essentially a single compound farnesene, 2,6,10 trimethyldodecane, a C15 iso-paraffin. Sugars are fermented using microorganisms selected to maximize production of farnesane, an unsaturated hydrocarbon. The farnesene is separated from the fermentation mixture and catalytically hydroprocessed to form the saturated analogue farnesane. Farnesane is finally purified by distillation; see Fig. 9.5.

The SPKs described in Annexes A1 and A2, although also iso-paraffinic, are comprised of a variety of carbon numbers in the jet fuel range and a number of isomers at each carbon number. One of the properties of petroleum-derived jet fuel is a smooth boiling range distribution. Blending 50 % of SPKs with Jet A preserves this property. However, blending 50 % of a single compound would flatten the boiling range distribution. Testing during the review process showed that the Jet A requirements could only be met with SIP blends of 10 % or less.

Annex A3 has the same organization as A1 and A2. Table A3.1 lists requirements that must be met by each batch of SIP before blending. The major differences between Table A3.1 and ASTM D1655 Table 1 are listed in Table 9.2 of this chapter. The differences reflect the single compound nature of SIP in the distillation and density requirements. The freezing point and thermal





TABLE 9.2 Differences between ASTM D7566 Annex A3.1 and ASTM D1655 Table 1.

Property	Test Method	ASTM D1655 Jet A	ASTM D7566 Annex A3.1 SIP
Acidity, total mg KOH/g max	ASTM D3242	0.10	0.015
Physical distillation,°C	ASTM D86		
T10, max		205	250
FBP, max		300	255
T90–T10, min		No requirement	5
Density @ 15°C, kg/m³	ASTM D4052	775-840	765-780
Freezing point,°C max	ASTM D2386	-40	-60
Thermal stability,°C	ASTM D3241		
Control temperature, min		260	355
Net heat of combustion, MJ/kg min	ASTM D3338	42.8	43.5

stability requirements ensure that the SIP has the same high purity as that used in the evaluation program.

Table A3.2 covers hydrocarbon composition and trace materials. As with HEFA SPK, all batches of SIP must be tested to these requirements.

9.5 Semisynthetic Jet Fuel Blends

After certification to the requirements of an annex, a synthetic blend component is blended with Jet A or conventional blending components to create a semisynthetic jet fuel blend. The maximum allowable concentration of the synthetic blend component is listed in **Table 9.3**.

Table 1 of ASTM **D7566**, listing detailed requirements of aviation turbine fuels containing synthesized hydrocarbons, is divided into two parts. Part 1, basic requirements, is identical to

TABLE 9.3 Maximum synthetic blend component concentration.

Annex	Maximum Synthetic Blend Component, Volume %
A1 FT SPK	50
A2 HEFA SPK	50
A3 SIP	10

ASTM D1655 Table 1. Part 2, extended requirements, lists additional requirements intended to ensure that semisynthetic blends have properties consistent with the experience base of petroleumderived jet fuel (Table 9.4).

Petroleum-derived jet fuels have a range of aromatics content with a minimum at about 8 %. With 50 % blends of FT and HEFA allowed, there was concern that aromatics content of a blend could drop below 8 %. The minimum was set to ensure that semisynthetic blends are within the range of experience. The distillation boiling range requirements are set for the same reason.

The synthetic blend components have relatively poor lubricity as is typical for high purity hydrocarbons. The lubricity requirement is included to ensure that all semisynthetic blends have adequate lubricity.

Although the C15 iso-paraffin farnesene (SIP) has a very low freezing point, it has relatively high viscosity at low temperatures. Low temperature viscosity of jet fuel is a very important property, and this requirement is set to ensure that a semisynthetic blend of SIP will have acceptable viscosity.

9.6 Additives

Only additives listed in ASTM D1655 are allowed in Jet A and at approved concentrations. Each synthetic blending component approved in the annexes is required to have an approved

TABLE 9.4 ASTM D7566 Table 1, Part 2–Extended requirements.

Property	Test Method	ASTM D1655 Jet A	ASTM D7566 Table 1 Part 2
Aromatics, vol % min	ASTM D1319	No requirement	8
Physical distillation,°C	ASTM D86		
T50–T10, min		No requirement	15
T90–T10, min		No requirement	40
Lubricity, wsd mm max	ASTM D5001	No requirement	0.85
Viscosity –40°C, max (SIP only)	ASTM D445	No requirement	12

antioxidant as a precautionary measure to prevent gum formation. However, the ASTM **D7566** semisynthetic blends have the same additive requirements as ASTM **D1655** Jet A.

References

- ASTM D1655, Standard Specification for Aviation Turbine Fuels, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [2] ASTM D7566, Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [3] ASTM D4054, Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [4] Defence Standard 91-91, Turbine Fuel, Kerosine Type, Jet A-1 (NATO Code: F-35, Joint Service Designation: AVTUR) UK Ministry of Defence, London, 2011.

Chapter 10 | Discussion on Uses of the Specifications for Diesel Fuels (ASTM **D975**) and Fuel Oils (ASTM **D396**)

Steven R. Westbrook¹

In 2013, the United States Energy Information Administration (EIA) projected that world energy consumption will increase 56 % by the year 2040 [1]. According to the EIA report, liquid fuels are now—and will continue to be—the most-used energy source, followed by coal and natural gas. The EIA projects that nearly 80 % of world energy, through 2040, will come from fossil fuels. ExxonMobil projected that worldwide diesel fuel demand will continue to grow through 2040 because diesel technology is able to handle heavy transportation loads better [2].

Diesel engine technology is more efficient than gasoline engine technology. Diesel engines are generally more durable than gasoline engines, resulting in longer useful lifetimes for diesel engines. These factors combine to make diesel engines and diesel fuel the preferred transportation fuel throughout much of the world.

Along with increased use of diesel engines, most countries have continued to tighten diesel engine vehicle emissions. These changes in emissions regulations have led to worldwide changes in diesel engine technology and diesel fuel specifications. In general, these hardware and fuel changes have evolved together.

The use of non-petroleum diesel fuels and blending components is also on the rise. Chief among these is the increasing use of biodiesel. However, simply because a liquid will burn in a compression ignition engine does not guarantee that it will give acceptable performance for extended periods of use.

In the United States and around the world, the increased demand for diesel fuel, the increased use of non-petroleum-based fuels, changing diesel engine technology, and tighter regulations all combine to emphasize the importance of high-quality diesel fuel specifications.

10.1 Types of Specifications

Specifications are the basis for a contract between a seller and a purchaser of fuel. Several different types of specifications can be found across the spectrum from fuel production to ultimate use in an engine. These include the following:

• Producer Specifications—Refiners and other fuel producers have specifications that control the quality of fuel they produce. These are not published. They are used to ensure that the fuel produced meets all applicable specifications during the distribution and use of the fuel.

• Consensus Specifications (Standards)—These are written and published by standards development organizations (SDO) such as ASTM International and the International Organization for Standardization (ISO). As a general rule, these specifications contain the minimum requirements for a fuel to provide acceptable performance under the scope of the specification. It is important to note that these specifications are not legal documents in and of themselves. Only when used in a contract or by a regulatory body do they obtain legal status. In those cases, the user of the specification or the regulatory body is responsible for enforcement, not the SDO. The ASTM D975 specification specifically discusses this in Section 1.2, as follows:

1.2 This specification, unless otherwise provided by agreement between the purchaser and the supplier, prescribes the required properties of diesel fuels at the time and place of delivery.

1.2.1 Nothing in this specification shall preclude observance of federal, state, or local regulations which can be more restrictive.

- Pipeline Specifications—Most fuel that is produced and distributed in the United States moves through a pipeline at some point. When the fuel leaves the pipeline, it is stored at a terminal awaiting further distribution. Pipeline companies and terminal operators have specifications for the fuel that flows through their systems. These specifications are meant to ensure the quality of the fuel. They also are meant to protect the pipelines and storage tanks (i.e., prevent corrosion) as well as to maintain the integrity of all fuels passing through the pipeline.
- Engine Manufacturer Specifications—Diesel engine and truck manufacturers have company specifications. Typically, these are based on consensus standards. In some cases, additional requirements are included to provide additional equipment protection. Additionally, several organizations jointly have published the World Wide Fuel Charter (WWFC). These include the Truck and Engine Manufacturers Association, the European Automobile Manufacturers, and the Japan Automobile Manufacturers Association. According to the fifth

¹ Southwest Research Institute, 6220 Culebra Rd, San Antonio, TX 78228-0510 DOI: 10.1520/MNL6920150008

edition, published in 2013, the WWFC "provides fuel quality recommendations published by the members of the Worldwide Fuel Charter Committee as a service to worldwide legislators, fuel users, and producers."

- User Specifications—These are fuel specifications (or purchase specifications) developed by end users of diesel fuel in diesel engines. However, it should be noted that fuels that meet these specifications are often not available in the market, depending on the specification requirements. Examples of end users include the military, trucking companies, and municipal bus companies. These users typically buy large volumes of fuel and store it in their own tanks. Long-haul truckers, who buy fuel at various locations, are less likely to have fuel-purchase specifications because they have less control over the quality of the fuel they buy. User specifications are often based on engine manufacturers' specifications for the equipment they use. Often there are additional requirements based on individual needs.
- Government Regulations/Requirements—Regulatory agencies at all government levels—from federal through state down to municipal—issue diesel fuel regulations. In some cases, the regulations cover very limited aspects of fuel quality. Diesel fuel sulfur limits, set by the U.S. Environmental Protection Agency (EPA), are an example. Some regulations simply mimic, or even directly reference, existing consensus standards such as ASTM D975 [3]. Still others require or incentivize certain fuel properties. The various regulations regarding the addition of biodiesel to petroleum diesel fuel are examples of this.

The enforcement of a specification ultimately depends on the type of specification and the nature of the agreement between seller and buyer. The two parties to a fuel purchase will typically have procedures/agreements in place regarding compliance to the specification. Often times this involves testing representative samples of the fuel to confirm specification compliance. When the transaction is between a seller and the general public, the enforcement is usually performed by governmental or regulatory agencies. As an example, most states have agencies to enforce the relevant fuel specifications within their state. Routine sampling and analysis of fuel from filling stations and truck stops is at the heart of the enforcement. Federal agencies, such as the EPA, also conduct sampling/testing programs to monitor fuel quality.

10.2 Standardized Test Methods

Specifications are a collection of requirements/controls on the chemical, physical, and performance characteristics of the fuel. Each of these characteristics is measured using a given test method. When a fuel is analyzed for specification conformance, both parties to the transaction want to be sure that the analytical results are reliable. The best way to do that is to use standardized test methods. When both parties know how the analysis was conducted, they both understand what the results mean. In some cases, there may be more than one standardized method for measuring a given property. In those cases, the specification typically will designate a referee method to be used when results from different methods do not agree.

10.3 Fuel Grades

The ASTM specification is designated D975, *Standard Specification for Diesel Fuel Oils*. It covers seven grades of diesel fuel oils suitable for various types of diesel engines. These grades are listed in Table 10.1. The variety of specified fuel grades allows users of the specification to select and specify the fuel that most closely meets the end use and regulatory requirements. The fuel does not have to meet the concept of "one size fits all." A fuel buyer can simply write a purchase order or contract to buy ASTM D975, Grade No. 2-D S15, and ask for quotes from potential suppliers. This "shorthand" designation, provided by a standard specification, eliminates the need for the two parties to "spell out" all the various property requirements.

10.4 Fuel Composition

Diesel engine technology is such that many types of liquids will burn and produce power in the engine. Depending on several factors, diesel engines may operate on any of the following, alone or in blends:

- Diesel fuel
- Biodiesel
- Raw vegetable oil
- Coal slurries
- Engine oil and used engine oil
- Propane
- Natural gas
- Aviation turbine fuel
- Certain industrial solvents
- Others

TABLE 10.1 Diesel fuel grades within ASTM D975.

Grade No. 1-D S15—A special purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S15 fuel.

Grade No. 1-D S500—A special purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 500 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S500 fuel.

Grade No. 1-D S5000—A special purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 5000 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S5000 fuels.

Grade No. 2-D S15—A general purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load.

Grade No. 2-D S500—A general purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 500 ppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load.

Grade No. 2-D S5000—A general purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 5000 ppm sulfur (maximum), especially in conditions of varying speed and load.

Grade No. 4-D—A heavy distillate fuel, or a blend of distillate and residual oil, for use in low- and medium-speed diesel engines in applications involving predominantly constant speed and load.

(Notice that gasoline is not in the list. A very specifically designed engine is needed to be able to burn both gasoline and diesel fuel.)

However, just because a liquid will burn in the engine does not mean that the engine manufacturer is prepared to warranty the engine for operation with that fluid. Many potential fuels may cause minor, and in some cases major, damage to the engine. A good fuel specification has some constraints to help protect against the use of liquids that may damage the engine. In the case of ASTM **D975**, these are primarily covered in Section 7:

7. Requirements

7.1 The grades of diesel fuel oils herein specified shall be hydrocarbon oils, except as provided in 7.3, with the inclusion of additives to enhance performance, if required, conforming to the detailed requirements shown in Table 1.

NOTE 4—Additives are generally included in finished diesel fuel to improve performance properties (cetane number, lubricity, cold flow, and so forth).

7.2 Grades No. 2-D S15, No. 2-D S500 and No. 2–D S5000— When a cloud point less than –12°C is specified, as can occur during cold months, it is permitted and normal blending practice to combine Grades No. 1 and No. 2 to meet the low temperature requirements. In that case, the minimum flash point shall be 38°C, the minimum viscosity at 40°C shall be 1.7 mm²/s, and the minimum 90 % recovered temperature shall be waived.

7.3 Alternative Fuels and Blend Stocks:

7.3.1 Fuels Blended with Biodiesel—The detailed requirements for fuels blended with biodiesel shall be as follows:

7.3.1.1 Biodiesel for Blending—If biodiesel is a component of any diesel fuel, the biodiesel shall meet the requirements of Specification D6751.

7.3.1.2 Diesel fuel oil containing up to 5 vol % biodiesel shall meet the requirements for the appropriate grade No. 1-D or No. 2-D fuel, as listed in Table 1.

7.3.1.3 Test Method **D7371** [4] shall be used for determination of the vol % biodiesel in a biodiesel blend. Test Method EN14078 [5] may also be used. In cases of dispute, Test Method **D7371** shall be the referee test method. See Practice **E29** [6] for guidance on significant digits.

7.3.1.4 Diesel fuels containing more than 5 vol % biodiesel component are not included in this specification.

7.3.1.5 Biodiesel blends with No. 4-D fuel are not covered by this specification.

Having these requirements in the specification allows engine manufacturers to warranty their engines for operation on fuel meeting ASTM **D975**. With standardized specifications, what is excluded/ disallowed from the fuel is usually just as important as what is included/allowed.

10.5 Definitions

By including certain definitions within ASTM **D975**, ASTM provides additional guidance regarding the composition of fuels covered under the specification. The following are found in Section 3 of ASTM **D975**:

- Biodiesel, n—Fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.
- Biodiesel blend (BXX), n—Blend of biodiesel fuel with diesel fuel oils.
 - Discussion—In the abbreviation, BXX, the XX represents the volume percentage of biodiesel fuel in the blend.
- Hydrocarbon oil, n—A homogeneous mixture with elemental composition primarily of carbon and hydrogen that may also contain sulfur, oxygen, or nitrogen from residual impurities and contaminants associated with the fuel's raw materials and manufacturing processes and excluding added oxygenated materials.
 - Discussion—Neither macro nor micro emulsions are included in this definition since neither are homogeneous mixtures.
 - Discussion—Examples of excluded oxygenated materials are alcohols, esters, ethers, and triglycerides.
 - Discussion—The hydrocarbon oil may be manufactured from a variety of raw materials, for example petroleum (crude oil), oil sands, natural gas, coal, and biomass.

10.6 Selected Diesel Fuel Properties

This section is a discussion of the significance of selected properties listed in ASTM D975. A more complete, more detailed, discussion can be found elsewhere [7]. Appendix X1 of ASTM D975 is also a discussion of the significance of the specification requirements.

10.6.1 CETANE NUMBER

Cetane number is a measure of the ignition quality of the fuel and influences combustion roughness and emissions. The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. Increase in cetane number over values actually required does not materially improve engine performance. Accordingly, the cetane number specified should be as low as possible to assure maximum fuel availability.

Cetane number can also be an indicator of fuel composition and contamination because composition has a significant effect on ignition quality. Straight-chain paraffins ignite readily under compression, but branched-chain paraffins and aromatics react more slowly. So a fuel with a low cetane number may be contaminated with high aromatic content fluids. The EPA recognized this compositional relationship and included applicable regulations in 40 CFR Part 80 to control aromatics content in S500 grades. They set a minimum cetane index value (as calculated by ASTM D976) of 40 as a means to limit aromatics content in the fuel. The alternative to this requirement was 35 % by volume maximum aromatics as measured by ASTM D1319. With the advent of biodiesel blends in ASTM D975, the EPA controls are less accurate or useful. However, they are federal regulations that remain in effect and so will remain a part of the ASTM D975 requirements.

10.6.2 FLASH POINT

The flash point as specified is not directly related to engine performance. It is, however, of importance in connection with legal requirements and safety precautions involved in fuel handling and storage. It is normally specified to meet insurance and fire regulations. Low flash point may indicate contamination with gasoline or other low-flash point fluids.

Grades No. 1 and No. 2 have different flash point requirements, 38°C and 52°C minimum, respectively. The differences are because of the compositional differences of the two grades. Grade No. 1 is a lighter, more volatile fuel grade. This difference was found to cause problems in some parts of the United States during winter months. Grade No. 1 fuel is sometimes blended into Grade No. 2 fuel in the winter in order to improve low temperature operability properties of the Grade No. 2 fuel. There were cases when enough Grade No. 1 was blended in that the flash point of the Grade No. 2 fell below the 52°C minimum. In an effort to formally recognize this situation and aid regulators, ASTM added the following footnote to Table 1 in ASTM D975:

When a cloud point less than -12°C is specified, as can occur during cold months, it is permitted and normal blending practice to combine Grades No. 1 and No. 2 to meet the low temperature requirements. In that case, the minimum flash point shall be 38°C, the minimum viscosity at 40°C shall be 1.7 mm²/s, and the minimum 90 % recovered temperature shall be waived.

The addition of this footnote to the table corrected an unforeseen problem brought on by common industry practices that seemed to conflict with current regulations and specifications. The slightly lower flash point caused no operational problems in engines but did cause problems for regulators. Had the 52°C minimum been strictly enforced, there would have been numerous problems related to low temperature operation (waxing).

10.6.3 SULFUR

The effect of sulfur content on engine wear and deposits appears to vary considerably in importance and depends largely on operating conditions. Fuel sulfur can affect emission control systems performance.

When the EPA initiated regulations to ultimately reduce the allowable sulfur level of diesel fuel from 5000 ppm to under 15 ppm (ultra-low sulfur diesel, or ULSD) over a period of several years, it started a series of changes to ASTM **D975**. Because the EPA regulations allowed for different limits depending on the application of the fuel (on-highway, off-highway, locomotive, marine, etc.), a new system of designating fuel grades was required. This was the

genesis of the "S" designations in each of the various grades. These changes also brought about the need for increasingly sensitive and accurate methods to analyze total sulfur levels. Eventually, the following information was added to aid the user with the selection of the appropriate sulfur test method(s) [3] (see ASTM D975-15b Sec. 3 and 5.18):

Sulfur Test Method	Grades
D129	No. 1-D S5000, No. 2-D S5000, No. 4-D
D1266	No. 1-D S500, No. 2-D S500
D1552	No. 1- D S5000, No. 2-D S5000, No. 4-D
D2622 (referee for S500, S5000, and No. 4 Grades)	All Grades
D3120	No. 1-D S15, No. 2-D S15 No. 1-D S500, No. 2-D S500 (If the fuel contains biodiesel, this method may not be applicable as it is limited to oxygenates with a boiling range of 26 °C to 274 °C)
D4294	No. 1-D S500, No. 2-D S500 No. 1- D S5000, No. 2-D S5000, No. 4-D
D5453 (referee for S15 grades)	All Grades
D7039	No. 1–D S15, No. 2–D S15 No. 1-D S500, No. 2-D S500
D7220	No. 1–D S15, No. 1–D S500 No. 2–D S15, No. 2–D S500

10.6.4 LUBRICITY

The large reductions in sulfur discussed earlier brought about other changes in the fuel as well. The most striking change was to a fuel property known as lubricity. Diesel fuel functions as a boundary lubricant in most components of fuel injection equipment such as pumps and injectors. Historically, this was not a property of concern to diesel engine operators because diesel fuel composition was such that it provided ample lubricity where needed. As sulfur limits were reduced, the refining processes used to reduce the sulfur brought about subtle changes in the fuel. Total aromatics content often went down as sulfur was removed. Hetero-atoms such as nitrogen-containing compounds were also often removed at the same time. These changes caused changes in the lubricity of the fuel. At the same time, diesel engine fuel systems were also changing. Tolerances in fuel pumps and injectors were getting tighter, and injection pressures were going up. All of these factors combined and resulted in significantly increased reports of fuel system hardware failures in Europe. The industry needed help with this problem and a change to ASTM D975 to address the fuel quality aspect. But fuel lubricity had not previously been in ASTM D975, and little was known about the property or the aspects of fuel composition that might have an effect. At the time, there was no standardized test method that was generally accepted as a measure of fuel lubricity. Eventually, a test method, ASTM D6079, was recognized as the standard test. It was the basis for including a lubricity requirement in ASTM **D975**. Although there remains some disagreement among experts regarding the sensitivity and precision of the test, the inclusion of the requirement in ASTM **D975** allowed fuel producers and engine manufacturers to establish processes to address the problem.

10.6.5 CONDUCTIVITY

In much the same way that the conversion to ULSD brought about the need for a lubricity requirement, it also caused the inclusion of another new property, conductivity, in ASTM D975. The processes used to produce ULSD and to keep it free of contaminants resulted in significant reductions in the amount of certain trace components and contaminants that had historically provided adequate electrical conductivity in the fuel. Electrical conductivity of fuels is an important consideration in the safe handling characteristics of any fuel. The risk associated with explosions due to static electrical discharge depends on the amount of hydrocarbon and oxygen in the vapor space and on the energy and duration of a static discharge. There are many factors that can contribute to the high risk of explosion. For ULSD fuels in particular, electrical conductivity can likely be very low before the addition of a static dissipater additive (SDA). The intent of this requirement is to reduce the risk of electrostatic ignitions while filling tank trucks, barges, ship compartments, and rail cars, where flammable vapors from past cargo can be present. Generally, it does not apply at the retail level where flammable vapors are usually absent.

10.6.6 CLOUD POINT

Cloud point is important in that it defines the temperature at which a cloud or haze of wax crystals appears in the fuel under prescribed test conditions that generally relate to the temperature at which wax crystals begin to precipitate from the fuel in use. The climate across the United States varies significantly from north to south or east to west. This results in widely differing high and low temperatures depending on location and time of year. Still, fuel producers must formulate their fuel to meet customers' seasonal and regional needs. Fuel users need to know that they can purchase fuel with adequate low temperature characteristics to avoid filter clogging. It is impractical for ASTM D975 to recommend a single cloud point for all diesel fuel across the United States year-round. Suggested levels had to include consideration of seasonal and regional differences. ASTM chose to make these considerations in the form of guidelines: Appendix X5: "Tenth Percentile Minimum Ambient Air Temperatures for the United States (Except Hawaii)."

The tenth percentile minimum ambient air temperatures were derived from an analysis of historical hourly temperature readings recorded over a period of 15 to 21 years from 345 weather stations in the United States. They are presented in both tables and maps. The tenth percentile minimum ambient air temperature is defined as the lowest ambient air temperature that will not go lower on average more than 10 % of the time. In other words, the daily minimum ambient air temperature would on average not be expected to go below the monthly tenth percentile minimum ambient air temperature days in a 30-day month. These data can be used to estimate low temperature operability

requirements. In establishing low temperature operability requirements, consideration should be given to the following factors. These factors, or any combination, can make low temperature operability more or less severe than normal. Field work suggests that cloud point (or wax appearance point) is a fair indication of the low temperature operability limit of fuels without cold flow additives in most vehicles.

- Long-term weather patterns (average winter low temperatures will be exceeded on occasion).
- Short-term local weather conditions (unusual cold periods do occur).
- Elevation (high locations are usually colder than surrounding lower areas).
- Specific vehicle design.
- Fuel system design (recycle rate, filter location, filter capacity, filter porosity, etc.).
- Fuel viscosity at low temperatures.
- Equipment add-ons (engine heaters, radiator covers, fuel line and fuel filter heaters, and so forth).
- Types of operation (extensive idling, engine shutdown, or unusual operation).
- · Low temperature flow improver additives in fuel.
- Geographic area for fuel use and movement among geographical areas.
- General housekeeping (dirt or water, or both, in fuel or fuel supply system).
- Impact failure for engine to start or run (critical versus non-critical application).

Despite the fact that these remain only (non-mandatory) guidelines, it is reasonable to assume that they have become the basis against which fuel suppliers blend their winter fuels, and the extra level of comfort that fuel users need for low temperature operation.

10.6.7 STABILITY

Diesel fuel stability is not a specification property within ASTM **D975**. Rather, there is relevant information presented in Appendix X3, Storage and Thermal Stability of Diesel Fuels. This appendix provides guidance for consumers of diesel fuels who may wish to store quantities of fuels for extended periods or use the fuel in severe service or high-temperature applications. Fuels containing residual components are excluded. Consistently successful long-term fuel storage or use in severe applications requires attention to fuel selection, storage conditions, handling, and monitoring of properties during storage and prior to use.

Normally produced fuels have adequate stability properties to withstand average storage and use without the formation of troublesome amounts of insoluble degradation products. Fuels that are to be stored for prolonged periods or used in severe applications should be selected to avoid formation of sediments or gums, which can overload filters or plug injectors. Selection of these fuels should result from supplier–user discussions. These suggested practices are general in nature and should not be considered substitutes for any requirements imposed by the warranty of the distillate fuel equipment manufacturer or by federal, state, or local government regulations. Although they cannot replace knowledge of local conditions or good engineering and scientific judgment, these suggested practices do provide guidance in developing an individual fuel management system for the middle distillate fuel user. They include suggestions in the operation and maintenance of existing fuel storage and handling facilities and for identifying where, when, and how fuel quality should be monitored or selected for storage or severe use. The inclusion of this information in ASTM D975 provides potentially valuable information to the fuel user that would require significant effort to gather otherwise.

10.7 Alternative Fuels and Blend Stocks

Modern technologies, combined with the societal desires to increase the use of alternative fuels, have resulted in numerous potential diesel fuels showing up in the market. Some of these are considered acceptable for general use and some are not. Because the end user often has little knowledge of the intricacies of fuel composition, it may be difficult for them to judge the acceptability of various alternative fuels. Likewise, some engine manufacturers might find it prohibitive to attempt to qualify and approve every alternative fuel in the marketplace. By using consensus standards, both parties can agree on those alternative fuels that each would consider acceptable. (It is important to note that non-inclusion of a particular alternative fuel in ASTM D975 in no way labels that fuel as unacceptable. All parties involved in the consensus process make changes to the specification on a case-by-case basis.) Section 7.3 in ASTM D975 contains the following regarding alternative fuels and blend stocks:

- Fuels Blended with Biodiesel—The detailed requirements for fuels blended with biodiesel shall be as follows:
 - Biodiesel for Blending—If biodiesel is a component of any diesel fuel, the biodiesel shall meet the requirements of Specification D6751.
 - Diesel fuel oil containing up to 5 vol % biodiesel shall meet the requirements for the appropriate grade No. 1-D or No. 2-D fuel, as listed in Table 1.
 - Test Method D7371 shall be used for determination of the vol % biodiesel in a biodiesel blend. Test Method EN 14078 may also be used. In cases of dispute, Test Method D7371 shall be the referee test method. See Practice E29 for guidance on significant digits.
 - Diesel fuels containing more than 5 vol % biodiesel component are not included in this specification.

• Biodiesel blends with No. 4-D fuel are not covered by this specification.

For those interested in proposing a new alternative fuel for consideration, ASTM **D975** also contains Appendix X7, Guidance on Evaluation of New Materials for #1D and #2D Grades of Diesel Fuels. The purpose of this appendix is to give some general guidance from Subcommittee D02.E0 on evaluation of new materials for blends in or replacements for Specification ASTM **D975**, Grades #1-D and #2-D type fuels.

10.8 Conclusion

Specifications, especially consensus specifications, facilitate the selling and buying of diesel fuel on an equal basis between seller and buyer. Both parties start from the position of knowing what the product needs to be (seller) or will be (buyer). This is the strength of consensus standards. The producer/seller need not survey every potential customer for their requirements. Likewise, the buyer can go into the marketplace and purchase fuel with confidence. If every filling station and truck stop sold fuel that met no specific standard, the possible problems for the user would be incalculable. It is important to recognize that the consensus process of standards development does not mean unanimity on every point. All parties work through the process to obtain a specification that benefits all to some degree.

References

- U.S. Energy Information Administration (EIA), "EIA Projects World Energy Consumption Will Increase 56 % by 2040," *Today in Energy*, July 25, 2013, https://www.eia.gov/ todayinenergy/detail.cfm?id=12251
- [2] Colton, B., *The Outlook for Energy: A View to 2040*, Exxon Mobil Corporation, Irving, TX, 2015.
- [3] ASTM D975-15b, Standard Specification for Diesel Fuel Oils, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [4] ASTM D7371-14, Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method), ASTM International, West Conshohocken, PA, 2014, www.astm.org
- [5] CSN EN 14078, Liquid Petroleum Products—Determination of Fatty Acid Methyl Esters (FAME) Content in Middle Distillates—Infrared Spectroscopy Method.
- [6] ASTM E29-13, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications, ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [7] Rand, S. J., Ed., Significance of Tests for Petroleum Products, 8th Ed., ASTM International, West Conshohocken, PA, 2010.

Chapter 11 | Discussion on Uses of the Specifications for Biodiesel Fuel Blend Stock B100 (ASTM **D6751**) and Biodiesel Blends B6 to B20 (ASTM **D7467**)

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The purpose of this chapter is to provide users of the ASTM standards for biodiesel with a summary of the importance of the ASTM biodiesel standards, practical information about how they help to ensure performance of biodiesel and biodiesel blends in equipment or applications for which the standards were developed, and how the standards are being used by buyers, sellers, equipment companies, and regulatory authorities. This chapter will provide a short background on biodiesel and the biodiesel industry in the United States and general reasons why consumers are incorporating increasing amounts of biodiesel in conventional middle distillate type fuels such as on- and off-road diesel and home heating fuel. The chapter will also summarize how and why the standards were developed, how the standards address equipment and user needs, and some details regarding how the standards are being used in the commercial marketplace in the United States.

11.1 Background on Biodiesel and the Biodiesel Industry

The commercial biodiesel industry began in earnest in the early 1990s in order to produce domestic, renewable fuels to reduce dependence on imported crude oil, to reduce environmental impacts, and to reduce the adverse health impacts of exhaust emissions from conventional fuels. Prior to that time period (in the 1970s), early studies had been done on the use of raw vegetable oils or animal fat sources as potential extenders or emergency replacements for distillate fuels. This work was undertaken as a result of the first petroleum shortage and resulting concerns regarding conventional petroleum-based diesel (petrodiesel) fuel. This work in vintage diesel engine technology showed that the energy content, density, combustion, and general properties of oils and fats were such that they could be burned in these older diesel applications in an emergency. However, due primarily to their much higher viscosity (approximately 10 times higher viscosity than petrodiesel), the use of raw, unprocessed vegetable oils or fats could cause injector coking and fuel system-related stability problems and were not generally suitable for long-term use. Chemically transforming the raw oil or fat into a fatty acid methyl ester (i.e., biodiesel) could address the viscosity and stability issues associated with raw oils

and fats and potentially make them acceptable for long-term use. However, once petroleum prices and availability issues subsided, interest waned.

Advancing concern for cleaner air and energy independence led to the passage of the U.S. Clean Air Act Amendments of 1990 and the Energy Policy Act of 1992. The latter was a direct response to unrest in the Middle East and the Desert Storm conflict that occurred during the presidency of George H. W. Bush. This created interest in alternatives for diesel fuel. Previous positive work with methyl esters from oils and fats—combined with excess supplies of by-product soybean oil from processing soybeans into highprotein soybean meal for humans and animals (soybeans are 80 % high protein meal and only 20 % soybean oil)—spurred the formation of the National Soy Diesel Development Board in the United States in 1992. (The name was later changed to the National Biodiesel Board [NBB].) The ASTM Biodiesel Task Force was formed soon after and has been in operation since 1993.

The first ASTM biodiesel specification for pure biodiesel (B100) was adopted in 2001. The industry consensus ASTM standards for biodiesel have been the cornerstone in the development of biodiesel as a commercial fuel and fuel component in the United States and globally. In 2014, more than 1.5 billion gallons of pure biodiesel were produced by more than 200 U.S. manufacturing plants, according to the NBB. This growth was mainly due to local, state, and national policies encouraging or mandating biodiesel and also due to relatively few in-use problems with biodiesel meeting the ASTM specifications. The increase in biodiesel would not have been possible without ASTM standards and the technical information needed to secure them.

11.2 Development of the Biodiesel Standards: Based on User and Equipment Needs

After detailed discussions with potential customers in the early 1990s, it became clear that one of the first steps needed to develop a commercial biodiesel industry in the United States was to formulate a set of physical and chemical properties for biodiesel that would give confidence to customers. Users of the fuel wanted to be sure it would work in their existing diesel engine or home heating unit as well as, if not better than, conventional petrodiesel or fuel

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oil. This set of properties would then also be used by other major sectors in the marketplace (i.e., fuel blenders, equipment manufacturers, and regulators) for other purposes discussed in more detail later in this chapter.

The ASTM Biodiesel Task Force (TF) contains representatives from most major sectors, and these representatives are intimately involved in the development and the approval of ASTM biodiesel standards. This helps to ensure that the needs of each group especially the users and equipment companies—can be met through the use of the ASTM standards that are developed through the industry consensus process built into each ASTM specification. Because most biodiesel is used as a blend with conventional diesel or middle distillate fuels, there are several important factors that have been identified by the ASTM Biodiesel TF:

- It is important to have a stand-alone specification for pure biodiesel. The biodiesel will most likely be produced by one commercial entity and used by another for blending with petrodiesel. Therefore, a trading standard for the biodiesel blend stock is needed.
- 2. If both biodiesel blend stock and petrodiesel meet appropriate standards, the resulting biodiesel blend should require very little quality control after blending. As much as possible, blending biodiesel into petrodiesel should be treated similarly to the blending of other middle distillate products.
- 3. Development of the standard should be based on the end product's physical and chemical attributes required for applications by users—as opposed to being based on biodiesel feedstock and processing methods.
- 4. Because millions of existing engines and equipment have been designed to existing petroleum-based specification(s), biodiesel blend stocks and resulting blends should have physical and chemical properties similar to existing petrodiesel.
- 5. Some items contained in the existing petroleum-based specification are not applicable to biodiesel due to the different chemical or physical nature of biodiesel, and these should be eliminated. One example of this includes the distillation curve. Biodiesel is comprised of only four to six individual molecules that all boil at similar temperatures versus petrodiesel, which is comprised of hundreds of compounds that boil over a large range. Another example is the aromatics content. Biodiesel has zero aromatics while petrodiesel normally contains 10 % to 40 % aromatics.
- 6. Some specifications that did not exist for petroleum-based diesel may be needed for biodiesel. Examples of this include the acid value and the total and free glycerin and phosphorous content, all of which can be present in minor amounts in biodiesel but are not normally found in petrodiesel.
- 7. Finally, as new requirements are adopted for conventional fuels for new engines, injection equipment, and exhaust after-treatment, they should also be considered for biodiesel as well. Most equipment changes result from the need for improved emissions control, better fuel economy, and better performance in general. Lower sulfur content and the implementation of lubricity standards to address highly hydrotreated petroleum-based fuel are two examples.

The aforementioned factors allowed the development of the biodiesel standard so that it could be used by all the major industry stakeholders to meet their needs.

In the past, the term "biodiesel" had been used to refer to a coal slurry, a pure vegetable oil, a mixture of vegetable oils and petrodiesel, the esters of natural oils, and mixtures of esters with petrodiesel, just to mention a few. With negative feedback from equipment companies regarding a variety of these materials in the past, and more positive experience with the methyl esters of vegetable oils in the United States and Europe, biodiesel was defined narrowly by ASTM to eliminate these other potentially problematic materials: "Biodiesel, n—Fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100."

From the perspective of a user as well as an equipment company, this relatively tight definition was needed in order for both to feel confident in the performance of biodiesel. After a significant amount of cooperative testing and research with equipment companies—mostly large diesel engine makers—the first specification for pure biodiesel (B100) was approved by ASTM in 2001 as ASTM **D6751**, *Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels* [1]. It should be noted that the title of the standard is as a blend stock, not as a finished fuel. Those using it as a finished fuel should do this in consultation with the equipment manufacturer as is noted in the standard [1].

Soon after the ASTM D6751 [1] blend stock standard was adopted, stakeholders expressed a need for standards for the finished blended fuel. ASTM adopted finished fuel standards for blends up to B5 into the existing diesel fuel (ASTM D975) [2] and burner fuel (ASTM D396) [3] standards in 2008. A separate standard, ASTM D7467 [4], was adopted for B6–B20 blends for on- and off-road diesel fuel that same year. ASTM continues to improve the biodiesel standards as changes occur with conventional fuels and equipment and as biodiesel blend levels in the market increase.

11.3 Critical Aspects of ASTM Biodiesel Standards for Users, Buyers, Sellers, and Others

The biodiesel standards have been designed for use in the same applications or equipment in which conventional diesel fuel or middle distillate type fuel oils are burned. In most cases, biodiesel is blended with conventional fuels in blends up to 20 % by volume. As such, the general considerations for diesel fuel and burner fuel also apply to biodiesel blends, and biodiesel blends should be compatible with equipment that has been used with regular diesel and heating fuel.

This section will focus on specific aspects and needs for biodiesel and biodiesel blends that are different from, or in addition to, those of conventional petroleum-based middle distillate fuels.

11.3.1 ASTM D6751, BIODIESEL BLEND STOCK (B100)

ASTM D6751 [1], the specification for biodiesel blend stock, is by far the most important specification to ensure fit-for-purpose biodiesel

blends. This specification has instituted controls that address concerns regarding previous problems with raw oils and fats. ASTM D6751 [1] provides chemical and physical properties that give satisfactory performance in diesel engines, home heating oil burners, and other equipment that uses traditional diesel or middle distillate fuel oils.

The B100 specification helps to ensure that biodiesel has been properly processed and has sufficiently low levels of potentially problematic minor oil and fat components. These are not found in petroleum derived fuels and, therefore, are not controlled by the parameters and limit values in existing fuel standards.

Biodiesel is produced from a variety of vegetable oils and animal fats. All natural vegetable oils (i.e., soy, corn, canola, cottonseed, etc.) and animal fats (i.e., poultry, pork, beef) come in the form of triglycerides. Each triglyceride contains three long straight-chain hydrocarbon fatty acids connected to a 3-carbon glycerin backbone. To produce biodiesel meeting ASTM **D6751** [1], each of the three fatty acid chains connected to the triglyceride is reacted with a short chain alcohol, usually methanol, to create three biodiesel molecules (i.e., the mono-alkyl ester) and one glycerin molecule. The reaction is carried out by using excess methanol to drive the reaction to completion and by being in the presence of a catalyst, which usually is sodium or potassium hydroxide that has been pre-dissolved in the methanol.

All oils and fats available in commercial volumes for biodiesel production naturally have very similar fatty acid chain lengths and structures. In general, the fatty acid chains are all straight chain hydrocarbons containing zero, one, two, or three double bonds, with the carbon chains being mostly 16 to 18 carbons long [5]. Biodiesel, therefore, is comprised almost entirely of only these five or six specific molecules, all of which provide similar energy content, boiling temperatures, viscosity, and flash point-and which burn in a similar way. It also naturally brackets the cetane number (generally between 50 and 65) and the cloud point (generally between -1°C [30°F] and 18°C [65°F]). Because vegetable oils and animal fats essentially have zero sulfur or aromatic compounds, the narrow ASTM biodiesel definition also helps to ensure an ultra-low-sulfur, zero-aromatic fuel. Lastly, the "mono-alkyl ester" functional group in the ASTM definition provides biodiesel with superior lubricity properties not normally associated with an ultra-low-sulfur fuel.

Petroleum-based middle distillate fuels, in contrast, are comprised of hundreds of different hydrocarbons of varying structures and chain lengths including straight, branched, cyclic and polycyclic, and aromatic and polyaromatic. The total number of carbons per molecule generally falls between 12 and 24 carbons.

In addition to the narrow definition, Table 1 of the ASTM **D6751** [1] specification has parameters that help ensure the fuel has been properly processed. The following aspects of biodiesel processing are critical to performance in a diesel engine or in a fuel oil burner and are addressed in ASTM **D6751** [1]:

1. Essentially complete conversion of the fat or oil to mono-alkyl esters is ensured through measurement of the total glycerin (ASTM D6584 [6]), which includes all bound glycerin

(i.e., mono-, di-, and triglycerides) as well as the unbound free glycerin.

- 2. Removal of the unbound glycerin is ensured through measurement of the free glycerin (ASTM D6584 [6]).
- 3. Removal of the catalyst is ensured through the measurement of the sulfated ash (ASTM D874 [7]).
- Removal of any excess alcohol is ensured through direct measurement of methanol by either gas chromatography (EN14110 [8]) or by use of a high flash point value, if alcohols other than methanol are used.
- 5. Sufficiently low level of free fatty acid components is ensured through measurement of the acid number (ASTM D664 [9]).

Other critical parameters that are controlled by the biodiesel specifications also have been identified:

- Sufficiently low level of other minor oil fat components that can affect filter clogging: This is controlled through a new test method developed specifically for biodiesel (ASTM D7501 [10], commonly called a cold soak filtration test, or CSFT) and through the use of the No. 1-B grade of biodiesel, which further limits the CSFT and mono-glycerides. Additional guidance is also contained in a non-mandatory appendix on cold flow considerations.
- Sufficiently high oxidation stability for storage and in-use considerations: This is ensured through the measurement of induction period stability (EN1575 [11]) with additional advice contained in a non-mandatory appendix on stability.
- Sufficiently low levels of water and sediment: This is ensured through the measurement of water and sediment (ASTM D2709 [12]) and through the workmanship clause.

Additional controls important for diesel combustion (viscosity, cetane, carbon residue, etc.) are included to ensure that final blends are fit-for-purpose.

11.3.2 ASTM D7467, BIODIESEL BLENDED IN 6 % TO 20 % BY VOLUME WITH CONVENTIONAL DIESEL (B6-B20)

From 2001 until 2008, the industry bought, sold, and consumed biodiesel and biodiesel blends through the purchase of ASTM D6751 [1] B100 blend stock and ASTM D975 [2] diesel fuel or by purchasing ASTM D396 [3] fuel oils and blending the two in various concentrations, generally in blends of 5 % or less, or in blends containing 6–20 % biodiesel by volume. Some believed that having blends of two streams that each have adequate specification should result in an acceptable finished product, similar to what is done when conventional Grade No. 1-D and Grade No. 2-D are blended for low temperature operation. ASTM D6751 [1] was designed for 20 % inclusion because that seemed to be a good overall trade-off between the availability of oils and fats for biodiesel production and the desire to use biodiesel blends in existing equipment without modification.

Due to desires of some users, engine and equipment manufacturers, regulators, and others for finished blended fuel standards for biodiesel blends up to 20 % biodiesel, in 2008, ASTM included
finished fuel standards for blends up to B5 in the existing ASTM D975 [2] and ASTM D396 [3] standards. The ASTM D7467 [4] standard covering B6–B20 blends with No. 1-D and No. 2-D type ASTM D975 [2] fuels in on- and off-road diesel fuel also passed in 2008.

ASTM **D7467** [4] requires that B100 meet ASTM **D6751** [1] prior to being blended. This ensures that most of the biodiesel specific potential issues are addressed at the B100 level and therefore do not need to be readdressed in the finished blend. This is extremely important because some of the critical biodiesel (B100) properties—such as total glycerin—are at such a low level in the B100 that it would be very difficult to identify them in the finished blend. For ASTM **D7467** [4], the petrodiesel component must meet ASTM **D975** [2] properties for everything except lubricity, sulfur, aromatics, and cetane, provided the finished B6–B20 blend meets the appropriate levels for those parameters. Blending with either No. 1-D or No. 2-D ASTM **D975** [2] fuel or a mixture of No. 1-D/No. 2-D is permitted.

With the aforementioned in mind, Table 1 of the ASTM **D7467** [4] standard contains all the same parameters and requirements that are in Table 1 of ASTM **D975** [2], as well as the same three EPA sulfur grades (S15, S500, S5000). To avoid confusion between the No. 1 and No. 2 grades of conventional and biodiesel blends, B6–B20 grades containing the widest of either the existing No. 1-D or No. 2-D limit values were adopted. In order to ensure that blended fuel always meets the intended specification, the T-90 was allowed to be 5°C higher for the B6–B20 blend due to the higher boiling point and higher flash point of the biodiesel component.

The only other change for ASTM **D7467** [4] compared to ASTM **D975** [2] is the addition of an acid number and an induction period stability requirement. If B100 meets ASTM **D6751** [1], the ASTM **D7467** [4] values for acid number and stability should fall within specification as well and should provide acceptable fuel quality. However, as the blend ages, it can lose storage stability and, in some cases, begins to form acids. The induction period and the acid number were included in ASTM **D7467** [4] to enable a user or regulator to measure these properties at the point of sale—without knowing the parent fuel quality—as a convenient means to confirm that fuel has not degraded and still is fit-for-purpose. A useful appendix providing stability guidelines also has been included in ASTM **D7467** [4]. The same cold flow guidelines provided in ASTM **D975** [2] also should be used for ASTM **D7467** [4] fuels.

11.4 How the ASTM Biodiesel Specifications Are Used in the Commercial Marketplace

The ASTM specifications for biodiesel are used every day in the commercial marketplace by a variety of stakeholders who use, regulate, and design equipment for diesel fuels. The biodiesel blend stock standard, however, is mostly used by intermediary entities such as fuel blenders and less by the end user of the finished product. The primary users of the biodiesel standards, similar to users of conventional diesel and gasoline, are comprised of five general categories. Multiple representatives from each category have been and continue to be involved in developing and improving ASTM biodiesel specifications:

- Users: Ease of purchasing contract and assurance of proper operation in their equipment.
- Biodiesel Producers: Clear definition of requirements for process and manufacturing control.
- Fuel Distributors/Blenders/Retailers: Ease of purchasing and quality control.
- 4. Equipment and Engine Manufacturers: Optimize design and manufacture compatible products.
- 5. Regulatory Agencies: Aid to regulate safety, protect the environment, and monitor fuel quality and product labeling requirements, as well as tax administration.

For biodiesel, the ASTM specifications have taken on another purpose that is not normally associated with conventional gasoline or diesel fuel. The ASTM standards are the basis for the biodiesel industry's voluntary fuel quality program, which is called BQ-9000 [12]. The BQ-9000 [13] fuel quality program has been critical in helping build confidence in the commercial marketplace that the fuels being sold meet the ASTM standards that have been developed.

In order for the biodiesel industry to sell fuel, customers demanded assurance from their vehicle or engine manufacturer that the use of biodiesel would not affect their engines or vehicles adversely. Many original equipment manufacturers (OEMs) made it clear that they would not endorse the use of biodiesel in their equipment without approved ASTM standards. Even after the ASTM D6751 fuel standard was adopted, independent fuel testing showed that a significant amount of the biodiesel for sale in the market did not meet the ASTM D6751 [1] standard. OEMs, as well as potential customers, needed further assurance that the biodiesel being produced actually met the ASTM specifications. The BQ-9000 [13] program—a combination of an International Standards Organization (ISO) 9000 type of fuel-quality management system that incorporates the mandatory requirement to meet the ASTM biodiesel specifications-was instituted and resulted in significant quality improvements.

Although companies selling products such as fuel in mass quantities normally provide a guarantee that the fuel will meet the standards, it would be cost prohibitive to analyze every truck of fuel for every property in the standards. As one of the long time ASTM members from Chrysler has said in many meetings, "We guarantee our cars will meet the industry standard crash test—but we don't actually test each car before we sell it!" With this in mind, the BQ-9000 [13] program requires testing of only the critical parameters for each batch or lot of biodiesel, rather than the full set of 20 properties in the ASTM D6751 [1] standard. The following is the list of critical parameters in the BQ-9000 [13] program:

- Cloud point
- Acid number
- Free glycerin

- Total glycerin
- Monoglycerides
- Sulfur
- · Oxidation stability
- Visual appearance
- Cold soak filterability test

ASTM will continue to improve the biodiesel standards as changes occur with conventional fuels and equipment and as biodiesel blend levels in the market increase and are used in other applications. These standards will be a key for users, buyers, sellers, equipment companies, regulators, and others as the biodiesel industry seeks to grow over time.

References

- ASTM D6751-15a, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [2] ASTM **D975-15b**, *Standard Specification for Diesel Fuel Oils*, ASTM International, West Conshohocken, PA, 2015, **www.astm.org**
- [3] ASTM D396-15b, Standard Specification for Fuel Oils, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [4] ASTM D7467-15a, Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20), ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [5] Howell, S. A., "Biodiesel," ASTM Manual 1: Significance of Tests for Petroleum Products, 8th Ed., S. J. Rand, Ed., ASTM International, West Conshohocken, PA, 2010.

- [6] ASTM D6584-13e1, Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography, ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [7] ASTM D874-13a, Standard Test Method for Sulfated Ash from Lubricating Oils and Additives, ASTM International, West Conshohocken, PA, 2013, www.astm.org
- [8] EN 14110, Fat and Oil Derivatives—Fatty Acid Methyl Esters (FAME)—Determination of Methanol Content, European Committee for Standardization, Brussels, Belgium, 2003, www.cenorm.be
- [9] ASTM D664-11a, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, ASTM International, West Conshohocken, PA, 2011, www.astm.org
- [10] ASTM D7501-12a, Standard Test Method for Determination of Fuel Filter Blocking Potential of Biodiesel (B100) Blend Stock by Cold Soak Filtration Test (CSFT), ASTM International, West Conshohocken, PA, 2012, www.astm.org
- [11] EN 15751, Automotive Fuels—Fatty Acid Methyl Ester (FAME) Fuel and Blends with Diesel Fuel-Determination of Oxidation Stability by Accelerated Oxidation Method, European Committee for Standardization, Brussels, Belgium, 2014, www.cenorm.be
- [12] ASTM D2709-96, Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge, ASTM International, West Conshohocken, PA, 2011, www.astm.org
- [13] "BQ-9000," BQ-9000 Biodiesel Fuel Quality Program, Jefferson City, MO, 2015, http://www.bq9000.com (accessed February 1, 2016).

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