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# Aviation Fuels

Technical Review



# **Chevron Products Company**

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Please note: This information is accurate as of fall 2004. It may be superseded by new regulations, specifications, or advances in fuel or engine technologies.

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# **General Introduction**

Man has long been captivated by the possibility of flight. From Icarus' wings to DaVinci's flying machines to lighter-than-air balloons, inventive minds worked to turn the dream into a reality. But what was lacking was a means of propulsion. This finally became available in the early years of the 20th century with the development of the internal combustion engine. This engine provided a compact and portable source of power that allowed man to overcome the pull of gravity.

The early aircraft engines were similar to those used in automobiles and burned the same fuel. The need for increased power led to the development of specialized engines and aviation gasolines (avgas) tailored to their requirements. In the 1940s, the turbine engine emerged as the answer to the quest for still more power. In a replay of avgas development, kerosine – the fuel used in the first aircraft turbine engines – was eventually replaced by specialized aviation turbine fuels (jet fuels).

In the last 90 years, aviation has grown from a novelty to an essential, even defining, element of modern society. It enables people and goods to move around the globe in hours, rather than the weeks or months that used to be required.

Aviation is powered by petroleum fuels. This is not an accident; the choice is based on petroleum's recognized advantages. Liquid fuels have higher energy contents per unit volume than gases, and are easier to handle and distribute than solids. Among liquids, liquid hydrocarbons offer the best combination of energy content, availability, and price.

This Review covers the performance, properties, specifications, composition, and manufacture of aviation fuels, both turbine fuel and aviation gasoline. Since engine and fuel are interdependent components of a single system, it also touches on engine basics. And it addresses the special precautions incorporated in the distribution system to ensure quality and cleanliness as fuel is moved from refinery to aircraft.

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# 1 · Aviation Turbine Fuel Introduction

Jet propulsion can be traced back to the 1st century B.C. when an Egyptian, Hero, is credited with inventing a toy that used jets of steam to spin a sphere. Sixteen centuries later, Leonardo da Vinci sketched a device that used a flux of hot gas to do mechanical work. By the 17th century, inventors were beginning to develop simple turbine systems to operate machinery.

The development of a turbine engine for aircraft began independently in Germany and Britain in the 1930s. In Germany, Hans von Ohain designed the engine that powered the first jet flight in 1939. Germany deployed the jet-powered Messerschmitt 262 late in World War II.

In Britain, Frank Whittle obtained a patent for a turbine engine in 1930. An aircraft powered by an engine he designed first flew in 1941. The first British jet fighter, the Gloster Meteor, also flew late in World War II.

# **Types of Fuel**

Illuminating kerosine, produced for wick lamps, was used to fuel the first turbine engines. Since the engines were thought to be relatively insensitive to fuel properties, kerosine was chosen mainly because of availability; the war effort required every drop of gasoline.

After World War II, the U.S. Air Force started using "wide-cut" fuel, which, essentially, is a hydrocarbon mixture spanning the gasoline and kerosine boiling ranges. Again, the choice was driven by considerations of availability: It was assumed that a wide-cut fuel would be available in larger volumes than either gasoline or kerosine alone, especially in time of war.

However, compared to a kerosine-type fuel, wide-cut jet fuel was found to have operational disadvantages due to its higher volatility:

- Greater losses due to evaporation at high altitudes.
- Greater risk of fire during handling on the ground.
- Crashes of planes fueled with wide-cut fuel were less survivable.

So the Air Force started to change back to kerosine-type fuel in the 1970s and has essentially completed the process of converting from wide-cut (JP-4) to kerosine-type (JP-8) system-wide. The U.S. Navy has used a high flashpoint kerosine-type fuel (JP-5) on aircraft carriers because of safety considerations since the early 1950s. See Figure 3.1 for a list of U.S. military jet fuels.

When the commercial jet industry was developing in the 1950s, kerosine-type fuel was chosen as having the best combinations of properties. Wide-cut jet fuel (Jet B) still is used in some parts of Canada and Alaska because it is suited to cold climates. But kerosine-type fuels – Jet A and Jet A-1 – predominate in the rest of the world.<sup>1</sup>

Figure 1.1
Hero's Toy

Water contained in the sphere is heated and the steam escaping through the jets causes the sphere to turn in the opposite direction. Jet A is used in the United States while most of the rest of the world uses Jet A-1. The important difference between the two fuels is that Jet A-1 has a lower maximum freezing point than Jet A (Jet A:  $-40^{\circ}$ C, Jet A-1:  $-47^{\circ}$ C). The lower freezing point makes Jet A-1 more suitable for long international flights, especially on polar routes during the winter.

However, the lower freezing point comes at a price. Other variables being constant, a refinery can produce a few percent more Jet A than Jet A-1 because the higher freezing point allows the incorporation of more higher boiling components, which in turn, permits the use of a broader distillation cut. The choice of Jet A for use in the United States is driven by concerns about fuel price and availability. Many years of experience have shown that Jet A is suitable for use in the United States.

# **Fuel Consumption**

The consumption of jet fuel has more than doubled in the United States over the past 25 years, growing from 32 million gallons per day in 1974 to 72 million gallons per day in 2000, declining to 68 million gallons per day in 2002. Most of this growth has occurred since 1984.<sup>2</sup>

Data for the worldwide use of jet fuel are available only for years after 1989 (*see Figure 1.2*). In 2001, the most recent year for which data are available, consumption was 189 million gallons per day, up 20 percent from 1990. Figure 1.2 shows how this total is distributed around the globe. The United States is the largest single market, consuming about 37 percent of the worldwide total.

Figure 1.2
World Apparent Consumption of Jet Fuel

			Consumpt	tion, Millic	n US Gall	ons/Day						
Region	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
North America	69.2	66.8	66.3	66.7	69.4	69.0	72.2	73.5	74.8	77.4	79.6	76.1
Central and South America	6.3	6.3	6.0	6.0	7.0	6.1	7.4	7.7	7.7	5.3	8.5	9.5
Western Europe	26.7	26.3	28.1	29.1	30.8	32.4	34.0	35.5	37.7	40.7	42.2	40.9
Eastern Europe and FSU	24.1	20.4	18.4	15.2	12.4	12.3	11.4	10.1	11.8	11.0	11.3	11.4
Middle East	6.6	6.5	6.2	6.7	7.9	6.5	7.8	5.5	6.3	6.1	6.7	6.9
Africa	4.6	4.8	5.1	5.0	5.2	5.2	4.9	5.7	5.0	5.7	5.6	6.2
Far East and Oceania	20.2	21.1	25.6	28.9	30.7	36.0	36.1	38.7	35.2	36.6	37.1	38.2
Total	157.6	152.2	155.6	157.5	163.4	167.5	173.7	176.7	178.4	182.8	191.1	189.1

Source: U.S. Energy Information Administration

# 2 · Aviation Turbine Fuel Performance

## **Performance Properties**

Since the primary function of aviation turbine fuel (*jet fuel*) is to power an aircraft, *energy content* and *combustion quality* are key fuel performance properties. Other significant performance properties are *stability*, *lubricity*, *fluidity*, *volatility*, *non-corrosivity*, and *cleanliness*. Besides providing a source of energy, fuel is also used as a hydraulic fluid in engine control systems and as a coolant for certain fuel system components.

#### **Energy Content**

An aircraft turbine engine generates power by converting chemical energy stored in the fuel into a combination of mechanical energy and heat (*see Chapter 6*). Since space is at a premium in most aircraft, the amount of energy contained in a given quantity of fuel is important.

The energy content of jet fuel can be measured: It is the heat released (also called the *heat of combustion*) when a known quantity of fuel is burned under specific conditions. The amount of heat released depends on whether the water formed during combustion remains in the vapor phase or is condensed to a liquid. If the water is condensed to the liquid phase, giving up its heat of vaporization in the process, the energy released is called the *gross energy content*. The *net energy content* is lower because the water remains in the gaseous phase (water vapor). Since engines exhaust water as vapor, net energy content is the appropriate value for comparing fuels.

Energy content can be expressed either *gravimetrically* (energy per unit *mass* of fuel) or *volumetrically* (energy per unit *volume* of fuel). The International Metric (SI) units are *megajoules per kilogram* (MJ/kg) and *megajoules per liter* (MJ/L). In the United States, the gravimetric unit is *British thermal units per pound* (Btu/lb), and the volumetric unit is *British thermal units per gallon* (Btu/gal).

Because the energy contents of individual hydrocarbons can differ, jet fuel composition has some effect on energy content (*see page 25*). The effect is usually predicted by fuel density, which is also a function of composition. Generally, less dense jet fuels have a higher gravimetric energy content, and more dense jet fuels have a higher volumetric energy content. This effect is more pronounced when different types of fuel are compared (*see Figure 2.1*).

Figure 2.1
Fuel Energy Content vs. Density

	Typical Density at 15°C (60°F) g/mL lb/U.S. gal		Typical Energy Content				
Fuel			Gravi MJ/kg	metric Btu/lb	Volu MJ/L	metric Btu/gal	
Aviation Gasoline	0.715	5.97	43.71	18,800	31.00	112,500	
Jet Fuel:							
Wide-cut	0.762	6.36	43.54	18,720	33.18	119,000	
Kerosine	0.810	6.76	43.28	18,610	35.06	125,800	

Fuels differ in density, and therefore, in energy content per unit weight or unit volume. Less dense fuels, such as avgas, have a higher energy content per unit weight and a lower energy content per unit volume. The relationships are reversed for more dense fuels.

Which is preferred for aviation fuel, a higher density fuel with a higher volumetric energy content? Or a lower density fuel with a higher gravimetric energy content? The answer is obvious for aircraft that take off with their fuel tanks full, as most military aircraft do. A fuel with a high volumetric energy content maximizes the energy that can be stored in a fixed volume and thus provides the longest flight range.

The answer is not so obvious for commercial airliners, most of which don't fill their fuel tanks before each flight. Instead, they take on enough fuel to reach their intended destination, plus an adequate safety margin. In this situation, is it more advantageous to use a less dense fuel with a high gravimetric energy content to minimize fuel weight? Or does the increased range provided by the same volume of a more dense fuel with a high volumetric energy content offset the added weight? The relationship among these variables is complex, and beyond the scope of this Review. But, in most cases, it turns out that the answer is the same as for the "full tank" case: A more dense fuel with a high volumetric energy content is preferred.

Jet fuel is a commodity product that is typically bought and sold by volume, with no price adjustment for density or energy content.

#### Combustion Characteristics

The principal difference between piston and jet engines is that combustion is intermittent in a piston engine and continuous in a jet engine. As a result, the engines have different fuel combustion quality requirements. In piston engines, combustion timing is critical to good performance. When combustion is continuous, combustion timing is no longer important.

In a jet engine, small carbonaceous particles are formed early in the combustion process. These particles continue to burn as they pass through the flame and are completely consumed under suitable conditions. But these particles become incandescent under the high temperature and pressure conditions of the combustion section. Absorption of this infrared radiation by the combustor walls augments the normal heat received by heat transfer from the combustion gases. High combustor wall temperatures or hot spots can lead to cracks and premature engine failures.

If these carbonaceous particles are not completely consumed by the flame, they can also be harmful if they impinge on turbine blades and stators, causing erosion. Carbon deposits can also plug the holes in the combustor wall that supply dilution air to the combustion section, disrupting the flow pattern of the combustion products.

Fuels with high aromatics content, and especially fuels with high naphthalenes content, form more of these carbonaceous particles. Since these carbonaceous particles are potentially harmful, both the total aromatic content and the total naphthalenes content of jet fuel are controlled.

Carbon particles that are not completely consumed are responsible for the visible smoke that some engines emit. Smoke formation is determined mainly by engine design and operating conditions, although for a given design, fuel composition can influence emissions. Better mixing

of fuel and air results in more complete combustion and, thus, less carbon formation. Newer engines emit much less smoke because of design changes that improve mixing.

### **Stability**

A stable fuel is one whose properties remain unchanged. Factors that can lead to deleterious changes in fuel properties include time (*storage stability*) and exposure to high temperatures in the engine (*thermal stability*).

Jet fuel instability involves multi-step chemical reactions, some of which are oxidation reactions. Hydroperoxides and peroxides are the initial reaction products. These products remain dissolved in the fuel, but may attack and shorten the life of some fuel system elastomers. Additional reactions result in the formation of soluble gums and insoluble particulates. These products may clog fuel filters and deposit on the surfaces of aircraft fuel systems, restricting flow in small-diameter passageways.

**Storage Stability** Instability of jet fuel during storage is generally not a problem because most fuel is used within weeks or months of its manufacture. Storage stability is an issue for the military, which often stores fuel for emergency use. And it can be an issue at small airports that don't use a lot of fuel. Jet fuel that has been properly manufactured, stored, and handled should remain stable for at least one year. Jet fuel subjected to longer storage or to improper storage or handling should be tested to be sure it meets all applicable specification requirements before use.

Because it is the more reactive fuel components that cause instability, storage stability is influenced by fuel composition. It is also influenced by storage conditions; instability reactions occur faster and to a greater extent at higher ambient temperatures. Antioxidants may be added to fuel to improve its storage stability (*see page 31*).

**Thermal Stability** Thermal stability is one of the most important jet fuel properties because the fuel serves as a heat exchange medium in the engine and airframe. Jet fuel is used to remove heat from engine oil, hydraulic fluid, and air conditioning equipment. As noted above, the resulting heating of the fuel accelerates the reactions that lead to gum and particulate formation. These gums and particles may deposit:

- On fuel filters, increasing the pressure drop across the filter and reducing fuel flow.
- In fuel injector nozzles, disrupting the spray pattern, which may lead to hot spots in the combustion chamber.
- In the main engine control, interfering with fuel flow and engine system control.
- On heat exchangers, reducing heat transfer efficiency and fuel flow.

These deposits may lead to operational problems and increased maintenance. Antioxidants that are used to improve fuel storage stability are not generally effective in improving thermal stability.

Engine problems related to inadequate fuel thermal stability typically become evident only after hundreds or thousands of hours of operation. The long time and the large volume of fuel consumed make it impractical to test fuel thermal stability under conditions identical to those that exist in engines. Instead, the fuel is subjected to more severe conditions in a bench test in order to be able to see a measurable effect in a reasonable period of time.

Test equipment has been developed to pump fuel over a heated aluminum surface and then through a filter to collect any solid decomposition products. The equipment is intended to model two sensitive areas of an engine: the surface of a fuel-oil heat exchanger and a fuel injection nozzle. The first standardized apparatus (ASTM D 1660) was called the *Coker*. It has now been replaced by the *Jet Fuel Thermal Oxidation Tester* (JFTOT; pronounced *jef'tot*) (ASTM D 3241).

#### Lubricity

*Lubricity* is the ability to reduce friction between solid surfaces in relative motion, so it is a measure of a material's effectiveness as a lubricant. Jet fuel must possess a certain degree of lubricity because jet engines rely on the fuel to lubricate some moving parts in fuel pumps and flow control units.

The lubrication mechanism is a combination of *hydrodynamic lubrication* and *boundary lubrication*. In hydrodynamic lubrication, a layer of the liquid lubricant prevents the opposing moving surfaces from contacting each other. Higher viscosity liquids provide more hydrodynamic lubrication than lower viscosity liquids. While jet fuel specifications do not include an explicit lower limit on viscosity, the distillation specification serves as a surrogate limit. Jet engines are designed to work with jet fuels within the normal viscosity range, and therefore, typical jet fuels provide adequate hydrodynamic lubrication.

When close tolerances squeeze out most of the liquid layer that provides hydrodynamic lubrication, boundary lubrication becomes important. Now, small areas of the opposing surfaces are in contact. Boundary lubricants are compounds that form a protective anti-wear layer by adhering to the metal surfaces.

Straight-run jet fuels (*see page 34*) are good boundary lubricants. This is not due to the hydrocarbons that constitute the bulk of the fuel, but is attributed to trace amounts of certain oxygen-, nitrogen-, and sulfur-containing compounds. Evidence for the role of trace quantities is the fact that adding as little as 10 ppm of a lubricity enhancing additive to a poor lubricity fuel can make it acceptable.

The naturally occurring compounds that provide jet fuel with its natural lubricity can be removed by hydrotreating – the refining process used to reduce sulfur and aromatic content (*see page 35*). However, low sulfur or aromatics levels in jet fuel are not, per se, signs of inadequate lubricity. The boundary lubricity of jet fuel cannot be predicted from bulk physical or chemical properties, it can only be measured in a specially designed test apparatus (*see page 23*). Fuels with similar sulfur and aromatics content can have different lubricity.

# Aviation Turbine Fuel Performance

#### **Fluidity**

Obviously, jet fuel must be able to flow freely from fuel tanks in the wings to the engine through an aircraft's fuel system. *Fluidity* is a general term that deals with the ability of a substance to flow, but it is not a defined physical property. Viscosity and freezing point are the physical properties used to quantitatively characterize the fluidity of jet fuel.

Jet fuel is exposed to very low temperatures both at altitude – especially on polar routes in winter-time – and on the ground at locations subject to cold weather extremes. The fuel must retain its fluidity at these low temperatures or fuel flow to the engines will be reduced or even stop.

**Viscosity** *Viscosity* is a measure of a liquid's resistance to flow under pressure, generated either by gravity or a mechanical source. "Thin" liquids, like water or gasoline, have low viscosities; "thick" liquids, like maple syrup or motor oil, have higher viscosities. The viscosity of a liquid increases as its temperature decreases.

Jet fuel at high pressure is injected into the combustion section of the turbine engine through nozzles. This system is designed to produce a fine spray of fuel droplets that evaporate quickly as they mix with air. The spray pattern and droplet size are influenced by fuel viscosity. If it is too high, an engine can be difficult to relight in flight. For this reason, jet fuel specifications place an upper limit on viscosity.

Fuel viscosity influences the pressure drop in the fuel system lines. Higher viscosities result in higher line pressure drops, requiring the fuel pump to work harder to maintain a constant fuel flow rate. Fuel viscosity also influences the performance of the fuel system control unit.

Freezing Point Because it is a mixture of many hundreds of individual hydrocarbons, each with its own freezing point, jet fuel does not become solid at one temperature the way water does. As the fuel is cooled, the hydrocarbon components with the highest freezing points solidify first, forming wax crystals. Further cooling causes hydrocarbons with lower freezing points to solidify. Thus, the fuel changes from a homogenous liquid, to a liquid containing a few hydrocarbon (wax) crystals, to a slush of fuel and hydrocarbon crystals, and, finally, to a near-solid block of hydrocarbons. The freezing point of jet fuel is defined as the temperature at which the last wax crystal melts, when warming a fuel that has previously been cooled until wax crystals form (see page 21). Thus the freezing point of fuel is well above the temperature at which it completely solidifies.

The primary criterion for fuel system performance is *pumpability* – the ability to move fuel from the fuel tank to the engine. Pumpability is influenced both by fuel fluidity and fuel system design. In lieu of a fuel system flow simulation test, the industry uses freezing point as an indicator of a fuel's low-temperature pumpability. Jet fuel typically remains pumpable approximately 4°C to 15°C (8°F to 27°F) below its freezing point.<sup>1</sup>

#### **Coefficient of Thermal Expansion**

Liquids increase in volume as their temperatures increase. The coefficient of thermal expansion is a measure of the rate of volume increase with temperature. A typical value for the coefficient of thermal expansion of kerosine-type jet fuel is 0.00099 per degree Celsius [(°C)-¹] [(0.00055°F)-¹]. At this rate, one gallon of jet fuel will expand 4.0 percent for an increase in temperature of 40°C [1.000 gallon at 0°C (32°F): 1.040 gallon at 40°C (104°F)].

Of course, the relationship is reversible. For example, as jet fuel cools in the aircraft's tanks during flight, it will occupy a smaller volume than it did on the ground. The coefficient of thermal expansion can be used to calculate the volume decrease.

1 Aviation Fuels, Maxwell Smith.

The U.S. Air Force is evaluating the use of additives that may prevent the formation of large wax crystals that are responsible for reduced fuel flow.

#### Volatility

*Volatility* is a fuel's tendency to vaporize. Two physical properties are used to characterize fuel volatility: vapor pressure and distillation profile. A more volatile fuel has a higher vapor pressure and lower initial distillation temperatures.

Volatility is important because a fuel must vaporize before it can burn. However, too high a volatility can result in evaporative losses or fuel system vapor lock.

Volatility is one of the major differences between kerosine-type and wide-cut jet fuel. Kerosine-type jet fuel is relatively non-volatile. It has a Reid vapor pressure<sup>2</sup> of about 1 kiloPascal (kPa)[0.14 pound per square inch (psi)]. Wide-cut jet fuel has a Reid vapor pressure as high as 21 kPa (3 psi).

Wide-cut jet fuel is better suited for cold weather applications because it has a lower viscosity and freezing point than kerosine-type jet fuel. In such applications, evaporative losses are less of a concern.

#### Non-corrosivity

Jet fuel contacts a variety of materials during distribution and use. It is essential that the fuel not corrode any of these materials, especially those in aircraft fuel systems. Typically, fuel tanks are aluminum, but fuel systems also contain steel and other metals. Fuel tanks may also have sealants or coatings, and elastomers are used in other sections of the fuel system. Engine and airframe manufacturers conduct extensive fuel compatibility testing before approving a material for fuel system use.

Corrosive compounds potentially present in jet fuel include organic acids and mercaptans. The specifications limit these classes of compounds. By-products of microbial growth also can be corrosive (*see* Microbial Growth, *page* 9).

Contamination from trace amounts of sodium, potassium, and other alkali metals in the fuel can cause corrosion in the turbine section of the engine.

#### **Cleanliness**

Fuel cleanliness means the absence of solid particulates and free water. Particulates – rust, dirt, etc. – can plug fuel filters and increase fuel pump wear. Water, in addition to not burning in an engine, will freeze at the low temperatures encountered in high altitude flights. The resulting ice may plug fuel filters and otherwise impede fuel flow. Water in the fuel also may facilitate the corrosion of some metals and the growth of microorganisms (*see page 27 for a more detailed discussion of water in fuel*).

In addition to being clean, fuel delivered to aircraft must also be free from contaminants. The most common sources of contamination encountered with aviation fuels are discussed in Appendix A. These include product mixes, surfactants, microbes, and dyes.

#### Microbial Growth

Jet fuel is sterile when it is first produced because of the high refinery processing temperatures. But it quickly becomes contaminated with microorganisms that are always present in air and water. Microorganisms found in fuels include bacteria and fungi (yeasts and molds). The solids formed by microbial growth are very effective at plugging fuel filters. Some microorganisms also generate acidic by-products that can accelerate metal corrosion.

Since most microorganisms need free water to grow, microbial growth is usually concentrated at the fuel-water interface, when one exists. Some organisms need air to grow (*aerobic* organisms), while others grow only in the absence of air (*anaerobic* organisms). In addition to food (fuel) and water, microorganisms also need certain elemental nutrients. Jet fuel can supply most of these; phosphorus is the only one whose concentration might be low enough to limit microbial growth. Higher ambient temperatures also favor microbial growth. Other factors affecting microbial growth and its control are discussed in ASTM D 6469, *Standard Guide for Microbial Contamination in Fuel and Fuel Systems*.<sup>3</sup>

The best approach to microbial contamination is prevention. And the most important preventive step is keeping the amount of free water in fuel storage tanks and aircraft fuel tanks as low as possible.

When microorganisms reach problem levels in aircraft fuel tanks, approved biocides may be used under controlled conditions. But biocides have their limits. A biocide may not work if a heavy biofilm has accumulated on the surface of the tank or other equipment, because then it doesn't reach the organisms living deep within the biofilm. In such cases, the tank must be drained and mechanically cleaned.

And even if the biocide effectively stops microbial growth, it still may be necessary to remove the accumulated biomass to avoid filter plugging. Since biocides are toxic, any water bottoms that contain biocides must be disposed of appropriately.

# **Safety Properties**

Jet fuel can be hazardous if not handled properly. First, and foremost, it is easy to ignite and it burns rapidly. Second, exposure to jet fuel liquid or vapor should be limited. Anyone planning to handle jet fuel should obtain and read the Material Safety Data Sheet (MSDS) issued by the supplier.

<sup>3</sup> See also "Guidelines for the Investigation of the Microbial Content of Fuel Boiling Below 390°C and Associated Water" Institute of Petroleum, 1996 and "Fuel and Fuel System Microbiology: Fundamentals, Diagnosis, and Contamination Control" Frederick J. Passmann editor, ASTM MNL47.

Liquid doesn't burn; only vapor burns. And vapor doesn't always burn – the mixture of vapor and air must be within the flammable <sup>4</sup> range. Mixtures with insufficient vapor (below the *lower flammability limit*) or too much vapor (above the *upper flammability limit*) will not burn. For kerosine-type jet fuel, the lower and upper flammability limits <sup>5</sup> are 0.6 volume percent vapor in air and 4.7 volume percent vapor in air, respectively. For wide-cut jet fuel, the lower and upper flammability limits are 1.3 volume percent vapor in air and 8.0 volume percent vapor in air, respectively.

In most circumstances, the hydrocarbon vapor-air mixture in an enclosed space over kerosine-type jet fuel will not be in the flammable range; the mixture will be below the lower flammability limit. However, high ambient temperature can heat the fuel enough to bring the vapor space into the flammable range. The flash point of a fuel is the lower flammability temperature of the fuel under the specific test conditions. However, this is not necessarily the lower flammability temperature under other conditions, such as in an aircraft fuel tank.

For the more volatile wide-cut fuel, the hydrocarbon vapor-air mixture in an enclosed space may be in the flammable range. The upper flammability temperature limit depends on the vapor pressure of the fuel. A fuel with a vapor pressure of 18 kPa (2.6 psi) will have an upper flammability temperature limit of approximately 18°C (64°F).

However, in the absence of specific information to the contrary, any jet fuel handling situation should be considered potentially hazardous and the appropriate safety measures observed.

#### Flash Point

The *flash point* is the lowest temperature at which the vapors above a flammable liquid will ignite on the application of an ignition source. At the flash point temperature, just enough liquid has vaporized to bring the vapor-air space over the liquid above the lower flammability limit. The flash point is a function of the specific test conditions under which it is measured. The flash point of wide-cut jet fuel is below 0°C (32°F) and is not typically measured or controlled. The minimum flash point of Jet A and Jet A-1 kerosine-type jet fuel is 38°C (100°F).

## **Electrical Conductivity**

Static electrical charge can be generated when dissimilar surfaces move across each other, for example, when fuel moves through a pipe, hose, valve, or fine filter. The rate at which the static charge dissipates is proportional to the liquid's ability to conduct electricity (*electrical conductivity*). Pure hydrocarbons are essentially nonconductors. While jet fuel is composed of hydrocarbons, it is a slightly better conductor because it contains trace amounts of ionizable<sup>6</sup> compounds, e.g., water, phenols, and naphthenic acids.

- 4 National Fire Protection Association and the Department of Transportation regulations include definitions of *flammable* and *combustible*, based on the flash point of the material.
- 5 Handbook of Aviation Fuel Properties, Coordinating Research Council.

# Aviation Turbine Fuel Performance

Conductivity of fuels is usually expressed in *conductivity units* (CU); 1 CU = 1 pico Siemens/ meter (1 pS/m) =  $1 \times 10^{-12}$  ohm<sup>-1</sup> meter<sup>-1</sup>. Kerosines may have conductivity ranging from less than 1 CU to perhaps 20 CU. For comparison, deionized water has a conductivity of about 10 million CU.

Filtering or rapidly pumping a liquid that is a relatively poor electrical conductor, like jet fuel, can result in a static charge being created much faster than it dissipates. When the accumulated charge exceeds the ionization potential of the air above the liquid, it can discharge from the liquid surface as a spark. The energy of the spark can initiate an explosion if the liquid is flammable and the composition of vapor and air in the vicinity is in the flammable range.

To prevent explosions triggered by a static discharge, well designed fuel handling systems use bonding and grounding (or *earthing*), pumping rate limits, and time for charge dissipation (*relaxation time*), before the fuel is exposed to air.<sup>7</sup> Military jet fuels and international Jet A-1 require the use of an additive to increase the electrical conductivity of the fuel. Conductivity improving additives are also called *anti-static* additives or *static dissipator* additives. Use of the additive reduces the hazard of charge accumulation for handling situations that are less than optimum. The additive does not prevent charge generation, rather it increases the rate of charge dissipation by increasing fuel conductivity.

#### **Emissions**

Aircraft engine emissions have not received as much attention in recent years as emissions from other energy sources. This is because aviation only contributes a small proportion of emissions compared to ground vehicles and stationary sources.<sup>8</sup>

There are two main sources of aircraft emissions, the jet engines and the auxiliary power unit (APU). Most jet fuel is burned in flight so most of the emissions occur at altitude, not at ground level. There is uncertainty about the effects of emissions at altitude, although this is an area of active research.<sup>9,10</sup>

When hydrocarbons are completely combusted, the products are carbon dioxide and water. However when jet fuel is burned, other emissions including sulfur oxides, nitrogen oxides, unburned hydrocarbons, and particulates (soot) are formed. This is due to both trace amounts of sulfur and nitrogen in the fuel and also engine design and operating conditions.

<sup>7</sup> See ASTM D 4865, Standard Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems, for more information.

<sup>8</sup> Aviation and the Environment, GAO-03-252, United States General Accounting Office.

<sup>9</sup> Atmospheric Effects of Aviation, National Academy Press, 1999.

<sup>10</sup> For Greener Skies: Reducing Environmental Impacts of Aviation, National Academy Press, 2002.

The International Civil Aviation Organisation (ICAO) has established limits for emissions of nitrogen oxides, carbon monoxide, unburned hydrocarbons, and smoke from commercial jet engines. These limits were established for a defined landing and take-off cycle (LTO) to limit emissions near ground level, but they also indirectly limit emissions at altitude.

Carbon dioxide is a greenhouse gas and is implicated in climate change. Aviation contributes a relatively small proportion of anthropogenic carbon dioxide. In 1992, aviation emissions were about 2% of the total and projections to 2050 have aviation contributing about 3% of the total. 11 Carbon dioxide emissions are directly related to the amount of fuel consumed and can be reduced by increasing efficiency of the engines and airframe.

**Water vapor** is the other major product of combustion. Emissions at ground level are not an issue, but water vapor emissions at cruise altitude can lead to formation of contrails and aviation-induced cirrus clouds<sup>12</sup>. The effect of these contrails and clouds is uncertain, but they are thought to contribute to climate change. This is another area of ongoing research.

**Sulfur oxides** are the result of combustion of sulfur containing compounds in the fuel, and thus are proportional to fuel sulfur content. SOx emissions are thought to contribute to aerosols and particulate formation<sup>13</sup>, although more research is needed to definitively answer this question.

Over the past decade there has been a worldwide trend to lower sulfur content in motor gasoline and diesel fuel with some countries requiring near-zero sulfur today or in the near future. These limits have been mandated by government regulations driven by the need to reduce harmful emissions. A similar reduction has not occurred for jet fuel; the specifications continue to allow a maximum of 3000 ppm sulfur although the worldwide average sulfur content in jet fuel appears to be between 500 and 1000 ppm.

There has been discussion within the aviation industry over the past few years about taking proactive steps to reduce the maximum sulfur content in the fuel specifications, but no changes have been made to date. Reducing sulfur content significantly could lead to changes in other fuel properties, which would have to be considered before introducing the change. The trend of sulfur content in jet fuel will be monitored over the next few years to provide guidance for change.

<sup>11</sup> Aviation and the Global Atmosphere, Intergovernmental Panel on Climate Change, Cambridge University Press, 1999.

<sup>12</sup> Aircraft Contrails Factsheet, United States Environmental Protection Agency, EPA430-F-00-005, September 2000.

<sup>13</sup> Influence of Fuel Sulfur on the Composition of Aircraft Exhaust Plumes, U. Schumann et. al., Journal of Geophysical Research, Vol. 107 No. D15, 2002.

**Nitrogen oxides** are mainly formed from oxidation of atmospheric nitrogen at the very high temperatures found in the combustor (*see Chapter 6*). Any fuel bound nitrogen<sup>14</sup> will also result in NOx formation. Nitrogen in the fuel is neither controlled or typically measured, but can range from near zero to perhaps 20 ppm.

Since NOx formation is controlled by the maximum local temperature reached in the combustor, it is determined primarily by engine design and operating conditions. Current engine design trends are intended to ensure more complete combustion more rapidly resulting in more uniform combustion temperatures and thus lowering NOx emissions.

NOx emission factors for modern commercial engines are about 4g NOx per kg fuel at idle<sup>15</sup>. A fuel with 20 ppm bound nitrogen will contribute 66 mg NO2 per kg fuel, about 1.5% of the total. As NOx emissions are higher at take off, climb, and cruise conditions, the fuel bound nitrogen contributes an even smaller percentage at these operating conditions.

NOx emissions are a concern because they contribute to the formation of ozone near ground level.

**Particulates** and unburned hydrocarbons are the result of incomplete combustion, as discussed on page 4. If present in high enough concentration, these particulates will be visible as smoke or soot coming out of the engine. Modern jet engine combustors are designed to significantly reduce visible smoke and thus emit fewer particulates than older engines.

Fuel properties have been found to have some effect on emissions <sup>16</sup>. Correlations to particulate emissions have been found among various fuel properties such as hydrogen content, hydrogen/ carbon ratio, smoke point, aromatics, and naphthalenes. However, the findings have not been consistent from one experiment to another. Overall, engine design and operating conditions play a greater role in particulate emissions than fuel properties.

Particulates at ground level can contribute to haze and smog formation and can be harmful if inhaled. The effect of particulates at cruise altitude is uncertain and is an area of ongoing research.

<sup>14</sup> Fuel bound nitrogen refers to molecules that contain nitrogen bound to other atoms, as opposed to atmospheric nitrogen dissolved in the fuel.

<sup>15</sup> ICAO Engine Emissions Databank.

<sup>16</sup> Particulate Matter Emitted from Aircraft Engines, L.G. Blevins, AIAA 2003-2764.

# 3 • Aviation Turbine Fuel Specifications and Test Methods

## **Specifications**

Product specifications are a mechanism by which producers and users of a product identify and control the properties necessary for satisfactory and reliable performance.

#### Civilian Jet Fuel

Two organizations have taken the lead role in setting and maintaining specifications for civilian aviation turbine fuel (*jet fuel*): the American Society for Testing and Materials (ASTM) and the United Kingdom Ministry of Defence (MOD). The specifications issued by these two organizations are very similar but not identical. Many other countries issue their own national specifications for jet fuel; these are very nearly or completely identical to either the ASTM or MOD specifications. In the Commonwealth of Independent States (CIS) and parts of Eastern Europe, jet fuel is covered by GOST specifications. The major jet fuel specifications are listed below.

American Society For Testing and Materials ASTM is made up of many committees. Subcommittee J of Committee D-2, Petroleum Products and Lubricants, is responsible for aviation fuel specifications. ASTM is a consensus standards organization. This ensures that the viewpoints of the large number of groups that are affected by and/or interested in the specifications are considered. These groups include:

- · Individual refiners.
- · Petroleum refining organizations.
- Petroleum marketing organizations.
- · Additive and equipment suppliers.
- · Aircraft and airframe manufacturers.
- · Aircraft engine manufacturers.
- Governmental regulatory agencies, like the Federal Aviation Administration (FAA).
- Special-interest groups and consultants.

Committee D-2 can also turn to the Coordinating Research Council (CRC) if it needs technical data to help establish a specification or develop a test method.

**ASTM D 1655** The *Standard Specification for Aviation Turbine Fuels* includes specifications for two kerosine-type jet fuels: Jet A and Jet A-1. Jet A is used for almost all commercial aviation flights within, or originating from the United States.

**UK MOD** Within the UK there is a joint civil and military jet fuel specification; UK's Civil Aviation Authority has agreed to delegate technical authority for the civil specification to the Ministry of Defence (MOD). The Technical Authority for Defence Standard 91-91 (and MOD's other aviation fuel specifications) lies with the Defence Fuels Group (DFG). QinetiQ are contracted to DFG to provide the technical and administrative support. Specification changes are made through consultation with the Aviation Fuels Committee (AFC) which meets once per year, usually in April. The AFC is supported by a small group of advisors representing fuel producers, users, OEMs and regulatory bodies. Proposed technical changes to specifications are debated by this group before those with merit are forwarded for full discussion by AFC. Defence Standard 91-91 is usually revised over an approximately three year period though import or urgent changes can be made by issuing amendments.

Defence Standard 91-91 The United Kingdom Ministry of Defence maintains this specification (formerly titled DERD 2494) for Jet A-1, which is used for most civil aviation fuels outside the United States and the CIS. There are minor differences between the DEF STAN 91-91 Jet A-1 and ASTM D 1655 Jet A-1 specifications.

**GOST 10227** This Russian specification covers the light kerosine-type fuel, TS-1, used in the CIS and parts of Eastern Europe, along with T-1, T-2, and RT grades of fuel.

Joint Checklist A group of oil companies, called the Joint Inspection Group (JIG), that operate aviation fuel systems internationally have combined the most restrictive requirements from ASTM D 1655 and DEF STAN 91-91 into a single document: *Aviation Fuel Quality Requirements for Jointly Operated Systems*. This publication is sometimes referred to as the *Joint Checklist*. Many refineries manufacture jet fuel to the Joint Checklist so that it can be used to meet either specification for Jet A-1.

**International Air Transport Association** IATA publishes a document entitled *Guidance Material for Aviation Turbine Fuels Specifications*. The guidance material contains specifications for four aviation turbine fuels: three kerosine-type fuels (Jet A, Jet A-1, and TS-1) and one wide-cut fuel (Jet B). Jet A meets the ASTM requirements, Jet A-1 meets the Joint Checklist requirements, TS-1 meets the Russian GOST requirements, and Jet B meets the Canadian CGSB requirements.

The IATA Aviation Fuels Working Group (AFWG) sponsors an International Specification Liason Group. This group meets regularly to exchange information about changes made to various jet fuel specifications.

**ASTM D 6615** This specification covers wide-cut jet fuel (Jet B). Jet B was previously part of D1655, but was moved to a separate specification in 2001. The Canadian General Standards Board specification CGSB-3.22 also covers a wide-cut Jet B. There are small differences between these Jet B specifications.

#### **Synthetic Fuels**

Jet fuel specifications have been developed based on experience with petroleum derived fuel and thus contain implicit assumptions about fuel properties and behavior. Fuel derived from a different source would have to be examined to see if these assumptions are still valid.

A synthetic fuel produced by the Fischer-Tropsch process is approved for use as a blend component with conventional jet in both ASTM D1655 and DEF STAN 91-91. This material was approved after a thorough review process. The approval is specific to a product produced at a particular location. In anticipation of new plants producing synthetic fuels, the industry is developing a generic approval process based on understanding gained in the initial approval.

# Military Jet Fuel

The governments of many countries maintain separate specifications for jet fuel for military use. The reasons for separate specifications include the operational and logistical differences between the military and civilian systems and the additional demands high-performance jet fighter engines place on the fuel. U.S. military jet fuels are listed in Figure 3.1.

Figure 3.1
U.S. Military Jet Fuels

Fuel	Year Introduced	Туре	RVP, psi	Freeze Point °C max	Flash Point °C min	Comments
JP-1	1944	kerosine	- ''	-60	43	obsolete
JP-2	1945	wide-cut	≦ 2	-60		obsolete
JP-3	1947	wide-cut	5 – 7	-60		obsolete
JP-4	1951	wide-cut	2 – 3	<b>-72</b>		U.S. Air Force fuel
JP-5	1952	kerosine		-46	60	U.S. Navy fuel
JP-6	1956	kerosine		-54		XB-70 program, obsolete
JPTS	1956	kerosine		-53	43	Higher thermal stability
JP-7	1960	kerosine		-43	60	Lower volatility, higher thermal stability
JP-8	1979	kerosine		-47	38	U.S. Air Force fuel
JP8+100	1998	kerosine		-47	38	U.S. Air Force fuel containing an additive that provides improved thermal stability

JP stands for Jet Propulsion.

There are currently two fuels in widespread use by the U.S. military: JP-5 by the Navy, and JP-8 by the Air Force. Both are kerosine-type fuels. The major difference between them is the flash point temperature, although there are also minor differences in other fuel properties. The minimum flash point temperature for JP-8 is 38°C, and for JP-5 is 60°C. The higher flash point for JP-5 affords an additional degree of safety in handling fuel on aircraft carriers.

Figure 3.2 lists U.S. military, NATO and joint service designation for Western military jet fuels. The major difference between military fuels and commercial fuels is in the use of additives (*see page 29*). Otherwise, JP-8 and Jet A-1 are very similar fuels.

Figure 3.2
U.S. Military, NATO and Joint Service Designation of Western Military Jet Fuels

U.S. Military Designation	NATO Code	Joint Service Designation
JP-8	F-34	AVTUR/FSII
JP-8 without FSII	F-35	AVTUR
JP-4	F-40	AVTAG/FSII
JP-5	F-44	AVTCAT/FSII

**Detailed Requirements** Figure 3.3 summarizes some of the requirements of D 1655 and DEF STAN 91-91. Both specifications include many footnotes to the requirements listed in Figure 3.3 and also address other fuel issues. Readers in need of details should refer directly to the current version of the specification of interest. Also, readers should remember that a product specification is a living document that undergoes periodic updates. ASTM standards include a suffix indicating the year of last revision, e.g., D 1655-04 was last revised in the year 2004. Figure 3.3 accurately reflects the specifications as of this writing, but it will become out-of-date in time.

The properties controlled by the specification are not all independent of one another. For example, as total aromatics content increases, density, final boiling point temperature, and freezing point increase, and smoke point decreases.

Figure 3.3 compares several of the specification properties of the major civilian jet fuels.

Figure 3.3
Selected Specification Properties of Jet Fuels

Fuel	Jet A	Jet A-1	TS-1	Jet B
Specification	ASTM D 1655	DEF STAN 91-91	GOST 10227	CGSB-3.22
Acidity, mg KOH/g	0.10	0.015	0.7 (mg KOH/100ml)	0.10
Aromatics, % vol, max	25	25.0	22 (% mass)	25.0
Sulfur, mass%	0.30	0.30	0.25	0.40
Sulfur, mercaptan, mass%	0.003	0.003	0.005	0.003
Distillation, °C:				
Initial boiling point	_	Report	150	Report
10% recovered, max	205	205	165	Report
50% recovered, max	Report	Report	195	min 125; max 190
90% recovered, max	Report	Report	230	Report
End point	300	300	250	270
Vapor pressure, kPa, max	_	_	_	21
Flash point, °C, min	38	38	28	
Density, 15°C, kg/m³	775-840	775-840	min 774@20°C	750–801
Freezing Point, °C, max	-40	-47.0	-50 (Chilling point)	<u>–51</u>
Viscosity, -20°C, mm²/sec, max	8	8.0	8.0 @ -40°C	
Net Heat of combustion, MJ/kg, min	42.8	42.8	42.9	42.8
Smoke point, mm, min	18	19.0	25	20
Naphthalenes, vol%, max	3.0	3.00	_	3.0
Copper corrosion, 2 hr @ 100°C, max rating	g No. 1	No. 1	Pass (3 hr @ 100°C)	No. 1
Thermal stability				
Filter pressure drop, mm Hg, max	25	25	_	25
Visual tube rating, max	<3	<3	_	<3
Static test 4 hr @ 150°C, mg/100 ml, m	ax —	_	18	_
Existent gum, mg/100 ml, max	7	7	5	_

#### **Civil Aviation Authorities**

Engines and airframes are certified for airworthiness by a national civil aviation authority. In Europe, this authority is the European Aviation Safety Agency (EASA). In the United States, this authority lies with the Federal Aviation Administration (FAA). Federal Aviation Regulations (FAR) issued by the FAA include the procedures to be followed for airworthiness certification. Testing is carried out by the equipment manufacturers and witnessed by the FAA. When testing is successfully completed, a *type certificate* (TC) is issued for the engine/airframe combination. This certificate includes, among other things, the specification for the fuel(s) approved for use in that aircraft.

Any change to a certificated engine or airframe requires FAA approval. After demonstration of airworthiness, the FAA will issue a *supplemental type certificate* (STC) covering a specific modification.

Many countries have bilateral agreements that recognize each other's certifications.

#### **Test Methods**

Figure 3.4 lists the test methods specified for each property. In all, D 1655 references more than 30 other ASTM test methods and DEF STAN 91-91 references a similar number of IP test methods. These methods are the only ones acceptable for determining compliance with the specification requirements. Their existence allows everyone testing the product to get the same answers, within the defined precision of the methods. Specification bodies will not adopt a new requirement for a product until a standard test method has been developed to measure it.

Many of the test methods were developed in the 1920s, 1930s and 1940s. To ensure they remain up-to-date in light of new technological developments, ASTM and IP review each method at least every five years, at which time it is either reapproved, revised, or canceled. The year of last review is added to the test method number as a hyphenated suffix. For example, D 86-04, *Standard Test Method for Distillation of Petroleum Products*, was originally published as a tentative method in 1921, and was last reviewed in 2004.

New methods based on new technology are being developed continually. At ASTM or IP, the development process starts with a technical review of the proposed method. Next, an interlaboratory test protocol (*round robin*) is conducted, in which a common set of samples is independently tested by a group of laboratories. The results are compiled and statistically analyzed. If the agreement among laboratories is acceptable, a precision statement is developed, giving the maximum difference to be expected between back-to-back tests in one laboratory (*repeatability*) and also the maximum difference between results obtained by different laboratories on the same sample (*reproducibility*). Finally, a report is written, documenting the work for future reference.

Other national and international standards organizations also sanction methods. In many cases, their methods are very similar to or identical to ASTM's and yield the same value for the property. Some of the GOST test methods are significantly different from ASTM methods, so values for these properties may not be directly comparable.

Figure 3.4
Test Methods Used for Jet Fuel Specification Testing

Many of the test methods described below have both ASTM and IP designations. In some cases the methods are equivalent, and either method can be used for specification compliance testing; however, this is not true in all cases. Refer to the appropriate specification for information about which test methods are required. Many of these ASTM and IP test methods have ISO equivalents.

Property	Standard Test Method	Description
Distillation	ASTM D 86 / IP 123 – Distillation of Petroleum Products	A 100 mL sample is placed in a round-bottom flask and heated at a rate specified for a sample with its vapor pressure characteristics. Vapor temperatures are recorded when the first drop of condensate is collected ( <i>initial boiling point</i> ) and at recovered volumes of 5 mL, 10 mL, 15 mL, 20 mL, and every subsequent 10-mL interval to 80 mL, 85 mL, 90 mL, 95 mL, and at the end of the test ( <i>end point</i> ). The amount of sample remaining in the flask at the end of the test and the amount lost during the test – both in percent by volume – are, respectively, recorded and calculated.
	ASTM D 2887 / IP 406 – Boiling Range Distribution of Petroleum Fractions by Gas Chromatography	A small portion of sample is injected onto a non-polar GC column, which separates compounds by boiling point. The elution time is converted to a boiling point by analyzing a mixture of n-paraffins of known boiling points under identical conditions.
Thermal Stability	ASTM D 3241 / IP 323 – Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)	Fuel is pumped over a heated aluminum alloy tube at a constant flow rate for 2.5 hours. After contacting the tube, the fuel is filtered to collect any solid decomposition products. The pressure drop across the filter is monitored during the test. At the end of the test, the tube is removed and visually examined for any stain or discoloration, which is rated by comparing it to a standard color scale. This visual tube rating and the pressure drop across the filter at the end of the test are reported as the test result.
Density	ASTM D 1298 / IP 160 – Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method	Fuel is transferred to a cylindrical container and a hydrometer is carefully lowered into the cylinder and allowed to settle. After the temperature of the sample has equilibrated, the value on the hydrometer scale positioned at the surface of the sample and the sample temperature are recorded. The hydrometer value is converted to density at 15.6°C or API gravity at 60°F using standard tables.
	ASTM D 4052 / IP 365 – Density and Relative Density of Liquids by Digital Density Meter	A small volume of a sample is introduced into an oscillating tube held at constant temperature. The change in oscillation frequency caused by the change in the mass of the tube is related to the density of the sample.

Property	Standard Test Method	Description
Viscosity	ASTM D 445 / IP 71 – Kinematic Viscosity of Transparent and Opaque Liquids	A sample is placed in a calibrated glass viscometer and held at a closely controlled temperature. The time required for a specific volume of the sample to flow through the capillary under gravity is measured. This time is proportional to the kinematic viscosity of the sample.
Vapor Pressure	ASTM D 323 / IP 69 – Vapor Pressure of Petroleum Products (Reid Method) Referee Method	A special cylinder with separate vapor and liquid chambers that can be joined together is used. The liquid chamber is filled with chilled sample and then immediately connected to the vapor chamber, which has been heated to 37.8°C (100°F). The assembled apparatus is immersed in a bath held at 37.8°C (100°F) until a constant pressure is observed. This pressure includes a contribution from air and water dissolved in the fuel.
	ASTM D 5191 – Vapor Pressure of Petroleum Products (Mini Method)	A chilled sample is introduced into an evacuated, thermostatically controlled chamber. The chamber and sample are heated to 37.8°C (100°F) and the resulting rise in pressure is measured. The sample size and chamber volume are chosen to duplicate the conditions of the Reid Method.
Flash Point	ASTM D 56 – Flash Point by Tag Closed Tester	A sample is placed in a lidded cup and heated at a slow, constant rate. At regular intervals, the lid is opened and an ignition source is directed into the cup. The lowest temperature at which the ignition source causes the vapor above the sample to ignite is the flash point.
	ASTM D 3828 / IP 303 – Flash Point by Small Scale Closed Tester	A sample is placed into a lidded cup and the cup is heated to a fixed temperature. After a specified time, the cup is opened, a test flame is applied, and an observation is made whether or not a flash occurs. The test is repeated with a fresh sample at other fixed temperatures until the flash point is established with the required precision [not greater than 0.5°C (1°F)].
Net Heat of Combustion	ASTM D 3338 – Estimation of Net Heat of Combustion of Aviation Fuels	The net heat of combustion of a sample is estimated from its API gravity, aromatics content, and distillation profile. The estimate relies on a correlation developed for a wide range of fuels.
	ASTM D 4529 / IP 381 – Estimation of Net Heat of Combustion of Aviation Fuels	The net heat of combustion of a sample is estimated from its aniline point, density, and sulfur content. The estimate relies on a correlation developed for a wide range of fuels.

Property	Standard Test Method	Description
Net Heat of Combustion (continued)	ASTM D 4809 – Heat of Combustion of Liquid Hydrocarbon Fuels by BombCalorimeter Referee Method	A weighed sample of fuel is placed in an oxygen bomb calorimeter under specified conditions. The fuel is ignited and the temperature increase of the calorimeter is used to calculate the heat of combustion.
Freezing Point	ASTM D 2386 / IP 16 – Freezing Point of Aviation Fuels Referee Method	A sample is placed in a special jacketed tube fitted with a stirring rod and a thermometer. The tube is placed in a low-temperature bath and stirred as the sample cools. When crystals of hydrocarbon appear, the tube is removed from the cooling bath and allowed to warm up slowly with continuous stirring. The temperature at which the hydrocarbon crystals completely disappear is the freezing point.
	ASTM D 5972 / IP 435 – Freezing Point of Aviation Fuels (Automatic Phase Transition Method)	A small portion of fuel is cooled at a constant rate and monitored optically. When the formation of hydrocarbon crystals is detected by the optical system, the sample is then heated at a constant rate until the crystals redissolve. The temperature of the fuel at this point is the freezing point.
Naphthalenes Content	ASTM D 1840 – Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet Spectrophotometry	A sample is dissolved in isooctane at a known concentration and the absorbance of the solution at 285 nanometers is measured and used to calculate the naphthalenes content.
Luminometer Number	ASTM D 1740 – Luminometer Numbers of Aviation Turbine Fuels	A sample is burned in an ASTM-CRC Luminometer lamp to obtain a curve of flame radiation vs. temperature rise across the burner. The Luminometer number is calculated from the difference in temperature rise between the test fuel and tetralin, divided by the difference in temperature rise between isooctane and tetralin. <i>Note: This method is no longer in the specification but is included here for historical reference.</i>
Sulfur	ASTM D 1266 / IP 107 – Sulfur in Petroleum Products (Lamp Method)	A sample is burned in a glass lamp with a cotton wick to oxidize the sulfur to sulfur dioxide. The combustion gases are bubbled though a solution of hydrogen peroxide to convert the sulfur dioxide to sulfuric acid. The amount of sulfuric acid formed is measured either by barium precipitation or titration.
	ASTM D 1552 – Sulfur in Petroleum Products (High-Temperature Method)	A sample is burned to oxidize the sulfur to sulfur dioxide. The sulfur dioxide is either absorbed by an acidic solution of potassium iodide and starch indicator and back titrated with standard potassium iodate solution, or collected in a cell where its infrared absorbance is measured.  Note: This method is no longer in the specification but is included here for historical reference.

Property	Standard Test Method	Description
Sulfur (continued)	ASTM D 2622 / IP 447 – Sulfur in Petroleum Products by Wavelength- Dispersive X-Ray Spectrometry	A sample is placed in an X-ray beam and the intensity of the sulfur X-ray fluorescence is measured and used to calculate the sulfur content of the sample.
	ASTM D 4294 / IP 336 – Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy	A sample is placed in an X-ray beam and the resultant characteristic X radiation is measured and used to calculate the sulfur content of the sample.
	ASTM D 5453 – Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Ultraviolet Fluorescence	A sample is burned to oxidize the sulfur to sulfur dioxide. The combustion gases are irradiated with ultraviolet light and the fluorescence of the sulfur dioxide is measured.
Mercaptan Sulfur	ASTM D 3227 / IP 342 – Mercaptan Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Method)	A hydrogen sulfide-free sample is dissolved in alcoholic sodium acetate and potentiometrically titrated with standard silver nitrate solution, which precipitates the mercaptan sulfur as silver mercaptide.
Copper Strip Corrosion	ASTM D 130 / IP 154 – Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test	A polished copper strip is immersed in a sample for two hours at 100°C (212°F) and then removed and washed. The condition of the copper surface is qualitatively evaluated by comparing it to standards.
Acidity	ASTM D 3242 / IP 354 – Acidity in Aviation Turbine Fuel	A weighed amount of sample is dissolved in titration solvent and titrated with alcoholic potassium hydroxide to a colorimetric endpoint. The amount of acidity in the fuel is expressed as mg KOH/g.
Existent Gum	ASTM D 381 / IP 131 – Gum Content in Fuels by Jet Evaporation	A measured quantity of fuel is transferred to a weighed beaker, placed in a heated bath, and evaporated under a flow of steam. The resulting residue is weighed and reported as existent gum.
Aromatics Content	ASTM D 1319 / IP 156 – Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption	A small amount of sample is placed at the top of a special glass adsorption column packed with activated silica gel. Prior to this, the top layer of gel has been treated with fluorescent dyes. Isopropyl alcohol is used to transport the sample and the fluorescent dyes down the column. The hydrocarbons separate into bands of aromatics, olefins, and saturates because of their different affinities for the gel. The fluorescent dyes, which also selectively separate, make the boundaries of the aromatic, olefin, and saturate zones visible under ultraviolet light.

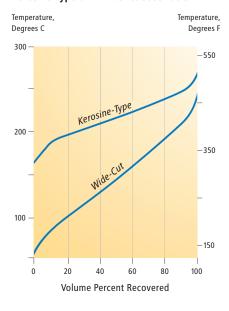
Property	Standard Test Method	Description
Aromatics Content (continued)	ASTM D 6379 / IP 436 – Aromatic Hydrocarbon Types in Aviation Fuels – High Performance Liquid Chromatography with Refractive Index Detection	A small amount of sample is injected onto a polar HPLC column which separates the aromatics from the saturates. A refractive index detector is used to quantitate the aromatics by comparison to a previously prepared calibration curve.
Smoke Point	ASTM D 1322 / IP 57 – Smoke Point of Kerosine and Aviation Turbine Fuel	The sample is burned in a wick-fed lamp. The smoke point is the maximum height of flame that can be achieved without smoking.
Electrical Conductivity	ASTM D 2624 / IP 274 – Electrical Conductivity of Aviation and Distillate Fuels	A sample is placed in a cell containing two electrodes. A voltage is applied across the electrodes and the resulting current is expressed in terms of the conductivity of the sample.
Water Reaction	ASTM D 1094 / IP 289 – Water Reaction of Aviation Fuels	A sample is shaken with an aqueous buffer solution in a clean glass cylinder at ambient temperature and then allowed to stand to let the mixture separate into hydrocarbon and aqueous phases. After five minutes of standing, the change in volume of the aqueous layer is measured. The appearance of the hydrocarbon/aqueous interface also is examined for the presence of bubbles or film. Note: This method is in the process of being removed from both the DEF STAN and ASTM specifications because it has been found ineffective in detecting surfactants that may disarm coalescers (see page 81). It is being replaced by D3948.
Water Separability	ASTM D 3948 – Determining Water Separation Characteristics of Aviation Turbine Fuels by Portable Separometer	Using a semiautomatic Micro-Separometer instrument, a fuel sample is mixed with water, forced through a fiberglass coalescing medium, and rated. The MSEP rating indicates the relative ease of coalescing water from the sample. The instrument is calibrated with a water-free fuel sample.
Lubricity	ASTM D 5001 – Measurement of Lubricity of Aviation Turbine Fuels by the Ball-on-Cylinder Lubricity Evaluator (BOCLE)	A non-rotating steel ball is held against a cylindrical ring. The cylindrical ring is rotated at a fixed speed while partially immersed in the fuel. At the end of the test, the ball is removed and examined for wear. The size of the wear scar is related to the lubricity of the fuel (a large wear scar means poor lubricity).
Particulate Matter	ASTM D 2276 / IP 423 – Particulate Contaminant in Aviation Fuel by Line Sampling	Fuel from a field sampler is fed through a membrane with a pore size of 0.8 micrometers. The membrane is compared to examples in a rating booklet to rate its color and color intensity.
	ASTM D 5452 – Particulate Contamination in Aviation Fuels by Laboratory Filtration	Fuel from a field sampler is fed through a pair of matched-weight membranes with a pore size of 0.8 micrometers. The membranes are dried under standard conditions and weighed. The weight difference between the two membranes is a measure of the particulate content of the sample.

# 4 · Aviation Turbine Fuel Composition

Figure 4.1

Typical D86 Distillation Curves –

Kerosine-Type and Wide-Cut Jet Fuels



#### **Base Fuel**

Aviation turbine fuel is a mixture of many different hydrocarbons. Modern analytical techniques are not powerful enough to separate all the individual molecular species present in jet fuel, so we don't know how many there are, but a good guess is a thousand or more. The range of their sizes (molecular weights or carbon numbers) is restricted by the distillation, freezing point, and sometimes naphthalenes and smoke point requirements for the product. Kerosine-type jet fuel has a carbon number distribution between about 8 and 16 carbon numbers; wide-cut jet fuel, between about 5 and 15 carbon numbers. Typical boiling curves of kerosine-type and wide-cut jet fuel are shown in Figure 4.1.

Most of the hydrocarbons in jet fuel are members of the paraffin, naphthene, or aromatic classes (*see Appendix B*). When jet fuels of the same type differ in bulk properties, it is because they contain different proportions of compounds from these three classes. This section discusses how class properties influence the properties of the whole fuel and affect its performance in a turbine engine.

## **Class Properties**

Figure 4.2 lists the boiling point and freezing point of representative jet fuel hydrocarbons. Boiling point increases with carbon number for compounds in the same class. For compounds of the same carbon number, the order of increasing boiling point by class is isoparaffin, n-paraffin, naphthene, and aromatic. The boiling point difference between isoparaffin and aromatic hydrocarbons of the same carbon number [40–50°C (72–90°F)] is larger than the boiling point difference

Figure 4.2
Boiling Point and Freezing Point of Representative Jet Fuel Hydrocarbons

Compound Name	Formula	Hydrocarbon Class	Boilin °C	g Point, (°F)	Freez °C	ing Point, (°F)
n-Octane	C <sub>8</sub> H <sub>18</sub>	n-Paraffin	125.7	(258.2)	-56.8	(-70.2)
2-Methylheptane	C <sub>2</sub> H <sub>18</sub>	Isoparaffin	117.6	(243.8)	-109.0	(-164.3)
1-Methyl-1- ethylcyclopentane	C <sub>8</sub> H <sub>16</sub>	Naphthene	121.5	(250.7)	-143.8	(-226.8)
Ethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	Naphthene	131.8	(269.2)	-111.3	(-168.4)
o-Xylene	C <sub>8</sub> H <sub>10</sub>	Aromatic	144.4	(292.0)	-25.2	(-13.3)
p-Xylene	C <sub>8</sub> H <sub>10</sub>	Aromatic	138.4	(281.0)	+13.3	(+55.9)
Cis-Decalin	C <sub>10</sub> H <sub>18</sub>	Naphthene	195.8	(384.5)	-43.0	(-45.4)
Tetralin	C <sub>10</sub> H <sub>12</sub>	Aromatic	207.6	(405.8)	-35.8	(-32.4)
Naphthalene	C <sub>10</sub> H <sub>8</sub>	Aromatic	217.9	(424.3)	+80.3	(+176.5)
n-Dodecane	$C_{12}H_{26}$	n-Paraffin	216.3	(421.4)	-9.6	(+14.8)
2-Methylundecane	$C_{12}H_{26}$	Isoparaffin	210.0	(410.0)	-46.8	(-52.3)
1-Ethylnaphthalene	$C_{12}H_{12}$	Aromatic	258.3	(497.0)	-13.8	(+7.1)
n-Hexylbenzene	C <sub>12</sub> H <sub>18</sub>	Aromatic	226.1	(439.0)	-61.0	(-77.8)
n-Hexadecane	$C_{16}H_{34}$	n-Paraffin	286.9	(548.4)	+18.2	(+64.7)
2-Methylpentadecane	C <sub>16</sub> H <sub>34</sub>	Isoparaffin	281.6	(538.9)	-7.0	(+19.4)
n-Decylbenzene	C <sub>16</sub> H <sub>26</sub>	Aromatic	297.9	(568.2)	-14.4	(+6.1)

Source: ASTM DS 4B Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds.

between compounds of the same class that differ by one carbon number [about 20°C (35°F)]. Thus, the compounds that boil near 225°C (430°F), the middle of the kerosine-type jet fuel boiling range, may be  $C_{10}$  aromatics,  $C_{11}$  naphthenes, and  $C_{12}$  paraffins.

Freezing point also increases with carbon number within each class but is strongly influenced by molecular shape. Compounds such as normal paraffins and unsubstituted aromatics freeze (crystallize) at much higher temperatures than other compounds with the same carbon number because they have a geometry that allows them to pack together easily into a crystalline structure.

Figure 4.3 lists the density and heat of combustion of representative jet fuel hydrocarbons. Density increases with carbon number for compounds in the same class. For compounds with the same carbon number, the order of increasing density by class is paraffin, naphthene, and aromatic.

Figure 4.3

Density and Heat of Combustion of Representative Jet Fuel Hydrocarbons

		Density	Net Energy Content at 25°C			
Hydrocarbon	Carbon	at 20°C,	Gravi		Volu	ımetric
Class	Number	g/cm³	MJ/kg	(Btu/lb)	MJ/L	(Btu/gal)
n-Paraffin	8	0.7027	44.42	(19,090)	31.21	(112,000)
Isoparaffin	8	0.6979	44.38	(19,080)	30.97	(111,100)
Naphthene	8	0.7809	43.57	(18,730)	34.02	(122,100)
Naphthene	8	0.7879	43.40	(18,660)	34.20	(122,700)
Aromatic	8	0.8801	40.81	(17,550)	35.92	(128,900)
Aromatic	8	0.8610	40.81	(17,550)	35.14	(126,100)
Naphthene	10	0.8967	42.62	(18,320)	38.22	(137,100)
Aromatic	10	0.9695	40.52	(17,420)	39.06	(140,200)
Aromatic	10	1.1750	40.12	(17,250)	47 .14	(169,100)
n-Paraffin	12	0.7488	44.11	(18,960)	33.03	(118,500)
Isoparaffin	12	0.7458	44.08	(18,950)	32.87	(117,900)
Aromatic	12	0.8602	41.80	(17,970)	35.96	(129,000)
n-Paraffin	16	0.7735	43.95	(18,890)	33.99	(122,000)
Aromatic	16	0.8554	42.23	(18,160)	36.12	(129,600)
	n-Paraffin Isoparaffin Naphthene Naphthene Aromatic Aromatic Naphthene Aromatic Naphthene Aromatic n-Paraffin Isoparaffin Aromatic n-Paraffin	n-Paraffin 8 Isoparaffin 8 Naphthene 8 Naphthene 8 Aromatic 8 Aromatic 8 Naphthene 10 Aromatic 10 Aromatic 10 n-Paraffin 12 Isoparaffin 12 Aromatic 12 n-Paraffin 16	Hydrocarbon Class         Carbon Number         at 20°C, g/cm³           n-Paraffin         8         0.7027           Isoparaffin         8         0.6979           Naphthene         8         0.7809           Naphthene         8         0.7879           Aromatic         8         0.8610           Naphthene         10         0.8967           Aromatic         10         0.9695           Aromatic         10         1.1750           n-Paraffin         12         0.7488           Isoparaffin         12         0.7458           Aromatic         12         0.8602           n-Paraffin         16         0.7735	Hydrocarbon Class         Carbon Number         at 20°C, g/cm³         Gravi MJ/kg           n-Paraffin         8         0.7027         44.42           Isoparaffin         8         0.6979         44.38           Naphthene         8         0.7809         43.57           Naphthene         8         0.7879         43.40           Aromatic         8         0.8801         40.81           Aromatic         8         0.8610         40.81           Naphthene         10         0.8967         42.62           Aromatic         10         1.1750         40.12           n-Paraffin         12         0.7488         44.11           Isoparaffin         12         0.7458         44.08           Aromatic         12         0.8602         41.80           n-Paraffin         16         0.7735         43.95	Hydrocarbon Class         Carbon Number         at 20°C, g/cm³         Gravimetric MJ/kg         (Btu/lb)           n-Paraffin         8         0.7027         44.42         (19,090)           Isoparaffin         8         0.6979         44.38         (19,080)           Naphthene         8         0.7809         43.57         (18,730)           Naphthene         8         0.7879         43.40         (18,660)           Aromatic         8         0.8801         40.81         (17,550)           Aromatic         8         0.8610         40.81         (17,550)           Naphthene         10         0.8967         42.62         (18,320)           Aromatic         10         0.9695         40.52         (17,420)           Aromatic         10         1.1750         40.12         (17,250)           n-Paraffin         12         0.7488         44.11         (18,960)           Isoparaffin         12         0.8602         41.80         (17,970)           n-Paraffin         16         0.7735         43.95         (18,890)	Hydrocarbon Class         Carbon Number         at 20°C, g/cm³         Gravimetric MJ/kg         Volumetric MJ/kg           n-Paraffin         8         0.7027         44.42         (19,090)         31.21           Isoparaffin         8         0.6979         44.38         (19,080)         30.97           Naphthene         8         0.7809         43.57         (18,730)         34.02           Naphthene         8         0.7879         43.40         (18,660)         34.20           Aromatic         8         0.8801         40.81         (17,550)         35.92           Aromatic         8         0.8610         40.81         (17,550)         35.14           Naphthene         10         0.8967         42.62         (18,320)         38.22           Aromatic         10         0.9695         40.52         (17,420)         39.06           Aromatic         10         1.1750         40.12         (17,250)         47.14           n-Paraffin         12         0.7488         44.11         (18,960)         33.03           Isoparaffin         12         0.8602         41.80         (17,970)         35.96           n-Paraffin         16         0.7735

Source: TRC Thermodynamic Tables, Thermodynamics Research Center, Texas A&M University.

For compounds of the same carbon number, the order of increasing energy content per unit weight by class is aromatic, naphthene, paraffin. On a volume basis, the order is reversed, with paraffins having the lowest energy content per unit volume and aromatics the highest. This same relationship holds for fuels (*see page 3*). Lighter (less dense) fuels, like gasoline, have higher energy content on a weight basis, whereas heavier (more dense) fuels, like diesel, have higher energy content on a volume basis.

Viscosity is related more to carbon number than to hydrocarbon class. For a given carbon number, naphthenes generally have slightly higher viscosity than paraffins or aromatics.

#### **Hydrocarbon Missile Fuels**

JP-9 and JP-10 are specialty fuels that have been developed for demanding applications, such as aircraft-launched missiles. The required properties are: maximum volumetric energy content, clean burning, and good low-temperature performance. To achieve these properties, the fuels are formulated with high-density naphthenes in nearly pure form. These fuels only are used in limited volumes and in situations where price is a minor consideration.

JP-10 is essentially a single-hydrocarbon exo-tetrahydrodicyclopentadiene. It has a minimum volumetric heat content of 39,434 MJ/m³ (141,500 Btu/gal). For comparison, Jet A or JP-8 has a volumetric energy content of about 35,000 MJ/m³ (125,800 Btu/gal), about 11 percent lower. JP-9 is a blend of three hydrocarbons: methylcyclohexane, perhydronorbornadiene dimer, and exotetrahydrodicyclopentadiene (JP-10). JP-9 has a minimum volumetric heat content of 39,573 MJ/m³ (142,000 Btu/qal).

JP-9 is a mixture of these three compounds:

JP-10 exo-tetrahydrodicyclopentadiene

methylcyclohexane

perhydronorbornadiene dimer

Figure 4.4 summarizes the relationships between hydrocarbon class and jet fuel properties. Normal paraffins have poor volumetric energy contents and very poor low-temperature flow properties. Aromatics have very good volumetric energy contents but poor combustion quality and low-temperature flow properties. Isoparaffins and naphthenes are intermediate, with these properties falling between those of normal paraffins and aromatics.

Figure 4.4

Potential Contribution\* of Each Hydrocarbon Class to Selected Jet Fuel Properties
(For hydrocarbons in the jet fuel carbon number range)

	Hydrocarbon Class			
Jet Fuel Property	n-Paraffin	Isoparaffin	Naphthene	Aromatic
Energy content: Gravimetric	+	+	0	_
Volumetric	-	-	0	+
Combustion quality	+	+	+	_
Low-temperature fluidity		0/+	+	0/-

<sup>\* &</sup>quot;+" indicates a beneficial effect, "0" a neutral or minor effect, and "-" a detrimental effect.

# **Property/Composition Relationships**

For mixtures, the values of some properties are weighted averages of the property's values for all the individual components. Properties that obey this relationship are called bulk properties. Density is a bulk property; to a first approximation, the density of a mixture is the volume average of the densities of all the components.<sup>1</sup>

The values of other properties are determined by individual components present in small, or trace amounts (less than 1000 ppm, and often less than 100 ppm), and are not reflective of the bulk composition of the mixture.

Figure 4.5 shows which of the important jet fuel properties are bulk properties, and which depend on the presence or absence of trace components. The trace components may be present in the hydrocarbon base fuel as manufactured or come from another source, such as additives or contaminants.

Figure 4.5
Relationship of Jet Fuel Properties to Composition

Property	Relation to Composition	Property	Relation to Composition
Energy content	Bulk	Lubricity	Trace
Combustion characteristics	Bulk	Stability	Trace
Distillation range	Bulk	Corrosivity	Trace
Density	Bulk	Cleanliness	Trace
Fluidity	Bulk	Electrical conductivity	Trace

<sup>1</sup> This is a very good approximation when all the components of a mixture are chemically similar, e.g., a mixture of hydrocarbons. It is not as good when some of the components are chemically very different from the rest, e.g., a mixture of alcohols and hydrocarbons.

# **Chemistry of Jet Fuel Instability**

Thermal stability is a very important jet fuel property (*see page 5*). Instability involves the formation of peroxides and hydroperoxides, soluble gums, and, most critically, insoluble material that may either coat surfaces or form particulates.

Our knowledge about the details of the instability reactions is incomplete, although this is an area of ongoing research. They are believed to be multi-step reactions, some of which – perhaps including the initiating ones – are oxidation reactions. The reactants are believed to be certain nitrogen- and/or sulfur-containing compounds, organic acids, and reactive olefins. They are present at concentrations so low – parts per million at most – that identification by current analytical techniques is virtually impossible. Contaminants can also play a role. Oxidation reactions are accelerated by the presence of certain dissolved metals, especially copper, that function as catalysts.

Failure of the thermal stability test (*see page 6*) involves the formation of higher molecular weight compounds with limited fuel solubility. The development of insolubles depends on both trace and bulk fuel properties. The chemistries and molecular weights of the reaction products are determined by the reactants, which are present only in trace amounts. But once the reaction products have formed, it is the solvency of the fuel, which is a function of its bulk composition, that determines whether the products will be soluble or insoluble.

Contrary to intuition, two fuels, that by themselves are stable, can be less stable when combined. Each fuel may contain some, but not all, of the reactants required to form insolubles. Only when the fuels are mixed are all the reactants present, enabling the conversion to proceed. The solvency of the blend may also play a role.

### **Water in Jet Fuel**

Water can occur in three different forms in jet fuel: dissolved in the fuel, as a separate liquid phase (*free water*), and as a fuel-water emulsion. Some amount of dissolved water is present in all fuels. This dissolved water is not a problem; free water or a water emulsion are potentially hazardous and must be avoided.

#### **Dissolved Water**

Water is very slightly soluble in jet fuel, and conversely, jet fuel is very slightly soluble in water. The amount of water that jet fuel can dissolve increases with the aromatics content<sup>2</sup> of the fuel and temperature.

Fuel in contact with free water is saturated with water, i.e., the fuel has dissolved all the water it can hold. A typical water-saturated kerosine-type fuel contains between 40 and 80 ppm dissolved water at 21°C (70°F). If the temperature of the fuel increases, it can dissolve more water. Conversely,

<sup>2</sup> Water is more soluble in benzene than in any other hydrocarbon. Monoaromatics will dissolve five to ten times more water than saturates of the same carbon number.

if the temperature of water-saturated fuel decreases, some of the water dissolved in the fuel will separate as free water.

In the absence of free water, jet fuel can pick up water from the air. The amount depends on the *relative humidity*<sup>3</sup> of the air. Fuel in contact with air with a relative humidity of 50 percent will contain only half as much water as water-saturated fuel at that temperature.

The above statements assume that the fuel is in equilibrium with free water or moist air. Fuel close to a fuel-water or fuel-air interface will reach water equilibrium in a matter of minutes. However, if the volume of fuel is large and the area of the interface is limited – conditions that exist in a large fuel storage tank – some of the fuel will be many feet from the interface. In the absence of mixing, it will take a lot longer for this portion to reach water equilibrium. In fact, fuel in a large tank may never come to complete water equilibrium since ambient temperature and relative humidity are constantly changing.

#### Free Water

In jet fuel, free water exists as a separate liquid phase. Since water is denser than jet fuel, free water, under the influence of gravity, forms a lower layer and the jet fuel an upper layer. If jet fuel and water are mixed, normally they will quickly separate again. The speed of the separation and the sharpness of the fuel-water interface are indications of the fuel's *water separability*.

As mentioned above, when water-saturated jet fuel cools, free water separates out, taking the form of many very small droplets sometimes called *dispersed water*. Even if they are not stabilized by surfactants (*see below*), the droplets coalesce slowly because of their small size. The suspended droplets give the fuel a hazy appearance. The haze will disappear if the fuel is warmed enough to redissolve the water.

#### **Emulsion**

An emulsion is a mixture of two immiscible liquids in which very small droplets of one – less than 100 micrometers in diameter – are dispersed in the continuous phase of the other. An everyday emulsion is mayonnaise, a mixture of egg yolk (droplet) in oil (continuous phase). But here, it is emulsions of water (droplet) in jet fuel (continuous phase) that are of interest.

While immiscible liquids normally separate if they have different densities and/or surface tensions, an emulsion can persist for a long time. The mixture is stabilized by surfactants that congregate at the surface of the droplets, preventing them from coalescing.

Liquids that are immiscible have very different polarities. In the case of water and jet fuel, water is polar<sup>4</sup> and jet fuel is non-polar. Some molecules contain both a polar group (polar head) and a

- 3 Relative humidity is the percentage of water vapor present in air, relative to the maximum amount the air can hold at the same temperature.
- 4 When used to describe molecules, polarity refers to the distribution of electric charge in the molecules. Molecules with an even distribution, such as hydrocarbons, are non-polar. Molecules with a partial separation of charge, with one portion slightly positive and another portion slightly negative, are polar. Polar molecules found in jet fuel typically contain sulfur, nitrogen, or oxygen atoms in addition to carbon and hydrogen.

# Aviation Turbine Fuel Composition

non-polar group within the same molecule. This duality causes the molecule to migrate to the interface between a pair of immiscible liquids, with the polar group interacting with the polar liquid and the non-polar group interacting with the non-polar liquid. These molecules are called surfactants (a contraction of *surface active agents*) because they are active at the surface between the immiscible liquids. And because they work at the interface, not in the bulk liquid, trace amounts can affect the properties of a large volume of liquid.

Some surfactants found in jet fuel occur naturally in crude oil, such as naphthenic acids and phenols. Others may be introduced in the refining process, such as sulfonic acids. Still others may be introduced through contamination in the fuel distribution system. The amount of contamination need not be large because, as noted above, surfactants are effective in trace amounts. Surfactants are commonly removed from jet fuel by passing the fuel through clay (*clay treating*).

Surfactants can cause problems even if they don't lead to the formation of a fuel-water emulsion. They can impair the ability of a filter/separator to remove free water from jet fuel (*see page 81*). In this situation, the surfactants are said to "disarm the coalescer." Since it is imperative that only clean, dry fuel is delivered to aircraft, tests have been developed to detect the presence of surfactants in jet fuel through their ability to stabilize emulsions.

#### **Additives**

Additives are fuel-soluble chemicals added in small amounts to enhance or maintain properties important to fuel performance or fuel handling. Typically, additives are derived from petroleum based raw materials and their function and chemistry are highly specialized. They produce the desired effect in the parts per million (ppm) concentration range. (One ppm is 0.0001 mass percent.)

Additives are used in varying degrees in all petroleum derived fuels, but the situation with aviation fuels is unique in that only those additives specifically approved may be added to jet fuel. All jet fuel specifications list approved additives along with allowed concentrations. Some approved additives are required to be added, some are optional, and others are approved for use only by agreement between buyer and seller. Figure 4.6 lists additives approved for use in some of the major jet fuel specifications.

Before an additive can be approved for use in aviation fuel, it must undergo extensive testing to show both that it is effective and that it does no harm to any other fuel properties. To guard against harmful additive interactions, an additive must be tested at four times its maximum dosage in the presence of other additives before it is approved.

Use of additives is the principal difference between commercial and military jet fuels. U.S. military jet fuels will contain three or more additives. International Jet A-1 contains a static dissipator additive and may also have an antioxidant. Jet A in the United States usually contains no additives at all, or perhaps only an antioxidant.

#### **Surfactants**

$$R - C O - H$$

naphthenic acid

sodium naphthenate

phenol

$$\begin{array}{c} O \\ \parallel \\ S = O \\ \mid \\ OH \end{array}$$

benzene sulfonic acid

$$\begin{array}{c} 0 \\ \parallel \\ S = 0 \\ \downarrow \\ 0 \end{array}$$

sodium benzene sulfonate

R represents a hydrocarbon group that is part of the molecule.

Figure 4.6
Approved Additive Types for Jet Fuels\*

Additive Type	Jet A ASTM D 1655	Jet A-1 DEF STAN 91-91	JP-4 MIL-DTL 5624	JP-5 MIL-DTL 5624	JP-8 MIL-DTL 83133
Antioxidant	Allowed	Required**	Required**	Required**	Required**
Metal deactivator	Allowed	Allowed	Agreement	Agreement	Agreement
Electrical conductivity/ static dissipator	Allowed	Required	Required	Agreement	Required
Corrosion inhibitor/ lubricity improver	Agreement	Allowed	Required	Required	Required
Fuel system icing inhibitor	Agreement	Agreement	Required	Required	Required
Biocide	Agreement	Agreement	Not allowed	Not allowed	Not allowed
Thermal stability	Not allowed	Not allowed	Not allowed	Not allowed	Agreement‡

- \* Consult the appropriate specification for detailed requirements.
- \*\* Required in any fuel, or fuel component, that has been hydroprocessed, otherwise optional.
- ‡ When thermal stability additive is in JP-8, the fuel is called JP-8+100.

#### Fuel System Icing Inhibitor

Ice can form in fuel tanks at the very low temperatures encountered at high altitude. Generally, this ice is formed from water that was dissolved in the fuel when it was loaded onto the aircraft but separated from the fuel as the fuel temperature dropped. Most commercial aircraft have heaters on their main fuel filters to melt any ice that is collected. However, many military aircraft do not have these heaters and are susceptible to reduced fuel flow if ice crystals form.

Fuel system icing inhibitors (FSII, pronounced "fizzy") work by combining with any free water that forms and lowering the freezing point of the mixture so that no ice crystals are formed.

The only FSII currently approved for Jet A, Jet A-1, and U.S. military fuels is di-ethylene glycol monomethylether (di-EGME). A similar compound, ethylene glycol monoethylether, is allowed in Russian TS-1 fuel.

di-EGME is only slightly soluble in fuel but is very soluble in water, which leads to various handling problems. Since the additive is only slightly soluble in fuel, it must be added in small amounts with good mixing to ensure that it is completely dissolved in the fuel, especially when it is added at low ambient temperatures. In practice, the additive must be injected at a controlled rate into a flowing stream of fuel.

If a fuel containing FSII comes into contact with free water, the additive will be extracted out of the fuel and form a viscous phase with the water, an obviously unacceptable situation. To avoid contact with free water, FSII is usually not added to fuel at a refinery but at some point in the fuel distribution system. For the military, it may be added at the airport or on delivery to the aircraft itself. Similarly, when required by small jets, it may be added during delivery to the aircraft. FSII is not used in jet fuel by large commercial carriers.

#### di-EGME

 $CH_{3}-O-CH_{2}-CH_{2}-O-CH_{2}-CH_{2}-OH\\$ 

di-ethylene glycol monomethyl ether (di-EGME)

## Thermal Stability

As mentioned in Chapter 2, jet fuel is used as a heat sink in turbine engines. Engines used in high-performance military aircraft place higher thermal stress on the fuel than engines used in commercial aviation. Engines being designed for future military aircraft will place even greater thermal stress on the fuel.

Recognizing this need, the U.S. Air Force initiated a program in the early 1990s to develop a fuel with improved thermal stability. This program led to the introduction of an additive package that improves the thermal stability of fuel by about 100°F (60°C), from about 325°F to 425°F, as determined in a battery of thermal stability tests. The additive package contains a dispersant that helps to keep potential insolubles in solution, preventing them from forming gums and sediment. The additive is generically known as "+100" (plus one hundred). U.S. Air Force fuel containing the additive is called JP8+100. This additive is not currently approved for use in commercial aircraft.

#### **Antioxidants**

Oxygen in the small amount of air dissolved in the fuel attacks reactive compounds in the fuel. The initial attack sets off a chain of oxidation reactions. Antioxidants work by interrupting this chain of reactions, preventing the formation of peroxides, soluble gums, or insoluble particulates. Peroxides can attack elastomeric fuel system parts, gums can lead to engine deposits, and particulates can plug fuel filters.

It is important to note that while antioxidants are effective at improving storage stability of jet fuel, they are not effective at improving its thermal stability.

Olefins, the most reactive class of hydrocarbons, are the most susceptible to oxidative degradation. However, straight-run fuels contain little, if any, olefins, and hydrotreated fuels contain none. In addition, straight-run fuels often contain natural antioxidants, so these fuels usually have good oxidative stability and thus do not need antioxidants.

However, hydrotreating, even mild hydrotreating to remove mercaptans, can also remove these natural antioxidants, possibly resulting in a less stable fuel. For this reason, antioxidants are sometimes added to hydrotreated fuel. To be most effective, the chemical should be added to the fuel immediately after it has been hydrotreated.

Antioxidants are required in any fuel or fuel-blend component that has been hydrogen treated under the DEF STAN Jet A-1 and U.S. military specifications. Antioxidants are optional in non-hydrogen treated fuel under these specifications and optional for all Jet A fuel.

The approved antioxidants for aviation fuel are hindered phenols. The maximum allowed concentration is 24 mg/L.

2,6-ditertiary butyl-4-methyl phenol

#### **Metal Deactivator**

N,N'-disalicylidene-1,2-propane diamine

#### Metal Deactivator

Metal deactivators are *chelating agents* – chemical compounds that form stable complexes with specific metal ions. More active metals, like copper and zinc, are effective catalysts for oxidation reactions, and degrade fuel thermal stability. These metals are not used in most jet fuel distribution systems or turbine engine fuel systems. However, if fuel becomes contaminated with these metals, metal deactivators inhibit their catalytic activity. The only approved metal deactivator is N,N′-disalicylidene-1,2-propane diamine.

## Corrosion Inhibitors/Lubricity Improvers

The tanks and pipelines of the jet fuel distribution system are constructed primarily of uncoated steel. Corrosion inhibitors prevent free water and oxygen in the jet fuel from rusting or corroding these structures.

Lubricity additives are used to compensate for the poor lubricity of severely hydrotreated jet fuel. They contain a polar group that adheres to metal surfaces, forming a thin surface film of the additive. The film acts as a boundary lubricant when two metal surfaces come in contact (*see page 6*). These compounds are usually carboxylic acids, whose compositions are proprietary.

Both corrosion and lubricity are surface phenomena. Perhaps it is not too surprising that corrosion inhibitors also improve lubricity.

#### **Electrical-Conductivity Additive**

Since the naturally poor electrical conductivity of jet fuel (*see page 10*) presents a potential safety hazard in certain circumstances, additives have been developed that improve the fuel's conductivity. Conductivity additives are often referred to as static *dissipator additives* (SDA). When the additive is used, the conductivity of the fuel must be between 50 and 450 CU at the point of delivery into the aircraft. The only additive currently approved for use in jet fuel is Stadis®450, whose composition is proprietary.

#### Leak Detection

Tracer A® can be used in Jet A and Jet A-1 to assist in detecting leaks in fuel handling systems. The additive is a gas that can be detected at very low concentrations. Tracer A is mixed with fuel as it is pumped through the distribution system. If any fuel leaks from the system, it will evolve the Tracer A® gas. The presence of this gas outside of a fuel system can be used to locate a leak.

#### **Biocides**

Biocides are designed to kill microorganisms, which include bacteria and fungi (yeasts and molds) (*see page 9*). Since biocides are toxic, any water bottoms that contain biocides must be disposed of appropriately. Currently approved biocides are Biobor<sup>TM</sup> and Kathon<sup>TM</sup>.

# 5 · Aviation Turbine Fuel Refining

Almost all jet fuel is made from petroleum. A small percentage is made from oil sands. Shale oil was refined into jet fuel in the 1970s and 1980s, but this is no longer economical. Recently, the Fischer-Tropsch process has been used to manufacture a synthetic jet fuel blend component (*see sidebar*). There is widespread interest in this process, so it may contribute increasing amounts of jet fuel in the future.

Refining is the process of converting crude petroleum, also called *crude oil* or simply *crude*, into high-value products. The most important are transportation fuels – gasoline, jet fuel, and diesel fuel. Other important products include aviation gasoline, liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt.

## **Raw Material**

As it comes out of the ground, crude oil can be as thin and light-colored as apple cider or as thick and black as melted tar. Thin crudes have relatively low densities and thus high API gravities (*see page 34*). Therefore, they are called high-gravity crudes; conversely, thick crudes with relatively high densities are low-gravity crudes. High-gravity crudes contain more of the lighter products and generally have a lower sulfur and nitrogen content, which makes them easier to refine. However, modern refining processes are capable of turning low-gravity crudes into high-value products. Refining low-gravity crudes requires more complex and expensive processing equipment, more processing steps and energy; therefore, it costs more.

All crude oils are composed primarily of hydrocarbons of the paraffin, naphthene, and aromatic classes. Each class contains a very broad range of molecular weights.

# **Refining Processes**

Today's refinery is a complex combination of interdependent processes, the result of a fascinating intertwining of advances in chemistry, engineering, and metallurgy. These processes can be divided into three basic categories:

- **Separation processes** The feed to these processes is separated into two or more components based on some physical property, usually boiling point. These processes do not otherwise change the feedstock. The most common separation process in the refinery is *distillation*.
- **Upgrading processes** These processes improve the quality of a material by using chemical reactions to remove any compounds present in trace amounts that give the material the undesired quality. Otherwise, the bulk properties of the feedstock are not changed. The most commonly used upgrading processes for jet fuel are *sweetening*, *hydrotreating*, and *clay treatment*.
- Conversion processes These processes fundamentally change the molecular structure of the feedstock, usually by "cracking" large molecules into small ones, for example, catalytic cracking and hydrocracking.

#### Gas to Liquids

Scientists long have tried to convert natural gas (methane) into liquid fuels. A conversion scheme was worked out in the 1920s by the German chemists Franz Fischer and Hans Tropsch. The Fischer-Tropsch process reacts methane with oxygen over a catalyst to create synthesis gas, a mixture of carbon monoxide and hydrogen. This gas mixture is then converted to a mixture of liquid hydrocarbons using another catalyst. The Fischer-Tropsch product has essentially no sulfur or aromatics.

The Fischer-Tropsch process has not seen wide commerical use to date. However it is receiving new interest lately because of its potential to bring "remote" natural gas to traditional markets. Researchers claim that recent advances make the process economically competitive, and as a result, several major projects are being planned. If the technology proves successful, it will provide a new source of high-quality kerosine.

#### **Density and Gravity**

Density ( $\rho$ ) is the mass of a unit volume of material at a selected temperature. For example, the density of water is 0.9990 grams per cubic centimeter ( $g/cm^3$ ) at 15.6°C (60°F). Relative density (RD) – also called specific gravity – is the ratio of the density of material at a selected temperature to the density of a reference material at a selected temperature. For the relative density of petroleum crudes and products in the U.S., the reference material is water, and both temperatures are 60°F (15.6°C).

RD (60/ 60°F) = 
$$\frac{\rho \text{ sample (60°F)}}{\rho \text{ water (60°F)}}$$

The U.S. petroleum industry often uses API gravity instead of relative density. The following equation relates API gravity, in degrees API (°API), to relative density.

$$^{\circ}API = \frac{141.5}{RD (60/60^{\circ}F)} - 131.5$$

While relative density measurements may be made on liquids at temperatures other than 15.6°C (60°F), the results are always corrected to 15.6°C (60°F), the standard temperature, when expressed as API gravity.

API gravity is an arbitrary scale developed by the American Petroleum Institute in the early years of the petroleum industry. Density had been used as a primary indicator of quality for liquid products. However, the higher value products have lower densities. The API gravity scale was constructed so that API gravity increases inversely to density, therefore products with higher value have higher API gravities. The numbers are also scaled so that most API gravities are between 10 and about 70, rather than less than one.

**Distillation** Distillation is by far the most important and widely used separation process in a petroleum refinery. In large part, petroleum products are defined by their boiling range, and distillation is the process used to separate a mixture with a wide boiling range into products with narrower boiling ranges. The separation is achieved by heating the liquid to vaporize the lightest components. These vapors flow into an overhead condenser, which cools the vapor back into a liquid, which is then collected.

Crude oil is made up of many thousands of components from light gases<sup>1</sup> that boil below ambient temperature, to very heavy materials that cannot be distilled even at temperatures above 538°C (1000°F).

In crude oil distillation, hot crude is pumped into a distillation column and the lightest hydrocarbons present,<sup>2</sup> usually propane and butane, rise to the top and are removed. Since gasoline is a little heavier, it does not rise quite so high and is drawn off from the side of the column. Kerosine and diesel, the next-heavier products, are drawn off at successively lower points on the column. The products obtained directly from crude oil distillation are called *straight-run* products, e.g., *straight-run jet*. The material that is too heavy to vaporize under atmospheric distillation conditions is removed from the bottom of the column (*atmospheric bottoms*).

The atmospheric bottoms can be fractionated further by a second distillation carried out under reduced pressure. The lower pressure in the distillation column allows some of the heavier components to be vaporized and collected. This process is called *vacuum distillation*, the overhead product is called *vacuum gas oil* (VGO), and the bottoms product is called *vacuum residue* (VR) or *vacuum resid*.

Because of the composition of the typical crude, refining by distillation alone has not been able to meet market demand for light fuel products since the early years of the 20th century. Distillation yields too much heavy product and not enough light product. In addition, the quality of light products produced by distillation alone is often poor. The petroleum refiner uses the upgrading and conversion processes to match the barrel to the market.

<sup>1</sup> In distillation discussions, the terms *light* and *heavy* are used as shorthand for *lower boiling* and *higher boiling*. They do not refer to the density of the materials, although, in general, the lower boiling material also will be less dense than the higher boiling material.

<sup>2</sup> Methane and ethane are often present in crude oil as it comes out of the production well. These lightest compounds are removed before the crude oil is transported by pipeline or tanker.

# **Upgrading Processes**

Sweetening<sup>3</sup> processes remove a particular class of sulfur-containing compounds called *mercaptans* from jet fuel. Mercaptans (*see page 87*) are undesirable because they are corrosive and also because of their offensive odor. Several processes have been developed to remove mercaptans by converting them to disulfides. These disulfides are not corrosive and their odors are not as strong as the mercaptans they replace.

Sodium plumbite and copper chloride have been used as catalysts<sup>4</sup> for this conversion in the past. In recent years, the Merox<sup>®</sup> (*mer*captan *ox*idation) process, which uses a cobalt-based catalyst, has almost completely replaced the older technologies. Most of these chemical sweetening processes do not change the total sulfur content of the fuel; they merely convert sulfur from one chemical form to another. Some versions of the Merox<sup>®</sup> process extract the disulfides that are formed and thus lower the total sulfur content.

*Hydroprocessing* is a generic term for a range of processes that use hydrogen and an appropriate catalyst to remove undesired components from refinery streams. The processes range from mild conditions that remove reactive compounds like olefins and some sulfur and nitrogen compounds, to more severe conditions that saturate aromatic rings and remove almost all sulfur and nitrogen compounds. Hydroprocessing breaks apart molecules containing sulfur and converts the sulfur to hydrogen sulfide, which is subsequently removed from the fuel.

Certain polar compounds can be removed from jet fuel by *clay treating*.<sup>5</sup> In this relatively simple process, the fuel is allowed to pass through a bed of clay. Certain classes of polar compounds, especially those that act as surfactants, adsorb onto the surface of the clay and thus are removed from the fuel. In the Merox<sup>®</sup> process discussed above, surfactants can be formed and it is usually necessary to clay treat the fuel after the Merox<sup>®</sup> process to remove them.

Clay treating may also be used on a smaller scale outside of a refinery, e.g., at a fuel terminal or an airport fuel storage facility, to remove surfactants from fuel. In these situations, the clay is contained in a canister or in a cloth bag. These containers are fitted into a filter vessel and the fuel is then pumped through them. Use of these containers makes it easier to handle the clay.

$$2RSH + \frac{1}{2}O_2 \xrightarrow{catalyst} RSSR + H_2O$$

Merox conversion

RSH 
$$\frac{H_2}{\text{catalyst}}$$
 RH + H<sub>2</sub>S

Hydroprocessing conversion

- 3 Sour, in the petroleum industry vernacular, refers to the smell of hydrogen sulfide (the familiar rotten-egg smell) and light mercaptans. Sweet, as the opposite of sour, implies the absence of this odor and, by extension, the absence of compounds that cause odor.
- 4 A *catalyst* is a material that speeds up or otherwise facilitates a chemical reaction without undergoing a permanent chemical change itself.
- 5 The term *clay filtration* is sometimes used in the industry, although this is a misnomer. Filtration is the removal of particulates from a fluid by physical exclusion or entrapment. It is true that clay treatment involves passing the fuel through a vessel similar to a particulate filter, but the similarity ends there. Clay treatment works by adsorption of polar compounds dissolved in the fuel onto the surface of the clay particles.

#### **Conversion Processes**

Hydrocarbons with higher boiling points (the larger ones left in the distillation bottoms) can be broken apart (*cracked*) into lower boiling hydrocarbons by subjecting them to very high temperatures. In the early days of refining, thermal cracking was a common process, but eventually heat was supplemented by a catalyst, transforming *thermal cracking* into *catalytic cracking*. Catalytic cracking produces higher quality products than thermal cracking. There are many variations on catalytic cracking, but *fluid catalytic cracking* (FCC) is probably the most widely used conversion process, worldwide.

Hydrocracking is another major conversion process. It is similar to catalytic cracking since it also uses a catalyst, but the reactions take place under a high pressure of hydrogen. The feed to the hydrocracking process is usually a heavy VGO. The large molecules in the VGO are broken down into smaller molecules by breaking carbon-carbon bonds and adding hydrogen atoms to the fragments. Other chemical changes also occur under hydrocracking conditions: The rings of some aromatic compounds are saturated, and most of the compounds containing sulfur and nitrogen are destroyed. The hydrocracking process yields a large percentage of product in the kerosine and diesel boiling range.

# **The Modern Refinery**

A schematic layout of a modern, fully integrated refinery with an emphasis on jet fuel is shown in Figure 5.1. Many refineries, especially smaller ones, will not have all of the processing units shown.

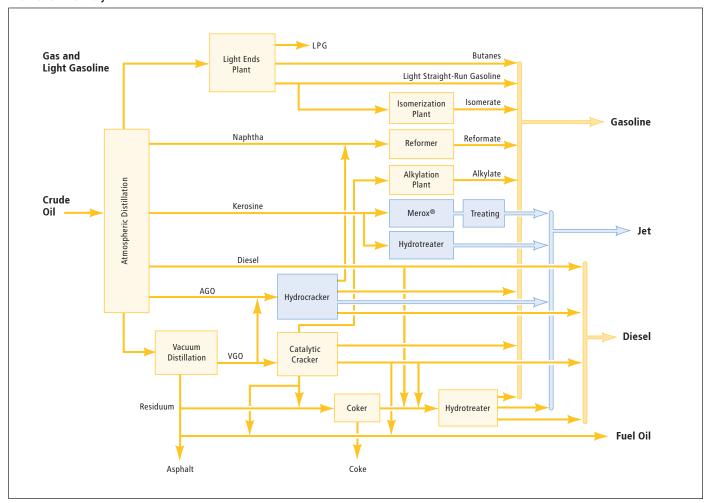
Crude oil is fed to the distillation column where straight-run light and heavy gasoline, kerosine, and diesel are separated at atmospheric pressure. The bottoms from the atmospheric column are vacuum distilled to obtain gas oils for FCC or hydrocracker feed. The gas oils may be hydrotreated to reduce sulfur and nitrogen to levels that will improve the performance of the FCC process.

Previously, the vacuum resid might have been used as a low-value, high-sulfur fuel oil for onshore power generation or marine fuel. But to remain competitive, refiners must wring as much high-value product as possible from every barrel of crude. As a result, the vacuum resid may be sent to a resid conversion unit, such as a resid cracker, solvent extraction unit, or coker. These units produce additional transportation fuel or gas oils, leaving an irreducible minimum of resid or coke.

#### Blending

The jet fuel produced by a refinery may be all straight-run or hydroprocessed product, or it may be a blend of straight-run, hydroprocessed, and/or hydrocracked product. Small amounts of heavy gasoline components also may be added. Straight-run kerosine from low-sulfur crude oil may meet all the jet fuel specification properties. But straight-run kerosine is normally upgraded by Merox treating, clay treating, or hydrotreating before it can be sold as jet fuel.





The refiner must blend the available streams to meet all performance, regulatory, economic, and inventory requirements. Sophisticated computer programs have been developed to optimize all aspects of refinery operation, including the final blending step. Refineries are optimized for overall performance, not just jet fuel production.

The refiner really has only limited control over the detailed composition of the final jet fuel. It is determined primarily by the composition of the crude oil feed, which is usually selected based on considerations of availability and cost. And the chemical reactions that occur in the conversion processes are not specific enough to allow for much tailoring of the products. Yet, despite these limitations, refineries daily turn out large volumes of products that meet all specification requirements.

# 6 · Aviation Turbine Engines

By the end of World War II, the aircraft piston engine was a fully developed power plant that was undergoing only incremental improvement. The introduction of the gas turbine engine paved the way for quantum leaps in aircraft performance. It enabled man to break the sound barrier and to routinely fly nonstop halfway around the world in a matter of hours. This chapter gives a brief overview of today's aircraft turbine engines.

#### Thrust

The force that powers flight is called thrust. Thrust is measured in newtons in the metric system and in pounds in the United States. One pound of thrust is the force necessary to offset the acceleration of gravity, 32 ft/sec², on a one-pound mass. A turbine engine producing 1000 pounds of thrust could suspend a mass of 1000 pounds in the air if the thrust were directed toward the earth, against the pull of gravity.

# **Principle of Operation**

Turbines are conceptually simple: They convert the kinetic energy of a moving fluid into mechanical energy by using the motion of the fluid to turn a rotor. The rotor, in turn, is connected to a device that does useful work. The moving fluid could be water, steam, air, or hot gases. Turbines driven by steam are widely used for electrical power generation.

An aircraft gas turbine engine generates hot, pressurized gas by burning fuel in a confined space. The gas, in the process of escaping from the engine, drives a turbine that, in turn, drives the compressor that compresses the air entering the engine. The hot compressed gas leaves the engine at high velocity, generating the thrust that pushes the aircraft forward.

The aircraft turbine engine is sometimes called a reaction engine because it exemplifies Newton's Third Law, which states: *For every action there is an equal but opposite reaction*. In this case, the action is the expulsion of the hot exhaust gas from the rear of the engine. The reaction is the thrust imparted to the engine – thrust that the engine transmits to the rest of the airframe.

Gas turbine engines consist of three sections, each with a different function: compression section, combustion section, and turbine section.

The compression section draws in and compresses ambient air and delivers the compressed air to the combustion section. There are two basic types of compressors: axial and centrifugal. In an axial compressor, air moves essentially parallel to the long axis of the engine as it passes through the compressor. In a centrifugal compressor, air is slung radially outward into a chamber, the diffuser, that redirects it to the combustion chamber.

Modern commercial engines often have two or three sets of compressors that work in series to achieve the desired degree of compression. At the end of the compression section, the air has a pressure of 30 to 35 atmospheres and a temperature of 550°C (1020°F) to 625°C (1160°F).

In the combustion section, fuel is continuously injected into the compressed air through a set of nozzles. The fuel evaporates as it mixes with the hot air, and then burns. The hot combustion gases are then forced into the turbine section by the high pressure at the outlet of the compressor. A more in-depth discussion of combustion is included below.

The turbine section contains a series of pairs of *stator vanes* and *rotor blades*. The vanes and blades are basically just extremely sophisticated airfoils. Stator vanes are stationary and accelerate the gas flow to push on the rotor blades. The rotors are connected to the compressor by a shaft. The push of the moving combustion gases against the rotor blades turns the turbine and, hence, the compressor. Finally, the hot mixture of combustion gases and air is accelerated through a nozzle at the rear of the engine. It is this exhaust stream that produces the thrust that drives the aircraft.

The combination of a turbine, the compressor it drives, and the connecting shaft is called a *spool*. An engine with two compressors will also have two independent turbines. The high-pressure compressor driven by the high-pressure turbine is the inner spool. The low-pressure compressor driven by the low-pressure turbine is the outer spool. The shafts of the two spools are concentric and rotate independently of each other at different speeds.

# **Engine Control Systems**

Besides providing the source of energy needed to power flight, fuel is also used to control various engine parameters. The main engine control meters fuel to the engine based on throttle demand coming from the cockpit, and also controls various engine operating parameters. Fuel is used as a hydraulic fluid to transmit pressure signals in the control and to position engine devices, such as compressor stator vane position or compressor air bleed valve position, to achieve desired operating conditions. Fuel is also used as a coolant or a heat sink in the engine.

## **Engine Types**

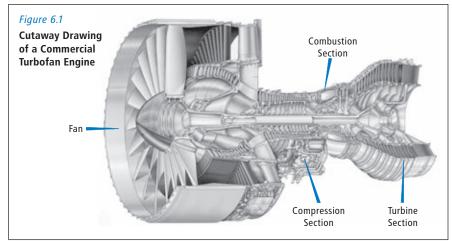
The earliest turbine engines had a single spool and were called *turbojet* engines. Turbojet engines perform well at high altitudes and high airspeeds, but are less efficient at low altitudes and low airspeeds.

Virtually all modern aircraft turbine engines are *turbofan* engines. A turbofan engine uses a turbojet as a core, but has a large fan mounted in front of the compressor section. This fan is visible in the front of a commercial airline jet engine. The fan, which, like the compressors, is driven by a turbine, acts like a propeller; it pushes air to create thrust. It differs from a conventional propeller in that it has lots of wide blades spaced closely together and is surrounded by a tight cowling.

The fan may be eight to twelve feet in diameter, more than twice the diameter of the core turbojet engine. Some of the air driven by the fan goes into the core while the rest goes around the outside of the core. This *bypass air* provides most of the thrust in high-bypass turbofan engines, perhaps 85 percent, while the hot exhaust gases provide only about 15 percent. Figure 6.1 is a cutaway drawing of a commercial turbofan engine.

#### Turbine Engines vs. Piston Engines

Gas turbine engines are smaller than piston engines of the same power and have a better power-to-weight ratio. However, turbine engines cost more to build than piston engines, and because they operate at high temperatures and rotation speeds, present engineering and materials challenges. Turbine engines work better under relatively constant load (aircraft flight); piston engines handle fluctuating loads better (rush hour traffic). In addition, turbine engines are better suited to large power requirements than piston engines, and have significantly better endurance capability.



Courtesy of Pratt & Whitney

Propellers are more efficient than turbojet engines at low altitudes and airspeeds. Turbofans combine the best features of both systems. Turbofans also are quieter than turbojets because the bypass air partially buffers the noise of the hot exhaust gases.

A *turboshaft* is the third major type of aircraft turbine engine. A turboshaft uses a turbojet engine, but the exhaust gases drive a low-pressure turbine, which connects to a gearbox. If the gearbox drives a propeller, then the engine is called a *turboprop*. The gearbox can also be connected to electric generators, pumping devices, or, in helicopters, a rotor. In these applications the engine is known as a turboshaft.

# **Combustion in the Engine**

Combustion, or burning, is a series of rapid oxidation reactions that release heat and, usually, light. Carbon dioxide and water are the final products of complete combustion. Combustion occurs in the gas phase; solids or liquids do not burn because there is not enough oxygen present in the condensed phase to support combustion. When solids or liquids appear to burn, it is really volatile components that have vaporized from the surface and mixed with air that are burning. A source of energy is needed to initiate combustion, but once combustion is established, it will continue as long as fuel and oxygen (air) are present in the required proportions.

Turbine engines have igniters to initiate combustion at startup. After this, combustion is sustained by the continuous injection of fuel into the flame. But this is an oversimplification. Continuous combustion requires a stable flame, which, in turn, requires matching the fuel and airflow rates to the flame propagation rate.

Hydrocarbon flame propagation rates are fairly slow, ranging from about 0.5 m/sec for a static mixture, to about 10 to 30 m/sec under turbulent flow conditions. Flame in the combustion zone

# **Aviation Turbine Engines**

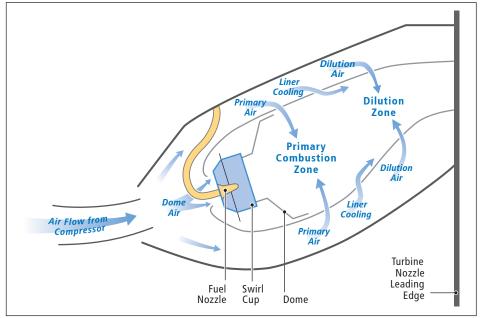
is stable only if its propagation velocity is greater than the velocity of the primary air. Otherwise, the flame would blow out and stable combustion would be impossible.

In the combustion section, airflow is divided so that only a portion enters the primary combustion zone around the fuel nozzle. This portion of the total airflow, made up of *dome air* and *primary air*, is approximately enough for stoichiometric<sup>1</sup> combustion of the fuel. A portion of the diverted air is used to cool the combustor liner. The remaining air is called *dilution air* and enters around the outside of the combustion chamber to cool and further mix the hot gases before they reach the turbine blades. Figure 6.2 shows a schematic diagram of airflow in the combustion section.

The velocity of air exiting the compressor section, about 150 m/sec, is much too high to support continuous combustion. This velocity is reduced to approximately 25 m/sec near the fuel nozzle by increasing the cross-sectional area at the entrance to the combustion section and diverting the secondary and dilution air around the primary combustion zone.

Fuel is fed into combustion chamber through injectors under a pressure of about 50 kg/cm<sup>2</sup> (700 psi). Under these conditions, fuel discharges from the nozzle with a velocity of about 30 m/sec, forming a jet of finely atomized fuel. Thus the velocity of the fuel spray, the velocity of the primary air, and the propagation velocity of a turbulent flame are closely matched. This allows the formation of a stable flame under very difficult conditions.

Figure 6.2
Schematic Diagram of Airflow in the Combustion Section



Courtesy of GE Aircraft Engines

It is easy to forget what a technological marvel modern flight is. When a Boeing 747-400 is cruising at 35,000 feet, each of the four engines is generating 12,000 pounds of thrust. To do this, the engine draws in 700 pounds of air each second, about 80 percent of which bypasses the core. The 120 pounds of air that enters the core is pressurized to more than 150 pounds per square inch and heated to more than 850°F in the compression section. One-andthree-quarter pounds of fuel is injected into the air and burned to heat the mixture of combustion gas to more than 2000°F. The turbines extract enough energy from these gases to turn the fan at about 3300 rpm, and the compressor at about 9500 rpm. When the gas mixture exits the turbine section, it has a velocity of 1400 feet per second and a temperature still over 1000°F.

One Second in the Life of a Turbine Engine

<sup>1</sup> *Stoichiometric* means chemically balanced, i.e., just enough oxygen is available to combine with all of the hydrocarbon present.

The highest flame temperatures, about 2050°C (3725°F), are found in the primary combustion zone in the region where the fuel-air ratio is near stoichiometric. The introduction of dilution air, coupled with the liner cooling air, reduces the temperature to about 1500°C (2730°F) at the entrance to the turbine section.

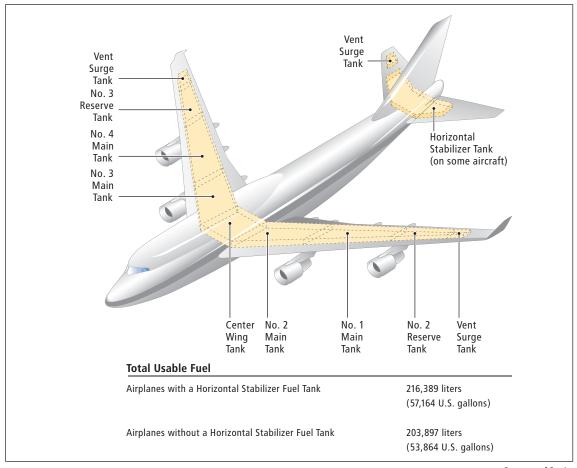
## **Fuel Tanks**

Commercial aircraft store fuel in their wings. Figure 6.3 shows the arrangement of fuel tanks in a Boeing 747-400. There are two main tanks and one reserve tank in each wing along with a center wing tank in the fuselage. Some 747-400s also have an additional fuel tank in the tail horizontal stabilizer. Each main tank has a pump that supplies fuel to a manifold that feeds the engines.

A Boeing 747-400 fully loaded with 216,389 liters (57,164 U.S. gallons) of fuel is carrying about 175,275 kg (386,411 lbs) at a fuel density of 0.810 g/mL (6.76 lbs/gal).

The Airbus A380, scheduled for commercial service in 2006, is expected to hold about 310,000 liters (81,900 U.S. gallons) of fuel.

Figure 6.3
Boeing 747-400 Fuel Tank Arrangement



Courtesy of Boeing

# 7 · Aviation Gasoline Introduction

Since the engines first used to power flight were based on the automotive engines of the day, they were fueled with automotive gasoline. The following decades saw large improvements in aviation engines and fuels. Much of the development was driven by the military's interest in aviation, both in the United States and in Europe. The primary goals were always better reliability and more power but without a proportional increase in engine size or weight.

Because engine and fuel are interdependent components of a single system, the path of progress resembled a game of leapfrog. "Engine development made it obvious that better fuels were needed, and when the improved fuel was used it immediately became evident that further engine development was necessary to make suitable use of the available fuel. As the engines caught up with the available fuel, it became evident that still better engine performance would result from even better fuel. As a result, the engine builder and user have, over a period of years, consistently demanded better and better fuel."

For fuels, the primary challenge was to improve antiknock properties so that the engines' power output would not be knock-limited. The major developments were the use of lead antiknock additive (tetraethyl lead), the identification of petroleum crudes with the best lead response, and the identification and production of specific hydrocarbons with good antiknock properties.

In 1930, the U.S. Army Air Corps specified a Fighting Grade gasoline with a minimum octane number requirement of 87. This is believed to be the first instance in which the antiknock properties of an aviation gasoline (*avgas*) were defined in terms of octane number.<sup>2</sup> By the start of World War II, fuels very similar to today's Grade 100 were in use.

Avgas reached its development peak during World War II. 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.

# **Grades of Fuel**

Grades of avgas are identified by their nominal minimum lean-mixture antiknock rating(s). Previously, both the lean- and rich-mixture ratings (*see page 58*) were used; now, only the lean-mixture rating is used.

In the decade following the war, six grades were in military and commercial use (*see Figure 7.1*). In the same decade, the turbine engine became the engine of choice for the military. As turbine engines also began to dominate commercial fleets, both ends of the avgas grade lineup were eliminated. Demand for the fuels with the higher antiknock ratings disappeared. And, at many commercial airports, an avgas tank was converted to jet fuel storage. But when some of the

<sup>1</sup> R. Schlaifer and S. Heron, *Development of Aircraft Engines and Fuels*, Graduate School of Business Administration, Harvard University, Boston, 1950, p. 552.

Figure 7.1

Grades of Aviation Gasoline in the United States

1950s	Today*
73	_
80/87	80
91/98	91
100/130	100, 100LL**
108/135	_
115/145	

<sup>\*</sup> ASTM D 910

older 80-octane-rated engines were fueled with Grade 100/130, they encountered spark plug fouling and exhaust valve deterioration because of its higher lead content.<sup>3</sup> A lower lead content version of Grade 100/130 (Grade 100LL) was developed in an effort to create a single universal grade of avgas.

Today, avgas is used mainly by small airplanes and light helicopters, but there is also a significant number of military and civilian transports powered by large piston engines that use avgas. There are two main specifications that cover avgas: ASTM D 910 and DEF STAN 91-90. These specifications describe basically the same products, although there are minor differences between the specifications for the same grade of avgas. As planned, Grade 100LL is the most popular, by far. Grade 100 and Grade 80 are used sparingly. D 910 recently reintroduced Grade 91 to facilitate its use in certification testing, but it is not intended to be a commercial product. A new specification for low-octane unleaded aviation gasoline, Grade 82UL, has recently been approved by ASTM (see page 56).

# **Fuel Consumption**

Air power was critical to the outcome of World War II, and toward its end, the Allies' production of avgas peaked at more than 25 million gallons per day.<sup>3</sup> Two years after the war, it had decreased sharply to about 5 million gallons per day. The growth of commercial aviation together with military use resulted in a gradual increase to about 14 million gallons per day in 1957. Then production began to decrease again as turbine engines replaced piston engines, first in military and later in commercial applications, returning to about 5 million gallons per day in 1970.

In 2002, total avgas production in the United States was 0.76 million gallons per day,<sup>4</sup> a very small amount compared to the production of turbine fuel (68 million gallons per day) or motor gasoline (372 million gallons per day). Worldwide use of avgas in 1996, by the most recent data available, is estimated to be about 2.2 million gallons per day.<sup>5</sup>

<sup>\*\*</sup> LL = Low Lead. Grade 100LL contains less tetraethyl lead antiknock additive than Grade 100.

<sup>3</sup> Alexander R. Ogston, *A Short History of Aviation Gasoline Development*, 1903–1980, Society of Automotive Engineers, Paper No. 810848, 1981.

<sup>4</sup> Energy Information Administration, U.S. Department of Energy.

<sup>5</sup> United Nations Energy Statistics Yearbook.

# 8 · Aviation Gasoline Performance

# **Performance Properties**

Since the primary function of aviation gasoline (*avgas*) is to power an aircraft, *energy content* is a key fuel performance property. Other important performance properties are *knock resistance*, *volatility, fluidity, stability, non-corrosivity*, and *cleanliness*.

# **Energy Content**

An aircraft piston engine produces power by converting chemical energy stored in the fuel into mechanical energy. Since space is at a premium in most aircraft, the amount of energy contained in a given quantity of fuel is important.

The energy content of avgas can be measured; it is the heat released (also called the *heat of combustion*) when a known quantity of fuel is burned under specific conditions. The amount of heat released depends on whether the water formed during combustion remains as a vapor or is condensed to a liquid. If the water is condensed to the liquid phase, giving up its heat of vaporization in the process, the energy released is called the *gross energy content*. The *net energy content* is lower because the water remains in its gaseous phase (water vapor). Since engines exhaust water as vapor, net energy content is the appropriate value for comparing fuels.

Energy content can be expressed either *gravimetrically* (energy per unit *mass* of fuel) or *volumetrically* (energy per unit *volume* of fuel). The international metric (SI) units are *megajoules per kilogram* (MJ/kg) and *megajoules per liter* (MJ/L). In the United States, usually the gravimetric unit is *British thermal units per pound* (Btu/lb) and the volumetric unit is *British thermal units per gallon* (Btu/gal).

Because the energy content of individual hydrocarbons can differ, fuels with different compositions may have different energy contents. But the gravimetric energy content of avgas doesn't vary much – typically, only a few percent. The energy content variation is small because the avgas specifications tightly constrain its chemical composition. (*See Figure 2.1 for typical avgas energy content.*)

The amount of power generated by a specific engine depends more on its design than on the fuel used. In general, the more air an engine can process, the more power it can produce. Therefore, major design considerations for power include engine cylinder size (*displacement*), engine compression ratio, and whether the incoming air is pressurized (*supercharged* or *turbocharged*).

#### Knocking

Normal combustion in a spark-ignition, internal combustion engine is initiated by a spark. The flame front fans out from the spark plug and travels across the combustion chamber rapidly and smoothly until almost all the fuel is consumed. Knocking — often called detonation in the aviation industry — is the sound produced by abnormal combustion.

Some of the unburned mixture ignites spontaneously (autoignites) and burns very rapidly. The resulting precipitous rise in cylinder pressure creates the characteristic knocking or pinging sound.\*

Conditions within an engine are not constant; they depend on how the engine is being operated. Knocking occurs when the fuel's antiknock rating is below the antiknock requirement of the engine at that given moment.

Combustion is a very rapid series of chemical reactions between fuel and oxygen. Factors that increase the rates of combustion reactions favor autoignition and knocking. These factors include higher temperatures (molecules have more energy to react), higher pressures (molecules are closer together), and more time after spark ignition (molecules have more time to autoignite). The corresponding engine conditions are high engine temperature, high compression ratio or turbocharging, and low engine speed or high spark advance.

Tetraethyl lead (TEL) is an effective antiknock additive because it interrupts the chain reactions that lead to autoignition.

## (continued next page)

\* Knocking due to autoignition is also called spark knock. Other types of abnormal combustion that are more dependent on engine conditions and less dependant on fuel characteristics are discussed on page 70.

#### **Knock Resistance**

Knock-free engine performance is essential to smooth, reliable engine operation. *Octane number* and *performance number* are measures of the ability of avgas to resist knocking as it burns in the combustion chamber (*see sidebar*).

Two laboratory engine tests (*see page 58*) are used to measure the antiknock performance of avgas: One measures performance at a lower fuel-air ratio (*lean-mixture* condition) that simulates cruising; the other at higher fuel-air ratios (*rich-mixture* conditions) that simulate take-off, where extra power is needed.<sup>1</sup> Two tests are required because knock-free performance in the lean fuel-air ratio regime does not guarantee knock-free performance in the rich regime in some engines.

The octane number scale is defined by two pure chemical reference fuels: normal heptane (*n-heptane*) with an octane number of zero, and isooctane (*2,2,4-trimethylpentane*) with an octane number of 100. The octane number of a blend of these two compounds is equal to the volume percentage of isooctane it contains. Isooctane also defines 100 on the performance number scale. The performance number scale above 100 is defined by mixtures of isooctane and tetraethyl lead.

The result from either test is called an octane number if it has a value of 100 or less, and a performance number if it has a value greater than 100.

The rich-mixture performance number scale is constructed to be approximately linear in maximum engine power output. Numbers above 100 indicate the additional knock-limited power, relative to isooctane, provided by an avgas with that rating. For example, an avgas with a performance number of 130 delivers about 130 percent of the knock-limited power available from isooctane.

Engine and fuel are interdependent components of a single system. Each engine is designed and certified for fuel with a specific minimum antiknock performance. Using a fuel with a lower antiknock performance will produce less knock-limited power and possibly damage the engine under severe knock conditions. Use of a fuel with a higher antiknock performance is not harmful, but provides no benefit.

# Antiknock, Turbocharging, and Compression Ratio

The development of higher octane number avgas led to higher performance engines mainly because it allowed the use of turbocharging (*see page 69*) and higher compression ratios. The power available from the four-stroke engine cycle is roughly proportional to the mass of air consumed. More air can be consumed per engine cycle by either increasing the displacement of the engine, or by increasing the pressure of the inlet air. This inlet air compression is called

1 The reference point for a discussion of fuel-air ratios is the fuel-air ratio for the stoichiometric mixture of air and fuel – the mixture containing just enough air (oxygen) to react with all the fuel. Mixtures with lower fuel-air ratios contain more air (oxygen) than needed to react with all the fuel; in terms of the fuel, the mixture is lean. Mixtures with higher fuel-air ratios contain insufficient air (oxygen) to react with all the fuel; in terms of the fuel, the mixture is rich.

# Aviation Gasoline Performance

supercharging or turbocharging. Supercharging leads to larger engine weight and volume and is thus undesirable, especially for aviation. Turbocharging has a much smaller weight and volume penalty. Since turbocharging leads to higher cylinder pressure and temperature, it thus requires a higher octane number fuel.

Use of a higher octane number fuel also allows use of an engine with a higher compression ratio. Increasing compression ratio alone in an engine does not consume more air, rather the same amount of air is consumed with higher thermal efficiency.

## Volatility

*Volatility* is a fuel's tendency to vaporize. Two physical properties are used to characterize avgas volatility: vapor pressure and distillation profile. A more volatile fuel has a higher vapor pressure and distills at lower temperatures.

Engines use one of two basic systems to deliver fuel into the cylinders: carburetion and fuel injection. A carburetor mixes fuel with air starting in the throat of the carburetor. This mixture is then drawn through an inlet manifold, where, ideally, complete mixing of fuel and air occurs, before entering the cylinders. A fuel-injection system injects fuel into the inlet manifold above the intake port of each cylinder. Air is still drawn in through the inlet manifold, but the mixing of fuel and air occurs primarily above each intake port, and is completed in the cylinder during the intake and compression strokes.

Carburetion was used exclusively in the early aviation engines, so the avgas volatility specifications were developed for carbureted engines. The same specifications are also suitable to fuel-injected engines because their volatility requirements are less demanding.

A more volatile fuel decreases the likelihood of starting and running problems, but increases the likelihood of vapor lock, icing, and boil-off problems. Consequently, setting the avgas volatility requirement is a balancing act. Figure 8.1 shows a typical avgas D 86 boiling curve along with the specification requirements and the associated performance properties discussed below.

(Knocking, continued from previous page)

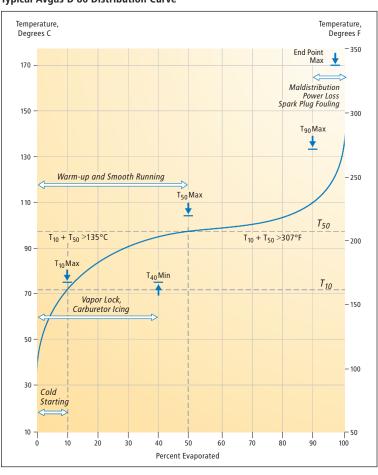
Occasional light knocking won't hurt an engine. Heavy or prolonged knocking can result in:

- · Loss of power.
- · Overheated engine parts.
- Engine damage, possibly leading to engine failure.

Knocking in an aircraft engine may not be audible, either during flight or on the ground, because of engine and propeller noise, wind, cabin insulation, etc. This increases the importance of using the correct grade of fuel and properly maintaining the engine.

Figure 8.1

Typical Avgas D 86 Distribution Curve



**Cold Starting** Liquids and solids don't burn; only vapors burn. This is true whether a fuel is in the atmosphere or confined in the cylinder of an engine. So, starting a cold engine requires a fuel with a high enough volatility to form a vapor-air mixture in the flammable range. The lower the ambient temperature, the higher the volatility of the fuel must be, or starting aids, such as engine heaters or primers, must be used.

Smooth Running For an engine to run smoothly, the fuel-air mixture must be distributed evenly among all the cylinders. Even-mixture distribution is an inherent characteristic of fuel-injected engines but not of carbureted engines. In both types of engines, the volatility of the fuel must be high enough for it to evaporate and mix with air before combustion. In a carbureted engine, the fuel must evaporate and mix with air to form a uniform mixture in the fraction of a second it spends in the carburetor and inlet manifold before it is drawn into a cylinder. If the fuel is only partially vaporized, some cylinders, depending on engine geometry, will receive a mixture of liquid fuel, fuel vapor, and air that is too rich, while others will receive a mixture of fuel vapor and air that is too lean. In addition, because tetraethyl lead is less volatile than the fuel,<sup>2</sup> the anti-knock additive will tend to be concentrated in the liquid fuel.

The uneven distribution of fuel and antiknock additive among the cylinders can result in rough running and poor fuel economy. It may even lead to knocking and engine damage. And if droplets of liquid fuel reach the cylinder wall, they will dilute the lubricating oil film, which may result in increased piston ring and cylinder wall wear.

**Vapor Lock** *Vapor lock* occurs when excessive gasoline vapor accumulates somewhere in the fuel system – fuel pump, fuel line, carburetor or fuel injector – and reduces or interrupts the fuel supply to the engine. When the fuel supply is reduced, the fuel-air ratio becomes too lean, which may result in loss of power, knocking, surging, or backfiring. When the fuel supply is interrupted, the engine stops and may be difficult to restart until the fuel system has cooled and the vapor recondensed, or purged by boosting the fuel supply pressure.

While the tendency of avgas to vapor lock increases with volatility, fuel overheating is the main cause of vapor lock. Local temperatures in the fuel system are determined by how hard the engine is working and how well the fuel system is isolated from the heat of the engine. Fuel residence time in the hot sections of the system, mechanical vibration, and other factors also play a significant role in vapor lock behavior.

The altitude at which the engine is operating has two opposing influences: ambient temperatures are lower at higher altitudes, which should improve fuel system cooling; but ambient pressures are also lower, making vaporization easier.

The design of an aircraft fuel system must take all the above factors into account to ensure that liquid fuel, with little or no free vapor, is delivered to the engine's fuel metering system.

# Aviation Gasoline Performance

Carburetor Icing In the absence of a heat source, an evaporating liquid cools its immediate surroundings. Carburetor icing becomes possible when the intake air temperature is reduced to below the freezing point of water. The air temperature is reduced both by evaporative cooling of the avgas and also expansion cooling as air passes through the carburetor venturi. Under certain conditions, especially intake air temperatures between about  $-4^{\circ}$ C and 15°C (25°F and 60°F) and high humidity, ice can form in the venturi and on the throttle plate. Icing does not occur when the air temperature is too low, below about  $-7^{\circ}$ C to  $-12^{\circ}$ C (20°F to 10°F), because then the air is too dry.

Ice formation can interrupt carburetion, causing the engine to stall. The icing tendency of a fuel increases with increased volatility because a greater fraction of the fuel vaporizes in the carburetor rather than in the intake manifold. Some engine designs avoid the icing problem by heating the intake air or the carburetor venturi and throttle plate.

**Fuel Boil-Off** The boiling point of a liquid is the temperature at which its vapor pressure is equal to the local atmospheric pressure. However, atmospheric pressure decreases exponentially with increasing altitude. At 3000 meters (10,000 feet), atmospheric pressure is only about 69 percent as great as at sea level, and at 6000 meters (20,000 feet), it drops to 46 percent of the sea-level value. Thus liquids boil at lower temperatures at higher altitudes.

Atmospheric temperature also decreases as altitude increases, which tends to counteract the decrease in pressure. However, it takes time for fuel to cool to ambient air temperature, while pressure equilibration is almost instantaneous since fuel tanks are vented to the atmosphere. An aircraft taking off from sea level with a fuel temperature of 38°C (100°F) and ascending rapidly to 6000 meters (20,000 feet) may experience fuel vapor pressure that is greater than the pressure in the fuel tank, i.e., the fuel will boil. Any boil-off that does occur will likely be confined to the fuel tank, since fuel pumps maintain the rest of the fuel system at a higher pressure.

If fuel does boil, the components with the highest vapor pressure evaporate first. Loss of these lightest components changes the composition of the remaining liquid and leaves it with a lower vapor pressure. When the fuel vapor pressure drops below the ambient pressure in the tank, boiling will stop. Fuel boiling also lowers the temperature of the remaining liquid through evaporative cooling. Both of these effects tend to minimize loss of fuel due to boiling. Only in extreme circumstances will loss of fuel exceed a few percent.

The solubility of air dissolved in fuel also decreases as pressure decreases. Normally this air will come out of solution smoothly and not cause a problem. However, if the fuel becomes supersaturated, air can be evolved very quickly and cause frothing of the fuel. This can lead to loss of fuel from vents, but the mechanism is different from actual fuel boiling.

#### Vapor Pressure

The vapor pressure of a pure compound is defined as the pressure exerted by its vapor in equilibrium with the liquid at a constant temperature. This pressure is independent of the amount evaporated, or vapor-liquid ratio, as long as there is liquid remaining. Vapor pressure increases as temperature increases. When the vapor pressure is equal to the external pressure (usually atmospheric pressure), the liquid boils.

But fuels, which are mixtures of many different hydrocarbons, do not behave the same as pure compounds. Each individual component in the fuel has its own vapor pressure. The vapor phase over a fuel does not have the same composition as the liquid phase. The vapor phase contains more of the high vapor pressure (low boiling point) compounds than the liquid.

As a fuel evaporates, its composition changes. The vapor pressure of the remaining liquid decreases as the extent of evaporation increases. For a complex mixture such as a fuel, vapor pressure is defined as the pressure of the vapor in equilibrium with its liquid at a specified temperature, as the vapor to liquid ratio approaches zero. This is the highest pressure that a fuel can exert.

In the petroleum industry, the true vapor pressure as defined above is difficult to measure in practice, and is therefore not often used. Instead, a related quantity called the Reid vapor pressure (RVP) is measured. The RVP of a fuel is typically a few percentage points lower than the true vapor pressure because of the way it is measured (see page 60).

## **Fluidity**

Like other liquids, 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 a solid at one temperature the way water does. As the fuel is cooled, the hydrocarbon components with the highest freezing points solidify first. Further cooling causes hydrocarbons with lower freezing points to solidify. Thus the fuel changes from a homogeneous liquid to a liquid containing a few hydrocarbon (wax) crystals, to a slush of fuel and hydrocarbon crystals, and finally, to a near-solid block of hydrocarbons at extremely low temperatures.

Avgas is exposed to low temperatures both at altitude and on the ground at locations subject to cold weather extremes. The fuel must retain its fluidity at these low temperatures or fuel flow to the engine will be reduced, or even stopped.

Air temperatures at altitude vary seasonally and with latitude, just as they do at ground level. The lowest average temperature at 3000 meters (10,000 feet) is about –25°C (–13°F), and at 6000 meters (20,000 feet) is about –42°C (–44°F), although extreme temperatures can be perhaps 20°C (36°F) lower. Given their low molecular weights and low freezing points (*see page 88*), most gasoline hydrocarbons won't crystallize at these temperatures. But the highest molecular weight components could. To avoid hydrocarbon crystallization, the avgas specifications require the freezing point of avgas to be less than –58°C (–72°F).

#### Storage Stability

Avgas instability involves multi-step reactions, some of which are oxidation reactions. Hydroperoxides and peroxides are the initial reaction products. These products remain dissolved in the fuel but may attack and shorten the life of some fuel system elastomers. Additional reactions result in the formation of soluble gums and insoluble particulates. These products may clog fuel filters and deposit on the walls of aircraft fuel systems, restricting flow in small-diameter passageways.

Instability of avgas during storage is generally not a problem because of the way the fuel is manufactured (*see page 66*), and most fuel is used within a few months of its manufacture. Storage stability can be an issue at locations where fuel is stored for occasional or emergency use. Avgas that has been properly manufactured, stored, and handled should remain stable for at least one year. Avgas subjected to longer storage or to improper storage or handling should be tested to be sure it meets all applicable specification requirements before use.

Changes that can occur during storage include:

- · Air oxidation of more reactive hydrocarbons.
- Air oxidation of tetraethyl lead to form an insoluble white solid.
- Evaporation of the more volatile hydrocarbon components.

Because it is the more reactive molecules that participate in instability reactions, storage stability is influenced by fuel composition. It is also influenced by storage conditions: Instability reactions occur faster and to a greater extent at higher ambient temperatures.

Storage of avgas in high ambient temperatures presents an additional challenge. The most volatile components can evaporate from the fuel and be lost to the atmosphere. If enough of the high vapor pressure components are lost, the TEL concentration could increase to above the specification maximum, and the vapor pressure could fall below the specification minimum.

# Non-corrosivity

Avgas contacts a variety of materials during distribution and use. It is essential that the fuel not corrode any of these materials, especially those in aircraft fuel systems. Engine and airframe manufacturers conduct extensive fuel compatibility testing before approving a material for fuel system use.

Certain sulfur compounds are potentially corrosive. They are limited by the specification copper corrosion test. By-products of microbial growth also can be corrosive.

## **Cleanliness**

Fuel cleanliness means the absence of solid particulates and free water. Particulates – rust, dirt, etc. – can plug fuel filters and increase fuel pump wear. Water, in addition to not burning in an engine, will freeze at the low temperatures encountered in high altitude flights. The resulting ice may plug fuel filters and otherwise impede fuel flow. Water also may facilitate the corrosion of some metals, and the growth of microorganisms in the fuel.

In addition to being clean, fuel delivered to aircraft must also be free from contaminants. The most common sources of contamination encountered with aviation fuels are discussed in Appendix A. These include product mixes, surfactants, and microbes.

Microbial Growth Avgas is sterile when first produced because of the high refinery processing temperatures. But it becomes contaminated with microorganisms that are always present in air and water. These include bacteria and fungi (yeasts and molds). The solids formed by microbial growth are very effective at plugging fuel filters. Some microorganisms also generate acidic byproducts that can accelerate metal corrosion.

Since most microorganisms need free water to grow, microbial growth is usually concentrated at the fuel-water interface, when one exists. Some organisms need air to grow (*aerobic* organisms), while others grow only in the absence of air (*anaerobic* organisms). In addition to food (fuel) and water, microorganisms also need certain elemental nutrients. Phosphorus is the only one whose concentration might be low enough to limit microbial growth. Higher ambient temperatures also favor microbial growth.

Microbial contamination of avgas is less common than in other petroleum products, presumably due to the toxicity of tetraethyl lead, but it does occur. The best approach to microbial contamination is prevention. And the most important preventive step is keeping the amount of water in the fuel storage tank as low as possible. No additives are approved as biocides in the major avgas specifications (*see page 54*).

# **Safety Properties**

Avgas can be hazardous if not handled properly. First and foremost, it is easy to ignite and it burns explosively. Second, exposure to avgas liquid or vapor can be unhealthy. Anyone planning to handle avgas should obtain and read the Material Safety Data Sheet (MSDS) issued by the supplier.

Liquid doesn't burn; only vapor burns. And vapor doesn't always burn - the concentration of vapor in air must be in the flammable<sup>3</sup> range. Mixtures with insufficient vapor (below the *lower flammability limit*) or too much vapor (above the *upper flammability limit*) will not burn. For avgas, the lower and upper flammability limits<sup>4</sup> are approximately 1.2 volume percent vapor in air and 7.0 volume percent vapor in air, respectively.

Except at temperatures below about -12°C (10°F),<sup>4</sup> the hydrocarbon vapor-air mixture in an enclosed space over liquid avgas will be above the upper flammability limit. However, in the absence of specific information to the contrary, any avgas handling situation should be considered to be potentially flammable, and the appropriate safety measures observed.

<sup>3</sup> National Fire Protection Association and the Department of Transportation regulations include definitions of *flammable* and *combustible* based on the flash point of the material.

<sup>4</sup> Handbook of Aviation Fuel Properties, Coordinating Research Council.

## Flash Point

The flash point is the lowest temperature at which the vapors above a flammable liquid will ignite on the application of an ignition source. At the flash point temperature, just enough liquid has evaporated to bring the vapor-air space over the liquid above the lower flammability limit. The flash point is a function of the specific test conditions under which it is measured. The flash point of avgas is about -40°C (-40°F), well below most ambient temperatures, and is typically neither measured nor controlled.

# **Electrical Conductivity**

Static electrical charge can be generated when dissimilar surfaces move across each other, for example, when fuel moves through a pipe or a fine filter. The rate at which the charge dissipates is proportional to the liquid's ability to conduct electricity (*electrical conductivity*).

Pure hydrocarbons are essentially nonconductors. Conductivity of fuels is usually expressed in *conductivity units* (CU), 1 CU = 1 pico Siemens/meter (1 pS/m) =  $1 \times 10^{-12}$  ohm<sup>-1</sup> meter<sup>-1</sup>. Avgas may have conductivity ranging from less than 1 CU up to perhaps 10 CU. For comparison, deionized water has a conductivity of about 10 million CU.

Filtering or rapidly pumping a liquid that is a poor electrical conductor can result in static charge being created much faster than it dissipates. When the accumulated charge exceeds the ionization potential of the air above the liquid, it can discharge from the liquid surface as a spark. The energy of the spark can initiate an explosion if the liquid is flammable and the composition of vapor and air in the vicinity is in the flammable range.

To prevent explosions triggered by a static discharge, well designed fuel handling systems use bonding and grounding, pumping rate limits, and time for charge dissipation (*relaxation time*) after filtration before the fuel is exposed to air.<sup>5</sup> Sometimes an additive is added to avgas to increase its electrical conductivity (*see page 65*). Conductivity improving additives are also called *anti-static* additives or *static dissipator* additives. Use of the additive reduces the hazard of charge accumulation for handling situations that are less than optimum. The additive does not prevent charge generation, rather it increases the rate of charge dissipation by increasing fuel conductivity.

<sup>5</sup> See ASTM D 4865, Standard Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems, for more information.

# 9 • Aviation GasolineSpecifications and Test Methods

# **Specifications**

Product specifications are a mechanism by which producers and users of a product identify and control the properties necessary for satisfactory and reliable performance. The first aviation gasoline (avgas) specifications were issued by the military because they sponsored much of the early development of aircraft engines and avgas.

Today there are two main avgas specifications: one maintained by ASTM International (American Society for Testing and Materials), and the other by the United Kingdom Ministry of Defence.

Specification bodies bring together the viewpoints of the large number of groups that are interested in and/or are affected by the specifications are considered. These groups include:

- · Individual refiners.
- Petroleum refining organizations.
- Petroleum marketing organizations.
- · Additive and equipment suppliers.
- · Aircraft and airframe manufacturers.
- · Aircraft engine manufacturers.
- · Governmental regulatory agencies.
- Special interest groups and consultants.

ASTM Subcommittee J of Committee D-2 (Petroleum Products and Lubricants) maintains D 910, Standard Specification for Aviation Gasolines.

The United Kingdom Ministry of Defence maintains the other avgas specification: Defence Standard 91-90 (formerly DERD 2485). Its requirements for the most important properties – knock ratings, distillation profile, and vapor pressure – are identical to those of D 910. There are minor differences between the two specifications for some other properties, and in their lists of approved additives.

Figure 9.1 summarizes the grade-specific property limits for avgas, and summarizes the property limits common to all three grades. Keep in mind that these figures are summaries. Readers in need of details should refer directly to the current version of the specification. Also keep in mind that a product specification is a living document that undergoes periodic updates. ASTM standards include a suffix indicating the year of last revision, e.g., D 910-04 was last revised in the year 2004. Figure 9.1 accurately reflects D 910 and DEF STAN 91-90 as of this writing, but they will become out-of-date in time.

Figure 9.1

Grade 100LL Avgas Requirements

Grade 100LL Avgas Requirements				
Property	ASTM D 910	ASTM Test Method	DEF STAN 91-90	IP Test Method
Knock rating, lean mixture Motor method octane number, min	99.5	D 2700	99.5	IP236
Knock rating, rich mixture Supercharge rating Performance number, min	130.0	D 909	130	IP119
Tetraethyl Lead Concentration mL TEL/L, max g Pb/L, max	0.53 0.56	D 3341 or D 5059	0.53 0.56	IP 270
Color	Blue	D 2392	Blue	IP17
Dye content Blue dye, mg/L, max Yellow dye, mg/L, max Red dye, mg/L, max	2.7 None None		2.7 None None	
Density at 15°C, kg/m3	Report	D 1298 or D 4052	Report	IP160
Distillation, °C Initial boiling point <u>Volume percent evaporated (VPE)</u>	Report	D86	Report	IP123
10, max 40, min 50, max 90, max Final boiling point Sum of temperatures at 10	75 75 105 135 170		75 75 105 135 170	
and 50 VPE, min	135		135	
Distillation yields, % vol. Recovery, min Residue, max Loss, max	97 1.5 1.5	D86	97 1.5 1.5	IP123
Vapor pressure at 38 °C, kPa Min Max	38.0 49.0	D 323, D 5190 or D 5191	38.0 49.0	
Freezing point, °C, max	-58	D 2386	-60	IP16
Sulfur content, % mass, max	0.05	D 1266 or D 2622	0.05	IP107
Net heat of combustion, MJ/kg, min	43.5	D 4529 or D 3338	43.5	IP12
Corrosion, copper strip, 2 hr. at 100 °C, max	No. 1	D 130	No. 1	IP154
Oxidation stability, after 5 hr. aging, mg/100 mL Potential gum, max Lead precipitate, max	6 3	D 873		
Oxidation stability, after 16 hr. aging, mg/100 mL Potential gum, max Lead precipitate, max			6 2	IP138
Water reaction, volume change, mL, max	± 2	D 1094	± 2	IP289

# The Beginning\*

Avgas specifications have come a long way since 1907, when the U.S. Navy issued Specification 24G5. It called for a "high-grade refined gasoline, free from all impurities, having a gravity of 70° Baume (0.702 relative gravity), and [leaving] no residue ... in a platinum dish after one hour in boiling water."

\* Alexander R. Ogston, A Short History of Aviation Gasoline Development, 1903–1980, Society of Automotive Engineers Paper No. 810848, 1981.

#### **Future Fuels**

In 1996, the U.S. Environmental Protection Agency (EPA) banned lead in motor gasoline. Although avgas was not included in the ban, concerns that the use of lead in avgas would eventually be restricted led the industry to begin looking for unleaded replacement fuels in the early 1990s.

An unleaded fuel that would satisfy the most critical piston engines in the existing aircraft fleet would need the same antiknock performance as Grade 100LL. The Coordinating Research Council is testing potential blend components for such a fuel. However, the challenge is daunting because the antiknock properties of tetraethyl lead are truly unique. Avenues of exploration include:

- Use of various oxygenates or aromatic amines to make up the octane number deficit of the hydrocarbon base fuel. Methyl *tertiary*-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), and m-toluidine <sup>1</sup> are under consideration.
- Use of a manganese-based antiknock additive [methylcyclopentadienyl manganese tricarbonyl (MMT)].

Ethanol is also being evaluated as a future fuel or fuel blend component for piston-powered aircraft. As of this writing, no viable fuels have emerged from this program.

## Grade 82UL

ASTM approved this specification for a low-octane unleaded (UL) avgas, D 6227, Standard Specification for Grade 82 Unleaded Aviation Gasoline, in 1998. Grade 82UL is not a replacement for Grade 80; it is intended only for aircraft piston engines specifically developed to use this unleaded avgas. Some of its important properties are summarized in Figure 9.2. Readers in need of details should refer directly to the current version of D 6227. Commercialization of this fuel will depend on the development of new engines and demand for the fuel.

Figure 9.2

Summary of D 6227 Requirements

Property	Requirement	Test Method
Knock value, lean mixture, motor method octane number, min	82.0	D 2700
Color	Purple	D 2392
Distillation, °C Volume percent evaporated:		D 86
10%, max	70	
50%, min	66	
50%, max	121	
90%, max	190	
End point, max	225	
Freezing point, °C, max	-58	D 2386
Vapor pressure, kPa		D 4953, D 5190, D 5191, D 5482
Min	38	
Max	62	

<sup>1</sup> Aromatic amines were used in avgas during World War II.

Aviation Gasoline Specifications and Test Methods

## **Civil Aviation Authorities**

Engines and airframes are certified for airworthiness by a national civil aviation authority. In Europe, this authority is the European Aviation Safety Agency (EASA). In the United States, this authority lies with the Federal Aviation Administration (FAA). Federal Aviation Regulations (FAR) issued by the FAA include the procedures to be followed for airworthiness certification. Testing is carried out by the equipment manufacturers and witnessed by the FAA. When testing is successfully completed, a type certificate is issued for the engine/airframe combination. This certificate includes, among other things, the specification for the fuel(s) approved for use in that aircraft.

Any change to a certificated engine or airframe requires FAA approval. After demonstration of airworthiness, the FAA will issue a supplemental type certificate (STC) covering a specific modification.

Many countries have bilateral agreements that recognize each others certifications.

#### **Test Methods**

Figure 9.1 lists the test methods specified for each property. These methods are the only ones that are acceptable for determining compliance with the specification requirements. Their existence allows everyone testing the product to get the same answers within the defined precision of the methods. Specifications will not adopt a new requirement for a product until a standard test method has been developed to measure it.

Many of the ASTM methods were developed in the 1920s, 30s, and 40s. To ensure they remain up-to-date in the light of new technological developments, ASTM reviews each method every five years, at which time it is either reapproved, revised, or canceled. The year of last review is added to the test method number as a hyphenated suffix. For example, D 86-04, *Standard Test Method for Distillation of Petroleum Products*, was originally published as a tentative method in 1921 but revised in 2004.

New methods based on new technology are continually being developed. At ASTM, the development process starts with a technical review of the proposed method. Next, an interlaboratory test protocol (*round robin*) is conducted in which a common set of samples is independently tested. The results from the participating laboratories are compiled and statistically analyzed. If the agreement among laboratories is acceptable, a precision statement is developed giving the maximum difference to be expected between back-to-back tests in one laboratory (*repeatability*) and also the maximum difference to be expected between results obtained by different labs on the same sample (*reproducibility*). Finally, a report is written documenting the work for future reference.

Other national and international testing organizations also sanction methods. In many cases, the methods of the other organizations are very similar or identical to ASTM's and yield the same value for the property. The DEF STAN specification typically reference IP test methods with ASTM test methods allowed as alternates. In may cases the two organization maintain technical equivalence between test methods; in this case they are considered "joint" methods.

#### History of Octane Testing\*

In the late 1910s and early 1920s, the initial systematic studies of the relationship between engine knocking and fuel quality were conducted by A.H. Gibson and Harry Ricardo in England and Thomas Midgely and Thomas Boyd in the United States. In 1927, Graham Edgar, following an extensive investigation of the detonation characteristics of pure hydrocarbons, proposed using normal heptane and isooctane to define a 100-point knock testing rating scale. At about the same time, the Cooperative Fuel Research Committee (CFR), sponsored jointly by automotive and oil organizations, specified a singlecylinder, variable-compression engine for knock testing. By 1929, oil companies were using the reference fuels and test engines to obtain octane ratings.

The CFR engine, when operated at specified speed and temperature conditions, became the basis for the CFR Motor Method for antiknock testing. The method used a knock meter to determine knocking. The CFR Motor method evolved into ASTM Method D 357. Standard Method for Knock Characteristics of Motor Fuels of 100 Octane Number and Below by the Motor Method. In 1968, D 357 was replaced by ASTM D 2700, Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel. In the 1930s, the CFR Motor Method was the specification method used by the U.S. Navy and commercial airlines to determine the (lean-mixture) antiknock rating of avgas. The U.S. Army Air

(continued next page)

\* Alexander R. Ogston, *A Short History of Aviation Gasoline Development, 1903-1980,* Society of

Automotive Engineers Paper No. 810848, 1981.

## **Specific Methods**

## Lean-Mixture Aviation Rating

ASTM D 2700 / IP 236 – Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel<sup>2</sup>

This method uses a standardized, single-cylinder, four-stroke-cycle, variable-compression-ratio, carbureted engine to rate a fuel's ability to resist auto-ignition. The engine is operated under specific conditions of speed, fuel-air mixture temperature, and spark timing. The fuel-air ratio and compression ratio of the engine are adjusted to produce a knock of standardized intensity for the test fuel, as measured by an electronic knock meter. Reference fuels are run to identify those with knock intensities that bracket the knock intensity of the test fuel. The result for the test fuel is then determined by interpolating between the octane numbers of the bracketing reference fuels and reported as a *Motor octane number*.

The method employs two sets of primary reference fuels:

- Primary reference fuels with octane numbers of 100 and less are blends of normal heptane (*n-heptane*), whose octane number is defined to be zero, and isooctane (*2,2,4-trimethylpentane*), whose octane number is defined to be 100. The octane number of each blend is equal to the volume percent of isooctane it contains.
- Primary reference fuels with octane numbers greater than 100 are blends of isooctane and tetraethyl lead. The method provides an equation to convert the concentration of tetraethyl lead in units of milliliters per U.S. gallon to octane number.

D 2700 includes a table to convert a Motor octane number to an *Aviation rating* equivalent to one that would be obtained using the now-discontinued D 614 method (*see sidebar*). For Motor octane numbers between 75 and 100, the conversion generally reduces the value by a fraction of a number and the result is reported as an octane number. For Motor octane numbers between 100 and 110, the conversion increases the value by up to 20 numbers and the result is reported as a *performance number*.

#### Rich-mixture Supercharge Rating

ASTM D 909 / IP 119 – Standard Test Method for Knock Characteristics of Aviation Gasolines by the Supercharge Method

This method uses a supercharged, single-cylinder engine operated at constant speed, compression ratio, air temperature, and spark timing. The inlet manifold air pressure and the fuel-air ratio are varied. The engine is connected to a dynamometer and power output at light knocking intensity is measured for a series of fuel-air ratios running from lean to rich.

The dynamometer measures the work available at the crankshaft, in units of *brake mean effective pressure* (BMEP). However, another unit – *indicated mean effective pressure* (IMEP) – is more

2 This is the test used to determine the "M" in the (R + M)/2 antiknock index posted on motor gasoline pumps at service stations.

#### Chapter 9

# Aviation Gasoline Specifications and Test Methods

indicative of fuel performance. "Indicated," in this context, refers to the gross work done on the piston by the expanding combustion gases. The difference between IMEP and BMEP – between gross work at the piston and net work at the crankshaft – is the work done to pump gases in and out of the cylinder and to overcome friction in the engine. These work losses are independent of fuel quality; they are functions of the engine and its mechanical condition. In practice, BMEP is measured and then fuel flow is shut off while the work losses are measured. The work losses are added to BMEP to obtain IMEP. Figure 9.3 is a typical curve obtained for a fuel by D 909. It plots IMEP vs. fuel-air ratio at light knocking intensity.

Primary reference fuels are run under the same conditions to obtain curves that bracket the curve of the test fuel. The rich-mixture supercharge rating of the test fuel is determined by interpolating between the bracketing reference fuel curves. The interpolation is performed at the fuel-air ratio that maximizes power output of the reference fuel with the lower rating.

The primary reference fuels are the same as those used for the motor octane method (D 2700). One set is blends of n-heptane and isooctane. The supercharge rating of a fuel in this set is defined as equal to the volume percent of isooctane it contains. The other set consists of blends of tetraethyl lead in isooctane. The supercharge rating of a fuel in this set is defined by the concentration of tetraethyl lead it contains.

For test fuels, the rich-mixture supercharge rating is reported as an octane number for ratings of 100 or less and as a performance number for ratings above 100. The method includes a table to convert concentrations of tetraethyl lead in isooctane in units of milliliters per U.S. gallon to performance numbers.

Since this use of two scales – octane number and performance number – can be confusing, an equation has been developed to convert rich-mixture supercharge octane numbers to performance numbers:

Performance Number = 
$$\frac{2800}{(128 - \text{octane number})}$$

Note that this equation indicates that performance numbers below 100 decrease more rapidly than octane numbers. A fuel with a supercharge octane number rating of 80 has a performance number of only 58.3.

#### **Distillation Profile**

30 percent, etc.

ASTM D 86 / IP 123 – *Test Method for Distillation of Petroleum Products*Avgas is a mixture of many individual hydrocarbons that have different boiling points.

Thus avgas boils or *distills* over a range of temperatures, unlike a pure compound, water, for instance, that boils at a single temperature. An avgas *distillation profile* is obtained by distilling the product under carefully defined conditions. The profile is a series of increasing vapor

temperatures for a fixed set of volume percentages evaporated – 5 percent, 10 percent, 20 percent,

Corps used a modification of this method that employed different speed and temperature settings and that used a thermal plug to determine knocking. The Air Corps method evolved into ASTM D 614, Standard Test Method for Knock Characteristics of Aviation Fuels by the Aviation Method. It was withdrawn in 1969, after a correlation had been developed between its results and those of D 2700. The current version of D 2700 includes a table to convert Motor octane numbers to aviation method (lean-mixture) ratings.

(History, continued from previous page)

In the late 1930s, the British first recognized the importance of specifying the antiknock rating of avgas under both lean-mixture and rich-mixture conditions. Following their lead, a CFR supercharge-rich mixture 3-C test was introduced in the United States in 1942. This method evolved into ASTM D 909, Standard Test Method for Knock Characteristics of Aviation Gasolines by the Supercharge Method, which was adopted in 1958.

Figure 9.3
Knock-Limited Power Curve
Obtained by ASTM D 909

In ASTM D 86, a 100 mL sample is placed in a round-bottom flask and heated at a rate specified for a sample with its vapor pressure characteristics. Vapor temperatures are recorded when the first drop of distillate is collected (*initial boiling point*), at recovered volumes of 5 mL, 10 mL, every subsequent 10 mL interval to 90 mL, 95 mL, and at the end of the test (*end point*). The amount of sample remaining in the flask at the end of the test and the amount lost during the test (both in volume percent) are, respectively, recorded and calculated. For avgas, the vapor temperature associated with each incremental volume percent recovered is converted to temperatures for each incremental volume percent evaporated by correcting for sample losses during the test. Figure 9.4 describes other avgas test methods.

Figure 9.4
Other Test Methods for Avgas

Many of the test methods described below have both ASTM and IP designations. In some cases the methods are equivalent, and either method can be used for specification compliance testing; however, this is not true in all cases. Refer to the appropriate specification for information about which test methods are required. Many of these ASTM and IP test methods have ISO equivalents.

Property	Standard Test Method	Description		
Density	ASTM D 1298 / IP 160 – Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method	Fuel is transferred to a cylindrical container and a hydrometer is carefully lowered into the cylinder and allowed to settle. After the temperature of the sample has equilibrated, the value on the hydrometer scale positioned at the surface of the sample and the sample temperature are recorded. The hydrometer value is converted to density at 15.6°C or API gravity at 60°F using standard tables.		
	ASTM D 4052 – Density and Relative Density of Liquids by Digital Density Meter	A small volume of a sample is introduced into an oscillating tube held at constant temperature. The change in oscillation frequency caused by the change in the mass of the tube is related to the density of the sample.		
Vapor Pressure	ASTM D 323 / IP 69 – Vapor Pressure of Petroleum Products (Reid Method)	A special cylinder with separate vapor and liquid chambers that can be joined together is used. The liquid chamber is filled with chilled sample and then immediately connected to the vapor chamber, which has been heated to 38°C (100°F). The assembled apparatus is immersed in a bath held at 38°C (100°F) until a constant pressure is observed. This pressure includes a contribution from air and water dissolved in the fuel.		
	ASTM D 5191 – Vapor Pressure of Petroleum Products (Mini Method) Referee Method	A chilled sample is introduced into an evacuated, thermostatically controlled chamber. The chamber and sample are heated to 38°C (100°F) and the resulting rise in pressure is measured. The sample size and chamber volume are chosen to duplicate the conditions of the Reid Method.		

Property	Standard Test Method	Description
Freezing Point	ASTM D 2386 / IP 16 – Freezing Point of Aviation Fuels	A sample is placed in a special jacketed tube fitted with a stirring rod and a thermometer. The tube is placed in a low-temperature bath and stirred as the sample cools. When crystals of hydrocarbon appear, the tube is removed from the cooling bath and allowed to warm up slowly with continuous stirring. The temperature at which the last hydrocarbon crystals are completely melted is recorded as the freezing point.
Sulfur	ASTM D 2622 – Sulfur in Petroleum Products by X-Ray Spectrometry	A sample is placed in a wavelength-dispersive X-ray spectrometer and the intensity of the sulfur X-ray fluorescence is measured and used to calculate the sulfur content of the sample.
	ASTM D 1266 / IP 107 – Sulfur in Petroleum Products (Lamp Method)	A sample is burned in a glass lamp equipped with a cotton wick. Burning converts the sulfur in the sample to sulfur oxides, which are subsequently converted to sulfuric acid by bubbling the combustion gases through a solution of hydrogen peroxide. The amount of sulfuric acid formed is determined either by barium precipitation or titration.
Copper Strip Corrosion	ASTM D 130 / IP 154 – Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test	A polished copper strip is immersed in a sample for two hours at 100°C (212°F) and then removed and washed. The condition of the copper surface is evaluated qualitatively by comparing it to standards.
Net Heat of Combustion	ASTM D 3338 – Estimation of Net Heat of Combustion of Aviation Fuels	The net heat of combustion of a sample is estimated from its API gravity, aromatic content, and distillation profile. The estimate relies on a correlation developed for a wide range of fuels.
	ASTM D 4529 – Estimation of Net Heat of Combustion of Aviation Fuels	The net heat of combustion of a sample is estimated from its aniline point, density, and sulfur content. The estimate relies on a correlation developed for a wide range of fuels.
	ASTM D 4809 – Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter Referee Method	A weighed sample of fuel is placed in an oxygen bomb calorimeter under specified conditions. The fuel is ignited and the temperature increase of the calorimeter is used to calculate the heat of combustion.

Property	Standard Test Method	Description
Oxidation Stability	ASTM D 873 / IP 138 – Oxidation Stability of Aviation Fuels (Potential Residue Method)	A 100 mL sample is placed in a tared beaker inside a pressure vessel and heated to 100°C (212°F) under 700 kPa (100 psi) of oxygen for five hours. The bomb is then cooled to room temperature and the pressure is released. The oxidized fuel is filtered through a tared sintered glass crucible. The residue in the crucible is weighed and reported as insoluble gum in mg/100 mL. The fuel is then evaporated to dryness in a tared beaker and any residue is weighed and reported as soluble gum in mg/100 mL. The potential gum is the sum of the soluble gum and insoluble gum.
Water Reaction	ASTM D 1094 / IP 289 – Water Reaction of Aviation Fuels	A sample is shaken with an aqueous buffer solution in a clean glass cylinder at ambient temperature and then allowed to stand to let the mixture separate into hydrocarbon and aqueous phases. After five minutes of standing, the change in volume of the aqueous layer is measured. The appearance of the hydrocarbon/aqueous interface is also examined for the presence of bubbles or film.
Electrical Conductivity	ASTM D 2624 / IP 274 – Electrical Conductivity of Aviation and Distillate Fuels	A sample is placed in a cell containing two electrodes. A voltage is applied across the electrodes and the resulting current is expressed in terms of the conductivity of the sample.
Lead Content	ASTM D 3341 / IP 270 – Lead in Gasoline – Iodine Monochloride Method	A sample is shaken with aqueous iodine monochloride solution, which converts tetraalkyl lead compounds to water-soluble dialkyl lead compounds. The aqueous phase is separated from the fuel and evaporated. Digestion with nitric acid converts the dialkyl lead compounds to inorganic lead compounds. The digestion residue is dissolved in a buffer and the lead content is determined by titration with EDTA using xylenol orange indicator.
	ASTM D 5059 – Lead in Gasoline by X-Ray Spectrometry	A sample is placed in an X-ray beam and the intensity of the lead X-ray fluorescence is measured. The concentration of lead is determined by a previously prepared calibration curve. Bismuth may be used as an internal standard to improve precision.
Color	ASTM D 2392 – Color of Dyed Aviation Gasolines	A sample's hue and color intensity are compared to those of colored-glass standards.

# 10 · Aviation Gasoline Composition

Aviation gasoline (avgas) is a mixture of many different hydrocarbon compounds. (See Appendix B) But not just any hydrocarbons will do. The specification requirements, especially for antiknock and volatility (Chapter 9), impose rather severe limitations on the compounds that can be used in avgas.

# **Composition**

#### **Carbon Number Distribution**

First, the distillation and vapor pressure requirements limit the boiling points and, therefore, the molecular weights or carbon numbers of the hydrocarbons. The carbon numbers range from about four (butane) to ten, with the most prevalent carbon number being eight, as shown in Figure 10.1.

# Classes of Hydrocarbons

Second, other requirements limit the hydrocarbons predominantly to the isoparaffinic and aromatic classes. Figure 10.2 explains why. For hydrocarbons in the avgas carbon number range, it shows the potential contribution of each class to three important avgas performance properties. Because the properties of isoparaffins correspond well to the three chosen avgas properties, isoparaffins are very beneficial. Aromatics are beneficial for antiknock properties but detrimental for low-temperature fluidity. Naphthenes, in general, are neutral to detrimental. Normal paraffins, except for butane, are very detrimental.

Figure 10.2 Potential Contribution\* of Each Hydrocarbon Class to Selected Avgas Properties (For hydrocarbons in the avgas carbon number range)

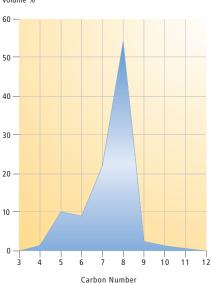
Avgas Property	n-Paraffin	Hydrocarb Isoparaffin	on Class Naphthene	Aromatic
Lean-mixture antiknock		+/++	0/-	+/++
Rich-mixture antiknock		+	0/—	++
Low-temperature fluidity	-	+/++	0/+	-

<sup>&</sup>quot;+" indicates a beneficial effect, "0" a neutral or minor effect, and "-" a detrimental effect.

# **Property/Composition Relationships**

For mixtures, the values of some properties are weighted averages of the property's values for all the individual components. Properties that obey this relationship are called *bulk* properties. Density is a bulk property; to a first approximation, the density of a mixture is the volume average of the densities of all the components.<sup>1</sup>

Figure 10.1



**Typical Avgas Carbon Number Distribution** Volume %

<sup>1</sup> This is a very good approximation when all the components of a mixture are chemically similar, e.g., a mixture of hydrocarbons. It is not as good when some of the components are chemically very different from the rest, e.g., a mixture of alcohols and hydrocarbons.

The values of other properties are determined by components present in small or trace amounts, typically less than 1000 ppm, and often less than 100 ppm, and are not reflective of the bulk composition of the mixture.

Figure 10.3 shows which of the important avgas properties are bulk properties and which depend on the presence or absence of trace amounts of components. The trace components may be present in the hydrocarbon base fuel as manufactured or come from another source, such as additives or contaminants.

Figure 10.3
Relationship of Avgas Properties to Composition

Property	Relation to composition	Property	Relation to composition
Energy content	Bulk	Stability	Trace
Knock resistance	Bulk*	Corrosivity	Trace
Distillation range	Bulk	Cleanliness	Trace

<sup>\*</sup> Bulk property of hydrocarbon components; trace property of tetraethyl lead antiknock additive.

# **Additives**

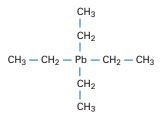
Additives are hydrocarbon-soluble chemicals added to a product in small amounts to enhance or maintain properties of fuel performance or fuel handling.

Typically, additives are derived from petroleum based raw materials and their function and chemistry are highly specialized. They produce the desired effect at the parts per million (ppm) concentration range. (One ppm is 0.0001 mass percent.)

Only additives specifically approved by the specification may be used in avgas. The approved additives are identified by their chemical formulas. For the leaded grades of avgas, tetraethyl lead additive and the identifying dye are mandatory; antioxidant, anti-icing, and electrical-conductivity additives are optional.

#### Antiknock Additive

The most important avgas additive is tetraethyl lead. It is added as part of a mixture that also contains ethylene dibromide and dye. Ethylene dibromide acts as a scavenger for lead. When avgas is burned in an engine, the lead in tetraethyl lead is converted to lead oxide. Without a scavenger, lead oxide deposits would quickly collect on the valves and spark plugs. If the deposits become thick enough, they can damage the engine. Ethylene dibromide reacts with the lead oxide as it forms and converts it to a mixture of lead bromide and lead oxybromides. Because these compounds are volatile, they are exhausted from the engine along with the rest of the combustion



tetraethyl lead

$$Br-CH_2-CH_2-Br$$

ethylene dibromide

# **Aviation Gas Composition**

products. Just enough ethylene dibromide is added to react with all of the lead. However, because the reaction does not quite go to completion, a small amount of lead oxide deposit is found in the cylinders of aircraft piston engines.

## Icing Inhibitor

Icing inhibitors are used to prevent the formation of ice in the fuel system. Either of two additives is allowed, isopropanol or di-ethylene glycol monomethyl ether (di-EGME). Generally, icing inhibitors are not added to avgas when it is manufactured. They are used at the discretion of the aircraft owner/operator. Since isopropanol is more expensive than di-EGME and it can also reduce the knock rating of the fuel, possibly to below the specification minimum, di-EGME is used more often when an icing inhibitor is required.

#### **Antioxidants**

Antioxidants, also called *oxidation inhibitors*, suppress the formation of peroxides and hydroper-oxides, soluble gums, and insoluble particulates in a fuel. These by-products are formed by multistep reactions, some of which – perhaps including the initiating ones – are oxidation reactions. Antioxidants interrupt the chain of oxidation reactions that lead to formation of gums and sediment. Fuels containing olefins are much more susceptible to forming the above by-products because olefins react more readily with oxygen than the other classes of hydrocarbons.

## Dyes

Dyes are used to color-code the different grades of avgas so they can be visually distinguished from one another and from other fuels. This is a safety measure to prevent misfueling of an aircraft.

The use of dye in avgas dates back at least to World War I. Two grades of avgas were in use then, Domestic Aviation Grade and Fighting Grade. The Fighting Grade was dyed red to distinguish it from the aviation grade.

## **Electrical-Conductivity Additive**

As a safety precaution, Stadis® 450 may be added in concentrations up to 3 mg/L to improve the electrical conductivity of avgas (*see page 53*). Conductivity additives are often referred to as *static dissipator* additives (SDA). Since a fuel treated with this additive may lose electrical conductivity over time, retreatment with the additive is allowed up to a maximum cumulative total of 5 mg/L. If avgas is treated with electrical-conductivity additive, its conductivity must be between 50 CU and 450 CU at the point of use.

# **Corrosion Inhibitors**

Corrosion inhibitors were approved for use in the military avgas specification. They were recently re-introduced into D 910 to control corrosion in the distribution system. These additives contain a polar group that adheres to metal surfaces, forming a thin film of the additive. These additives are usually carboxylic acids whose composition is proprietary.

#### di-EGME

di-ethylene glycol monomethyl ether (di-EGME)

2,6-ditertiary butyl-4-methyl phenol

# 11 · Aviation Gasoline Refining

Originally motor gasolines, and consequently, aviation gasolines (avgas), were manufactured by distilling petroleum crude to obtain a distillate with the desired boiling range. In the parlance of petroleum refining, distillates obtained directly from crude are called *straight-run* distillates. The hydrocarbon composition of a straight-run distillate and, therefore, its octane number, is determined by the composition of the crude. In terms of avgas requirements, all straight-run gasoline distillates have low octane numbers – in the 50 to 70 range. Crudes containing a relatively high proportion of aromatic hydrocarbons – *aromatic* crudes – yield straight-run gasoline distillates with higher octane numbers than *paraffinic* crudes.

The development of higher performance aircraft engines created the need for higher octane avgas. In the 1930s, two refining processes capable of producing higher octane number components came into use: catalytic cracking and alkylation. Both catalytically cracked gasoline and *alkylate* were used extensively in avgas during World War II.

The olefins that give catalytically cracked gasoline its high octane number tend to gradually oxidize to form gums and sediments. Catalytically cracked gasoline can be stabilized with antioxidants, but its poorer stability makes it a less desirable avgas component than alkylate.

## **Alkylation**

The *alkylation* process was developed in the 1930s specifically to produce an avgas component with high antiknock ratings. Isobutylene is reacted with isobutane in the presence of a strong acid to yield higher molecular weight, higher boiling isoparaffins, mainly trimethylpentanes. The predominant isomer is 2,2,4-trimethylpentane (isooctane), which, by definition, has an octane number of 100. The product of the alkylation process is called alkylate.

Usually the olefin feed is not pure isobutylene. The feed typically comes from the catalytic cracking process and may contain propylene, other isomers of butene, and isomers of pentene. Thus, while eight-carbon-number isomers predominate, the product may contain isoparaffins with carbon numbers from 7 to 12, or even higher, depending on feed composition and reaction conditions.

Higher carbon number isoparaffins are less desirable for avgas because of their lower octane numbers and higher boiling points. So, refineries producing avgas may distill the alkylate into two cuts: light alkylate or rerun alkylate, containing isoparaffins with nine carbons or fewer for avgas blending, and heavy alkylate.

Alkylate is a very important blending component of today's reformulated motor gasolines because of its relatively low vapor pressure, high octane number, and near-zero content of sulfur, aromatics, and olefins. Thus motor gasoline and aviation gasoline compete for alkylate in some refineries.

# **AVGAS Blending**

Today, avgas is a highly refined product specifically manufactured to meet the demanding performance requirements of aircraft engines. Avgas specifications make it difficult to meet all the requirements with a single refinery stream, even one such as light alkylate produced specially for avgas. So avgas, like motor gasoline and most other refinery products, is usually produced by blending two or more components to achieve the desired properties.

Grades 100 and 100LL avgas are based on alkylate. As such, it is mainly a synthetic product – few of the compounds in avgas come directly from crude oil. Toluene is often added to Grade 100LL to help meet the rich-mixture antiknock requirement. Grade 80 avgas may contain some straightrun gasoline distillate that has been subjected to additional purification after distillation, because of the lower antiknock requirements of this grade. Light hydrocarbons, such as butane or isopentane, typically are added to all grades to meet the minimum vapor pressure requirement. Finally, additives are added: the required concentration of the appropriate tetraethyl lead/ethylene dibromide/dye mixture plus any of the optional additives the refiner chooses to use (*see page 64*).

# 12 · Aircraft Piston Engines

There were tremendous advances in aircraft internal combustion (*piston*) engines from the beginning of powered flight in 1903 until the end of World War II. Engine power and reliability increased dramatically, while the important weight-to-power ratio fell steadily. Developments in engine design made since the end of World War II have resulted in continuous improvement in thermal efficiencies and fuel consumption in modern engines. This has allowed the development of high-performance aircraft to meet today's market demands.

This chapter will examine this type of engine in some detail. A relatively small number of two-stroke-cycle engines also have been used in aircraft. Diesel engines were used occasionally in the early years of aviation, and are getting a second look today. At least two manufacturers are developing diesel engines for aviation use. These engines would use jet fuel, which is similar to a light diesel fuel. This development is driven by a desire to move away from use of leaded avgas for a variety of reasons including environmental impact, reliability of supply, and price.

# **Internal Combustion Engines**

## Terminology

An internal combustion engine burns fuel in an enclosed chamber – the *cylinder* – which is integral to the engine. Most aviation piston engines are of the reciprocating piston type in which a piston moves back and forth in a cylinder. The engine's power is generated by the force exerted on the piston by the rapid expansion of gases resulting from the combustion of a compressed fuel-air mixture. The power from the motion of the piston is transmitted through a connecting rod to a crankshaft, which is coupled to the propeller.

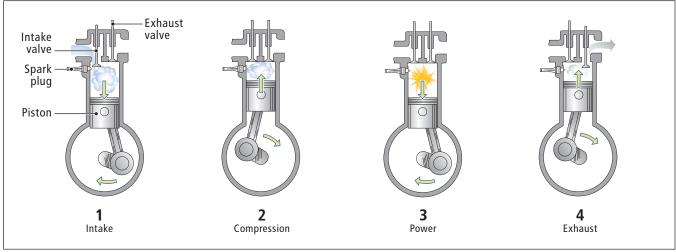
One complete movement of the piston in either direction is called a *stroke*. A piston at the point of its nearest approach to the cylinder head is at *top dead center* (TDC). Conversely, a piston at the other end of its stroke is at *bottom dead center* (BDC). The region of a cylinder below the piston crown at TDC and above it at BDC is the *swept volume*. An engine's *displacement* is the total swept volume of all cylinders. The *compression ratio* of an engine is the ratio between the volume in a cylinder when the piston is at BDC and the volume of the cylinder when the piston is at TDC. *Valves* are used to control gas flow into or out of the cylinder volume above the piston.

# Four-Stroke Combustion Cycle

One combustion cycle is made up of four piston strokes, which turn the crankshaft through two complete rotations (720 degrees). Figure 12.1 pictorially summarizes the four strokes - intake, compression, power, and exhaust. The first downward motion of the piston in the cycle – the *intake* stroke – draws the fuel-air mixture into the combustion chamber through the open intake valves. As the piston reverses direction and begins to move back up, the intake valves close. This upward motion of the piston is the *compression* stroke. Compression raises the pressure and temperature of the mixture. Near the top of the compression stroke, the spark plug produces a spark, igniting the mixture. The mixture burns and expands, which drives the piston downward for the third, or *power*, stroke. As the piston reaches BDC and begins to move back up again, the

exhaust valves open, beginning the *exhaust* stroke. The upward motion of the piston pushes the burned gases out of the engine into the exhaust manifold and eventually out the exhaust pipe.

Figure 12.1
Four-Stroke-Cycle Engine



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# Air System

Air is drawn into the engine through the intake system. It passes though an air filter to keep dust and contaminants out of the engine. A throttle (a disk attached to a rotatable shaft) is mounted in the air intake to control airflow. When the pilot opens the throttle, the disk tilts, allowing more air to enter the engine. With more air, the engine can use more fuel and produce more power to take off or climb.

An engine that uses intake air at atmospheric pressure is said to be *naturally aspirated*. The amount of air a naturally aspirated engine can use is limited by the local air density (barometric pressure) and pressure losses in the intake system. To get more air into an engine (boost the air pressure), small compressors are sometimes used to pressurize the intake air. If the compressor is driven off the engine crankshaft, the process is called *supercharging*. Another way to power the compressor is to put it on a common shaft with a turbine driven by the engine's exhaust gas. This process is called *turbocharging*. To maintain boost pressure at a relatively constant amount over a wide range of engine speeds, some sort of pressure regulation is needed. Turbocharging is preferred since it extracts energy from exhaust gases that would otherwise be wasted, so it is more efficient than supercharging, which takes energy from the crankshaft.

Since air density decreases along with atmospheric pressure as altitude increases, less and less air is drawn into a naturally aspirated engine as an aircraft climbs. This limits the maximum speed and altitude that can be achieved. This limitation was recognized even before World War I, but

#### Abnormal Combustion Phenomena

Chapter 8 described spark knock, the type of knocking involving the autoignition of the fuel-air mixture ahead of the flame front. But there are other abnormal combustion phenomena.

Surface ignition involves the ignition of the fuel-air mixture by a hot spot rather than by the spark. The hot spot ignites a portion of the mixture before it would normally burn. Potential ignition sources include: glowing combustion chamber deposits, sharp edges or burrs in the combustion chamber, or an overheated spark plug electrode. Heavy, prolonged spark knock can generate hot spots that produce surface ignition.

Surface ignition may occur either before or after spark ignition. Surface ignition before the spark is called preignition. When preignition occurs, ignition timing is lost and the upward movement of the piston is opposed by the 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 preignition is caused by a hot spot generated by prolonged, heavy spark knock, it is known as knock-induced preignition. It has the same adverse effect on engine operation as preignition from other sources. Knock-induced preignition is the most damaging side effect of spark knock.

(continued next page)

turbochargers were not developed until the mid-1920s. They were so successful that naturally aspirated engines were virtually obsolete in high-performance aircraft by the early 1930s.<sup>1</sup>

#### Carburetion

In the intake system of an engine, air mixes with a small amount of vaporized fuel to produce a homogeneous fuel-air mixture. The carburetor is the most successful of the many devices developed to discharge the correct amount of fuel into the intake air stream. The heart of a carburetor is a *venturi* – a converging-diverging nozzle. The diameter of the nozzle decreases to a minimum at the throat and then increases to the discharge end. As air passes through the venturi, its velocity increases up to the narrowest portion (throat) because the cross-sectional flow area decreases. As the air velocity increases, its pressure decreases, creating a vacuum that draws fuel out of the carburetor's fuel bowl through a tiny orifice called a *jet*. Additional jets are used to enrich the mixture during acceleration and to supply sufficient fuel at idle. A hand-operated primer is used on many engines to enrich the mixture for cold starts.

Carburetors do not control fuel flow precisely enough for critical or high-performance applications. In part this is because they are volume-flow based and difficult to calibrate for all operating conditions.

#### **Fuel Injection**

The second major type of fuel system design is the *fuel injection* system. Fuel injectors are mounted at the intake port of each cylinder, where they spray fuel onto the intake valves. To enrich the mixture during cold starts, an additional cold-start injector may be used. This injector adds additional fuel to the intake air for a short period of time while the engine warms up.

The primary advantage of fuel injection is more uniform fuel distribution to each cylinder compared to carburetion. Fuel-injected engines also respond more rapidly than carbureted engines when the pilot changes control settings. An additional advantage is the elimination of carburetor icing (*see page 49*). Disadvantages of fuel injection compared to carburetion are increased complexity, more moving parts, very narrow passages in an injector that may become plugged, and higher vapor lock tendencies.

Fuel injection systems used in general aviation are generally not as sophisticated as those used in modern automobile engines. They operate at lower pressure and provide a continuous flow of fuel to the intake ports, rather than the solenoid-actuated, timed injection typical of automobile systems.

The aircraft system uses an engine-driven fuel pump and typically includes an auxiliary electric fuel pump, which provides vapor suppression and backup for the engine driven pump. Fuel filters are installed both upstream and downstream of the main pump to remove particulate matter from the fuel that could cause injector plugging. A diaphragm pressure regulator maintains pressure and routes excess fuel back to the fuel tank on some systems.

# **Aircraft Piston Engines**

# **Engine Configurations**

Aircraft piston engines have been built in several different configurations. The in-line and "V" engines are very similar to those used in automobiles. Some early designs had separate cylinders to minimize weight; most later designs used the familiar engine block. As a rule, these usually were water cooled because the integral cylinder blocks are ideally suited to liquid cooling.

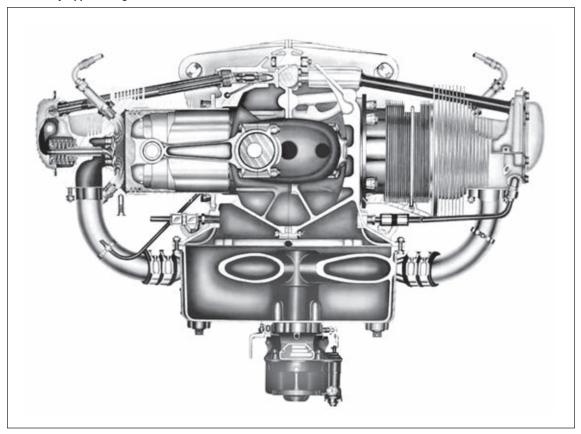
The radial engine configuration is unique to aviation. Here the crankshaft is in the circular centerpiece of the engine and the cylinders radiate out from it in a plane perpendicular to the crankshaft. In this design, each cylinder gets equal airflow, so most radials are air cooled. An interesting early design is the rotary engine, in which the engine block rotates about a fixed crankshaft.

Horizontally opposed engines are the third major configuration. These can be considered an extreme example of a "V" engine, in which the angle between the pistons is 180 degrees, as illustrated in Figure 12.2. The cylinders lie in a plane roughly parallel to the wings. Most horizontally opposed engines are air cooled. Horizontally opposed engines have been used in almost all small aircraft built since World War II.

(Abnormal, continued from previous page)

Surface ignition after the spark is postignition. Postignition reduces the combustion time, and a loss of combustion control can cause knock, engine roughness, and reduced power output. The extent of its effect depends on its location in the combustion chamber and the point in the cycle at which it occurs.

Figure 12.2
Horizontally Opposed Engine



# **Engine Development**

The engine that powered the Wright brothers' flight in 1903 was built to their design. It was a four-cylinder, in-line engine with an aluminum block to minimize weight. It weighed 179 pounds, had a displacement of 200 cubic inches, and produced 12 horsepower (hp) at 1090 revolutions per minute (rpm). In a few years this design was improved to yield engines of the same weight that delivered about 30 hp.

Engines delivering 100 hp were available within 10 years, and 1000 hp was achieved by the mid-1930s. By the end of World War II, engines delivering 3000 hp were in use. Figure 12.3 lists data for some representative engines.

In *A History of Aircraft Piston Engines*,<sup>2</sup> Smith lists more than 500 different engines. While not all of these went into production (or in a few cases, even left the ground), the number indicates the magnitude of the effort that went into developing more powerful and reliable engines while keeping weight to a minimum.

Figure 12.3
Engine Data Representative of the Development of Aircraft Piston Engines

Engine	Year	Design	Coolant	Number of Cylinders	Displacement, cubic inches	Horsepower (hp)	Weight, lbs	lb/hp
Wright	1903	In-line	Liquid	4	200	12	179*	14.9
Anzani	1910	Radial	Air	3	190	30	121	4.0
Gnome	1908	Rotary	Air	7	488	50	165	3.3
Bentley BR2	1918	Rotary	Air	9	1522	230	500	2.2
Rolls-Royce Condor	1918	"V"	Liquid	12	2138	650	1300*	2.0
Wright J-5 Whirlwind**	1925	Radial	Air	9	788	220	510	2.3
Rolls-Royce Merlin	1936	"V"	Liquid	12	1650	1030	1320*	1.3
Mercedes-Benz D-B 601	1938	"V"	Liquid	12	2069	1360	1540*	1.1
Napier Sabre	1940	"V"	Liquid	12	2240	2200	2500*	1.1
Allison V-1710	1941	"V"	Liquid	12	1710	1250	1595*	1.3
Pratt & Whitney R-4360	1945	Radial	Air	28	4360	3000	3600	1.2
Continental O-200	1959	Opposed	Air	4	201	100	188	1.9
Lycoming O-540	1959	Opposed	Air	6	542	250	396	1.6
Lycoming XR-7755	mid-1940s	Radial	Liquid	36	7755	4000	6050*	1.5
Lycoming IO-540-K	1960s	Opposed	Air	6	542	300	443	1.5
Lycoming TIO-540-J	1960s	Opposed	Air	6	542	350	518	1.5

<sup>\*</sup> These weights do not include the weight of liquid coolant, heat exchangers, and/or other accessories.

<sup>\*\*</sup> This engine powered the Spirit of Saint Louis in Charles Lindbergh's historic flight from New York to Paris in 1927. Sources: A History of Aircraft Piston Engines, Herschel Smith and Jane's All the World's Aircraft.

# **Aircraft Piston Engines**

As an example of this progress, compare a World War I Liberty engine to a World War II Rolls-Royce Merlin. Both had displacements of 1650 cubic inches, but the Liberty was rated at 400 hp, while the Merlin was capable of delivering 2200 hp. Improvements in engine design and fuel contributed approximately equally to this increase in power.<sup>3</sup> Most World War I fuels had a lean-mixture rating in the 50- to 70-octane number range, while the World War II Grade 115/145 plus water-alcohol injection yielded a rich-mixture rating of 175 performance number.

The development of more powerful piston engines came nearly to a halt with the successful introduction of turbine engines during World War II. Now the higher performance aviation applications use turbine power and the piston engine is used mainly for small aircraft.

# Appendix A • Aviation Fuel Distribution and Handling

# **Fuel Distribution System**

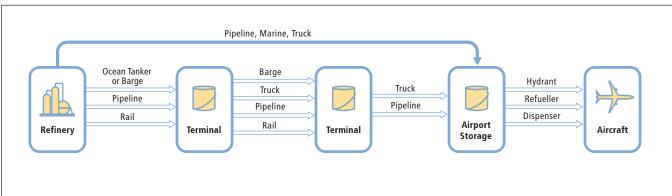
A batch of aviation fuel produced at a refinery is tested to ensure that it meets all of the applicable specification requirements. It must then be moved to an airport, and finally, pumped into the tank of an aircraft. The fuel may be shipped directly to an airport fuel storage facility, but usually the distribution chain includes one or more intermediate storage facilities (terminals), as illustrated in Figure A.1. Several modes of transportation may be used: pipeline, ship, barge, railroad tank car, and tanker truck, but not all modes are available for every destination. Quality checks are performed on the fuel at each point in the distribution system to guard against contamination.

## **Pipelines**

Pipelines are best suited for transporting large volumes of fuel. Batch shipments (*tenders*) of a product commonly exceed 400,000 gallons (10,000 barrels). For this reason, aviation turbine fuel (*jet fuel*) is commonly moved by pipeline. Aviation gasoline<sup>1</sup> (*avgas*) is usually moved by truck, railcar, or barge because of its smaller volumes.

Some refineries have dedicated<sup>2</sup> jet fuel pipelines running directly to nearby airports. However, jet fuel is often shipped via common-carrier multiproduct pipelines. That is, the pipelines are available to all shippers that meet their product quality requirements, and they handle tenders of different petroleum products, usually in a predetermined repetitive sequence.

Figure A.1
Jet Fuel Distribution System



- 1 Another reason to exclude avgas from multiproduct pipelines is the possibility that it could contaminate adjacent tenders of other products with lead. The U.S. Environmental Protection Agency requires that the lead content of motor gasoline not exceed 0.05 g/U.S. gal.
- 2 A dedicated system is one reserved exclusively for a single product. It has no interconnections to other pipes or storage tanks after the point where batches of fuel are isolated and tested for conformance to specification.

A tender may be produced by a single refiner, or it may be the aggregate of product from several refiners.<sup>3</sup> Adjacent tenders of different products usually are not physically separated from one another; the trailing interface of one tender is the leading interface of the next. The intermixing that occurs as the tenders move through the pipeline is confined to a well-defined zone. Heart cuts of the tender may be diverted to terminals along the route of the pipeline. At the terminus of the pipeline, the intermixture (*transmix*) may be segregated and returned to a refinery for reprocessing. More commonly, it is split among the adjacent tenders or incorporated into the tender of the less sensitive (non-aviation) product. The products remain on-test because the transmix volume is a small fraction of the tender volume and because the product sequence is chosen to minimize the differences between adjacent products (*see Figure A.2*).

When jet fuel is passed through a pipeline, it will typically become contaminated to some degree with particulate matter and water. Consequently, jet fuel tenders must be cleaned up at their destination.

#### Other Modes

Ships, barges, rail tank cars, and tank trucks are compartmentalized, so in cases of multiproduct transport, different products are physically prevented from intermixing. In some cases, the compartments are dedicated to a single product. In other cases, care must be taken to bring the residue of the product previously transported in a compartment to an acceptable level before a shipment of aviation fuel is loaded.

#### Intermediate Terminals

As noted, in a few cases aviation fuels are transported directly from a refinery to an airport. But more commonly they are distributed by a large multiproduct pipeline or ship or barge to an intermediate terminal from which they are transshipped to nearby airports. Transshipment may employ a smaller dedicated pipeline or tank trucks.

#### Storage Tanks

Aviation fuel storage tanks are typically designed to minimize the effects of particulate and water contamination that occur during fuel transfer, as illustrated in Figure A.3. Tanks have a low point on the bottom, a *sump*, where water and particulate are collected and removed. Tanks also use *floating suction* to draw fuel off the top of the tank rather than the bottom where water and particulate concentrate. This, along with adequate settling time, helps prevent some of the particulates and water from being transferred further into the distribution system.

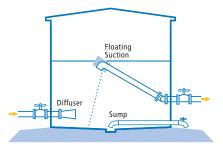
Figure A.2

Typical Multiproduct

Pipeline Product Sequence

Unleaded regular gasoline
Unleaded midgrade gasoline
Unleaded premium gasoline
Unleaded midgrade gasoline
Unleaded regular gasoline
Jet A
High-sulfur diesel fuel (dyed red)
Low-sulfur diesel fuel (undyed)
(Cycle repeats)

Figure A.3
Fuel Storage Tank



<sup>3</sup> The industry uses the term fungible to describe products whose batches are interchangeable because they are made to the same specification, although they may be produced at different refineries operated by different companies.

# **Receiving Fuel at Airports**

A very important step in the fuel distribution system is receipt into airport storage. As fuel is received, tests are conducted to confirm the identity of the fuel and also check for water and particulate contamination. At large airports, fuel is typically filtered both going into airport storage tanks and also going out of these tanks before being delivered to aircraft.

The Joint Inspection Group (JIG), a group of international fuel suppliers who jointly operate aviation fuel facilities at airports, has developed joint guidelines for receipt of fuel into storage and operation of airport depots. These guidelines are used mainly outside the United States.

In the United States, the Air Transport Association of America (ATA) Specification 103 covers jet fuel quality control at airports. These two documents are not identical, although there are plans to harmonize them.

#### Airport Fuel Dispensing

After the fuel reaches an airport's storage tanks, there are three ways of delivering it to aircraft: *hydrant* system (jet), *refueler* truck (avgas or jet), or a *dispenser* (avgas or jet). The hydrant system is used to fuel jet aircraft at most large commercial airports. A network of underground pipes connects the storage tanks to each gate. A hydrant unit, either a truck or cart, equipped with filtration and volume metering equipment, is used to fuel an aircraft. Hose connections are made between the hydrant and the unit, and the unit and the aircraft. Hydrant trucks typically are equipped with filter/separators or water-absorbing media to provide a final barrier to particulate and water contamination before fuel enters the aircraft's tanks.

The dispenser and refueler are used at smaller airports. Both have pumping, filtration, and volume metering equipment. A refueler truck carries fuel to an aircraft. A dispenser is a pump at a fixed location, similar to the familiar system used to deliver motor gasoline to cars but designed specifically to fuel aircraft.

# Regulations

Because petroleum products are both flammable and potential air and water pollutants, their distribution and storage are controlled by a multitude of regulations developed and administered by a variety of regulatory agencies. Figure A.4 is a partial listing of the subjects addressed by regulations. The operator of each facility has the responsibility to understand and comply with all pertinent regulations.

# Figure A.4

A Partial List of Subjects Addressed by Regulations Applicable to the Distribution and Storage of Aviation Fuels

Transportation of hazardous materials

Fire protection

Tank overfill prevention

Corrosion protection and release detection (underground storage tanks)

Protection of subsurface and navigable waters

Control of air emissions

Control of wastewater discharges

Storage, transportation, and disposal of hazardous waste

Safety and health of employees and adjacent communities

**Emergency response procedures** 

# **Contamination and Cleanup**

#### Contamination

On its journey from refinery to aircraft fuel tank, aviation fuel will spend time in storage tanks and also be transferred one or more times. Each time a transfer occurs, there is a potential for contamination of the fuel to occur. Particulate matter and water are the most common fuel contaminants. Other sources of contamination include: other petroleum products, surfactants, microbes, and dye. This section will describe each type of contamination briefly, and the procedures and equipment used to remove contaminants from aviation fuel.

Particulate Matter The dominant source of particulate matter is the solid corrosion products that slough off steel pipes and tanks (rust and scale). While protective coatings are being applied to the interior surfaces of more and more tanks, particularly those in critical service, the predominance of steel in industry facilities and the universality of water as a contaminant ensure that almost any distribution process will result in some rust contamination. Other sources of particulate matter are: refinery processing materials (catalyst fines and salts); airborne solids that enter through tank vents or slip past the seals of floating roof tanks (dust and pollen); solids from damaged hoses and filters (rubber particles and fibers); and solids from microbial infestation (cellular debris and microbial by-products).

**Water** Water in aviation fuels comes from a number of sources. Many refining processes employ water or steam, either directly or as heat exchanger coolant. Any free water picked up during processing is removed before the fuel leaves the refinery.

Because most pipelines are buried, tenders tend to be cooled during transmission. Cooling will cause droplets of free water to form if the jet fuel was close to being saturated with water when it was injected into the pipeline. Even if the jet fuel was dry on injection, it may pick up free water deposited in low spots in the pipeline by the tenders of other products.

Rain water may leak by the seals in floating-roof tanks. Water in moist air may condense in fixed-roof storage tanks, which must be vented. Air flows in and out of a fixed-roof tank as product is added or removed and as the air above the product expands or contracts in response to changes in ambient temperature. When warm, moist air enters during the day and is cooled at night, water may condense and "rain" into the fuel. The amount of water generated by the process depends on the relative humidity of the air and the difference between day and night temperatures; it can be significant for tanks where the climate is humid.

Other Petroleum Products If a batch of aviation fuel is contaminated with enough of another petroleum product to move one or more of the specification requirements off-test, there is no remedy. The batch must be returned to a refinery for reprocessing. So, aviation fuel lines and tanks are rigorously segregated from lines and tanks containing other products in the refinery and in the distribution chain.

There are situations in which small amounts of product mixing may occur:

- At the interface separating two products in a pipeline.
- When aviation fuel is loaded into a compartment of a vessel or truck that previously contained a different product.

These situations can be managed by keeping the relative amount of contamination small enough that it doesn't significantly alter the specification properties. However, even small amounts of contamination can be a problem for aviation fuels if the other product is dyed or contains additives or impurities that, because they are surfactants, degrade water separability.

**Surfactants** Surfactants (*see page 29*) are polar organic compounds that can stabilize a fuel-water emulsion by reducing the interfacial tension. Surfactants can also degrade the ability of filter/ separators (*see page 81*) to remove water, because they, like water, are attracted to and stick to the hydrophilic surfaces of the coalescing medium. Thus the presence of surfactants could potentially allow free water in jet fuel.

Surfactants may come from refinery processing, but these are removed at the refinery by clay treatment before release. Surfactants from other products can adsorb on pipeline walls and pumping equipment in a multiproduct pipeline, and later desorb into jet fuel. Surfactants may also be introduced from soap or detergent used in equipment cleaning.

Fuel is regularly tested for the effect of surfactants on water separability throughout the distribution system using a device called a microseparometer (*microsep or MSEP*) (see page 83).

Microbes Aviation fuels are sterile when first produced because of the high refinery processing temperatures. But they become contaminated with microorganisms that are omnipresent in air and water. Microorganisms found in fuels include bacteria and fungi (yeasts and molds). The solids formed by microbial growth are very effective at plugging fuel filters. Some microorganisms also generate acidic by-products that can accelerate metal corrosion.

Since most microorganisms need free water to grow, microbial growth usually is concentrated at the fuel-water interface, when one exists. Some organisms need air to grow (aerobic organisms), while others grow only in the absence of air (anaerobic organisms). In addition to food (fuel) and water, microorganisms also need certain elemental nutrients. Jet fuel can supply most of these; phosphorus is the only one whose concentration might be low enough to limit microbial growth. Higher ambient temperatures also favor microbial growth.

Microbial contamination in avgas is much less common than with jet fuel, although it does occur. Presumably, the lower occurrence in avgas is due to the toxicity of tetraethyl lead.

The best approach to microbial contamination is prevention. And the most important preventive step is keeping the amount of water in the fuel storage tank as low as possible. Biocides can be

used when microorganisms reach problem levels. But biocides have their limits. A biocide may not work if a heavy biofilm has accumulated on the surface of the tank or other equipment, because then it doesn't reach the organisms living deep within the biofilm. In such cases, the tank must be drained and mechanically cleaned.

And even if the biocide effectively stops microbial growth, it still may be necessary to remove the accumulated biomass to avoid filter plugging. Since biocides are toxic, any water bottoms that contain biocides must be disposed of appropriately.

Dye In the United States, diesel fuel may be dyed red for one of two reasons: to identify high sulfur diesel fuel intended for non-highway applications in EPA regulations, or to identify fuel that is not subject to the federal excise tax in Internal Revenue Service (IRS) regulations. If a tender of red-dyed diesel fuel is transported next to a tender of jet fuel in a multiproduct pipeline, the interface between the products will contain some amount of dye. If the cut between the jet fuel and the interface is not made properly, some of the red dye will contaminate the jet fuel.

As mentioned in Chapter 4, only additives that are specifically approved may be added to jet fuel. The presence of red dye in this situation is considered an unapproved additive in jet fuel, apart from the small amount of diesel fuel contamination it represents. A visual test of jet fuel appearance is done throughout the distribution system. Any pink or red color resulting from dye contamination is grounds for rejection of the fuel.

An industry sponsored program was conducted to determine the effect of trace levels of red dye on jet fuel properties and also on the performance of critical turbine engine components. This testing showed that trace amounts of red dye caused a decrease in thermal stability as measured by the JFTOT and an increase in fouling rate in engine fuel system components. As a result of this testing the restriction on red dye remains in effect; any visible pink or red color resulting from dye contamination is grounds for rejection of the fuel.

A yellow marker dye is used in Europe (Solvent Yellow 124, sometimes called the Euromarker) to indicate the tax status of certain fuels. This same marker has been proposed to be added to home heating oil in the United States in 2006 to distinguish it from other fuels. Since the chemistry of the yellow marker is similar to that of red dye, it is likely that it will also have a detrimental effect on fuel thermal stability. And since the yellow marker is not as easily visible in jet fuel as red dye, contamination is not as easy to detect.

**Pipeline Drag Reducer** Drag reducers are very high molecular weight hydrocarbon polymers that improve flow in pipelines by reducing the formation of turbulent eddies. Significant increases in flow are possible with just a few ppm of drag reducer. This additive is commonly used in gasoline and diesel tenders in some pipelines, but it is not approved in jet fuel.

Some pipelines delivering jet fuel to airports are nearing full capacity and would like to be able to use drag reducer to meet increasing future demand. A program to evaluate these additives for possible use in jet fuel was initiated. It was found that the drag reducer affected fuel spray patterns in jet engine nozzles and made it impossible to ignite the fuel under certain conditions. Because of the serious safety implications of this finding, the project was stopped and drag reducers are not permitted in jet fuel. Multi-product pipelines that use drag reducer in gasoline and diesel must stop injection of the additive before the jet interface arrives and not restart until after the jet has passed.

#### Cleanup

Contamination with particulate matter, and to a lesser extent, with water is unavoidable during distribution. Therefore, the aviation fuel distribution system includes processes to remove these contaminants:

- Filtration to remove particulate matter
- Filter/separator, water-absorbing media, and salt drier to remove water
- Clay treatment to remove surfactants

One or more of these processes may be used at each stage in the distribution chain: at the refinery, at the inlet or outlet of terminal tanks, at the inlet or outlet of airport storage tanks, and in equipment dispensing fuel into aircraft.

**Filtration** Passing a petroleum product through a filter with a pleated paper or synthetic fiber medium removes solids with particle sizes larger than the pore size rating of the filter.<sup>4</sup> Typically, filters with a nominal pore size of five micrometers (*microns*) are used for avgas and one micron or two microns are used for jet. These filters are commonly called *pre-filters*, because they are typically used before filter/separators, or *micronic filters*, because they are rated by the size of particulate removed, e.g., two microns.

The filter elements are hollow cylinders that screw into a base plate in the filter vessel, as shown in Figure A.5. Clean fuel flows out of the center of the filter elements into the bottom of the vessel.

In most fuel cleanup systems, particulate removal precedes water removal for cost reasons. If the particulate matter isn't removed, it would shorten the life of media used in the subsequent water removal process. Particulate removal media are less expensive than water removal media.

**Salt Drier** A salt drier is a vessel containing a bed of salt particles, usually sodium chloride, but calcium chloride is also used. As the fuel flows upward through the bed, free water in the fuel combines with the salt to form a concentrated salt solution (*brine*), as shown in Figure A.6. Droplets of brine, being much denser than the fuel, collect in a sump at the bottom of the vessel. Salt driers are most suitable for drying large volumes of fuel and therefore usually are installed at refineries or at high-volume terminals and airport storage facilities.

4 Particulate filters are designated by a nominal pore size or an absolute pore size, whichever is smaller. Typically, a filter captures 50 percent (by count) of particles the size of its nominal rating but 99 percent of particles the size of its absolute rating.

Figure A.5
Particulate Filter

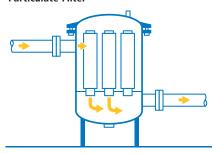
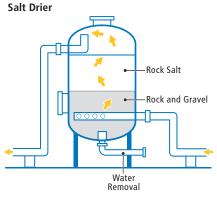


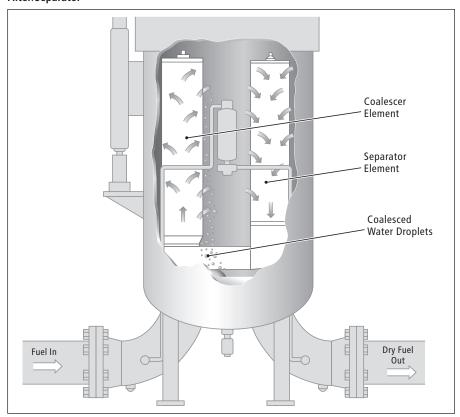
Figure A.6



# Aviation Fuel Distribution and Handling

**Filter/Separator** The filter/separator is the workhorse of the processes used to remove free water from aviation fuels. Two media are involved: First the fuel passes through a water-coalescing medium, which is composed of fibers with a hydrophyllic surface that serves to combine small drops of water into larger drops (*see Figure A.7*). Then it passes through a water-separation medium, which has an outer hydrophobic surface that rejects the larger water droplets. The rejected water is collected in a sump. A filter/separator does not remove dissolved water. Figure A.8 is a cutaway drawing of a typical filter/separator.

Figure A.8
Filter/Separator

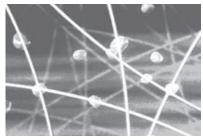


Courtesy of Velcon Filters, Inc.

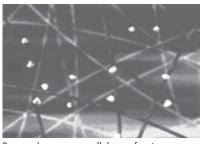
The filter/separator media will remove particulate matter larger than the pore sizes of the media, but, as noted above, this is not a cost-effective use of these materials.

The American Petroleum Institute (API) and the Institute of Petroleum (IP) have issued joint performance specifications for filter/separators (*API/IP Specification 1581*), as has the U.S. Defense Department (Mil Specs).

Figure A.7
Coalescence



Good coalescence – large drops of water



Poor coalescence – small drops of water

Courtesy of Velcon Filters, Inc.

Water-Absorbing Media Water-absorbing media, sometimes called a *filter monitor* or *fuse*, are designed to shut down a fuel system when free water is present. Filter monitors contain water-absorbing material that removes free water. As the water-absorbing material picks up water, it expands in volume, which reduces and finally stops the flow of fuel. The reduced flow warns the operator that the current batch of fuel may be unusually wet, and that the media should be replaced.

Unlike filter/separators, filter monitors are not disarmed by surfactants. Filter monitors are most often used at the point where fuel is loaded into an aircraft's tanks. Recent developments have shown that salts or excess di-EGME (*see page 30*) in the fuel can adhere to the water-absorbing media, interfering with the water-absorbing process.

The API and the IP have issued joint performance specifications and qualifications for waterabsorbing media in *API/IP Specification 1583*.

Clay Treater Clay treatment is used to remove surfactants (*see page 29*) from fuel. As noted above, surfactants can disarm coalescers and thus allow water to pass through. In a refinery, a clay treater is a large vessel containing tons of activated clay. As the fuel flows through the bed, the surface active compounds in the fuel are attracted to and held by (adsorbed) on the surface of the clay particles. In the fuel distribution system, smaller clay treaters are used that contain the clay in canisters or cloth bags for easier handling, as shown in Figure A.9, but they work in the same way as the larger refinery units.

**Quality Control** 

Because of the critical nature of aviation fuel use, the industry has developed several quality control guidelines. These include: Air Transport Association of America ATA 103 Standards for Jet Fuel Quality Control at Airports, IATA Fuel Quality Control and Fueling Service Guidance Material, Joint Inspection Group (JIG), and other guidelines.

These guidelines are designed to help ensure that only clean, dry, uncontaminated fuel is delivered to aircraft. They recommend practices for receiving fuel into airport storage and delivering it to an aircraft. They also recommend equipment for airport fueling facilities, facility system checks, and quick field tests to detect various forms of contamination.

ASTM has issued a *Manual of Aviation Fuel Quality Control Procedure, MNL5*. The manual contains information on many field test methods and operational procedures designed to assess fuel quality (*see Figure A.10*). It also contains general information on filtration equipment and recommended practices for its use, as well as a section on microbial contamination. Many individuals with extensive experience in all aspects of aviation fuel handling contributed to this valuable document.

Figure A.9
Clay Treater

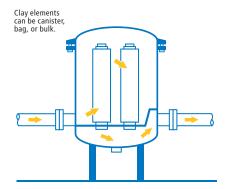


Figure A.10
Frequently Used Aviation Fuel Field Tests

Property	Standard Test Method	Description					
Visual Appearance	White Bucket Test	The sample is placed in an 8-liter (8-quart) white porcelain enamel bucket and the bucket is swirled to create a vortex in the sample.  (Particulates tend to concentrate at the center, or foot, of the vortex.)  The sample is inspected visually for clarity and color, and the bottom of the bucket is inspected for the presence of solids or water droplets.					
	ASTM D 4176 – Test Method for Free Water and Particulate Contamination in Distillate Fuels	The sample is placed in a clean, transparent, dry glass bottle and the bottle is swirled to create a vortex in the sample. The sample is inspected visually against a light background to determine whether its condition is "clear and bright."					
Density	ASTM D 1298 / IP 160 – Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method	Fuel is transferred to a cylindrical container and a hydrometer is carefully lowered into the cylinder and allowed to settle. After the temperature of the sample has equilibrated, the value on the hydrometer scale positioned at the surface of the sample and the sample temperature are recorded. The hydrometer value can be converted to density at 15°C using standard tables.					
Particulate Matter	ASTM D 2276 / IP 423 – Particulate Contaminant in Aviation Fuel by Line Sampling	Fuel from a field sampler is fed through a membrane with a pore size of 0.8 micrometers. The membrane is compared to examples in a rating booklet to rate its color and color intensity.					
	ASTM D 5452 – Particulate Contamination in Aviation Fuels by Laboratory Filtration	Fuel from a field sampler is fed through a pair of matched-weight membranes with a pore size of 0.8 micrometers. The membranes are dried under standard conditions and weighed. The weight difference between the two membranes is a measure of the particulate content of the sample.					
Water Separability	ASTM D 3948 – Determining Water Separation Characteristics of Aviation Turbine Fuels by Portable Separometer	Using a semiautomatic Micro-Separometer instrument, a fuel sample is mixed with water, forced through a fiberglass coalescing medium, and rated. The MSEP rating indicates the relative ease of coalescing water from the sample. The instrument is first calibrated with a sample of the fuel to be tested.					

Property	Standard Test Method	Description
Free Water	Test Kits	A number of commercial test kits to detect free water are available: Shell® Water Detector, Velcon Hydrokit,® Metrocator® Test Kit, and Gammon Aqua-Glo® Water Detection Kit.
Electrical Conductivity	ASTM D 2624 / IP 274 – Electrical Conductivity of Aviation and Distillate Fuels	The probe of a portable conductivity meter is immersed in a fuel sample and the conductivity is read from a meter or digital display

# Appendix B · About Hydrocarbons

# **Hydrocarbon Chemistry**

Hydrocarbons are organic compounds composed entirely of carbon and hydrogen atoms. There are four major classes of hydrocarbons: paraffins, olefins, naphthenes, and aromatics. The members of each class contain different numbers of carbon atoms but share some common structural feature. The classes differ in how the carbon atoms are arranged, i.e., bonded to one another, and in the ratio of hydrogen atoms to carbon atoms.

#### **Paraffins**

Paraffins have the general formula  $C_nH_{2n+2}$ , where "n" is the number of carbon atoms (carbon number). The carbon atoms in paraffins are joined by single bonds. The carbon atoms that form the "backbone" of the molecule are arranged in a zigzag pattern but usually are represented by a shorthand linear structure.

It is possible for paraffins with four or more carbon atoms to have the same number of carbon and hydrogen atoms, but to exist as two or more distinct compounds with different chemical and physical properties. These compounds, called structural isomers, differ in the arrangement of the carbon atoms. In normal paraffins the carbon atoms are bonded to form a chainlike structure. In isoparaffins the carbon atoms that form the molecule's backbone have the same chainlike structure as a normal paraffin, but other carbon atoms branch off from the chain. Normal octane and isooctane are two examples of eight-carbon structural isomers ( $C_8H_{18}$ ). Isooctane is the common name for 2,2,4-trimethylpentane; the numbers in the chemical name specify the locations of the three methyl groups attached to the pentane backbone. Paraffins are major constituents of both avgas and jet fuel.

#### **Olefins**

Olefins, also called alkenes, are similar to paraffins but contain at least two fewer hydrogen atoms and at least one double bond between adjacent carbon atoms. Olefins with one double bond have the general formula  $C_nH_{2n}$ . They rarely occur naturally in crude oil but can be formed by some refining processes. Like paraffins, olefins with four or more carbons can form structural isomers. Olefins typically are found only in trace quantities in both avgas and jet fuel.

#### **Naphthenes**

In naphthenes, also called cycloparaffins, some of the carbon atoms are arranged in a ring. The most prevalent naphthenes in petroleum products have rings of five or six carbon atoms. One-ring naphthenes have the same general formula as olefins,  $C_nH_{2n}$ . As with the normal paraffins, the carbon atoms in cycloparaffins naturally arrange themselves in a zigzag pattern, but the molecule is usually drawn as a planar structure. Naphthenes are typically found in low concentration in avgas (less than 1 percent) but are major constituents of jet fuel.

# **Paraffin**

 $\label{eq:ch3-CH2-CH2-CH2-CH2-CH2-CH3} $$\text{n-octane} $$ C_8H_{18}$$ 

$$\begin{array}{ccc} \text{CH}_3 & \text{CH}_3 \\ | & | \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ | & | \\ \text{CH}_2 \end{array}$$

2,2,4-trimethylpentane C<sub>8</sub>H<sub>18</sub>

#### **Olefin**

$$CH_2 = CH - CH_2 - CH_3$$
1-butene  $C_4H_8$ 

# **Naphthene**

cyclohexane C<sub>6</sub>H<sub>12</sub>

#### **Aromatics**

As in naphthenes, some of the carbon atoms in aromatics are arranged in a ring, but they are joined by aromatic bonds, not single bonds. The structure of benzene, the simplest aromatic, can be envisioned as the average of two discrete cyclohexatriene molecules, as it was thought to be in the early days of organic chemistry. However, the aromatic bond character is now known to be distributed evenly around the ring. The shorthand representation for benzene is a hexagon with an inner circle to represent the aromatic bonds.

#### **Aromatics**

Benzene C<sub>6</sub>H<sub>6</sub>

The ring of one-ring (*monocyclic*) aromatics like benzene always contains six carbon atoms; the general formula is  $C_nH_{2n-6}$ . In polycyclic aromatics each ring also contains six carbon atoms, but some of the carbons are shared by the adjacent rings. Naphthalene is the simplest two-ring (*dicyclic*) aromatic.

Avgas is limited to monoaromatics by distillation requirements. Typically, toluene is the only aromatic compound in avgas. Jet fuel is limited to monocyclic and dicyclic aromatic compounds by distillation requirements. Total aromatic content of Jet A and Jet A-1 is limited to 25% vol, and total naphthalenes content is limited to 3.0% vol by specifications.

Paraffins and naphthenes are classified as saturated hydrocarbons because no more hydrogen can be added to them without breaking the carbon backbone or a ring. Olefins and aromatics are classified as unsaturated hydrocarbons because hydrogen can be added to the carbon atoms joined by the double bond(s) and aromatic bonds. Such an addition converts the bonds to single bonds and, if all the bonds are converted, converts the compounds to saturated hydrocarbons.

#### Other Compounds

While hydrocarbons predominate in crude oil, compounds that contain other elements besides carbon and hydrogen also are present. These elements are called heteroatoms ("other atoms"). When heteroatoms are bound into molecular structures with carbon and hydrogen, the resulting compounds no longer are hydrocarbons.

Sulfur and nitrogen are the most common heteroatoms present in crude oil. Although sulfur- and nitrogen-containing compounds are present in small amounts, they play a large role in determining certain fuel properties, e.g., stability.



naphththalene C<sub>10</sub>H<sub>8</sub>

# **About Hydrocarbons**

One class of sulfur-containing compounds in crude oil is *mercaptan*. Mercaptans have a sulfur atom bonded to a hydrocarbon group and a hydrogen atom. Mercaptans can be oxidized to disulfides, which have two sulfur atoms bonded together, with each also bonded to a hydrocarbon group.

Other types of sulfur compounds are sulfides, in which a sulfur atom is bonded to two carbon atoms, and thiophenes, in which sulfur is bound in an aromatic ring.

Because of the way it is manufactured, avgas contains only trace amounts of heteroatoms. Jet fuel specifications allow up to 0.3 mass % sulfur and 0.003 mass % mercaptans, but typical jet fuels contain only half or less of the allowed maximum. Nitrogen compounds typically are found in only trace amounts in jet fuel.

R-S-H	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SH
mercaptan, e.g.,	butyl mercaptan
R-S-S-R	$CH_3 - S - S - CH_3$
disulfide, e.g.,	dimethyl disulfide
R-S-R	$CH_3 - S - CH_3$
sulfide, e.g.,	dimethyl sulfide

# **Hydrocarbon Properties**

The physical and chemical properties of hydrocarbons depend on class and carbon number. Often the variation of a property by carbon number within a class is predictable, but not always.

Figure B.1 lists some properties of a few representative hydrocarbons. The compounds were chosen to illustrate the range of the properties of interest. Because of the differences in their specifications, avgas and jet fuel have few hydrocarbons in common, and several hydrocarbons in the table may not occur in either product.





Figure B.1
Selected Properties of Some Hydrocarbons

Compound	Empirical	Compound	Boiling	g Point	Freezin	g Point	Density at 15°C,		nergy Itent		Energy ntent	Motor Octane
Name	Formula	Class	°C °F		°C °F		g/mL	MJ/kg	MJ/L	Btu/lb	Btu/gal	Number
Butane	C <sub>4</sub> H <sub>10</sub>	n-Paraffin	-0.5	31	-138	-217	0.583	45.73	22.66	19,660	95,710	89.6
2-Methylbutane	C <sub>5</sub> H <sub>12</sub>	Isoparaffin	28	82	-160	-256	0.624	44.89	28.01	19,300	100,540	90.3
Hexane	C <sub>6</sub> H <sub>14</sub>	n-Paraffin	68.7	156	-95.3	-140	0.663	44.73	29.66	19,230	106,430	26.0
2-Methylpentane	C <sub>6</sub> H <sub>14</sub>	Isoparaffin	60.3	140	-154	-245	0.657	44.66	29.34	19,200	105,300	73.5
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	Naphthene	80.7	177	6.6	44	0.783	43.45	34.02	18,680	121,990	77.2
Benzene	$C_6H_6$	Aromatic	80.1	176	5.5	42	0.822	40.15	33.00	17,260	127,040	115
Toluene	C <sub>7</sub> H <sub>8</sub>	Aromatic	111	231	-95.0	-139	0.873	40.52	35.37	17,420	127,000	103.5
Heptane	C <sub>7</sub> H <sub>16</sub>	n-Paraffin	98.4	209	-90.6	-131	0.688	44.57	30.66	19,160	109,930	0
Octane	C <sub>8</sub> H <sub>18</sub>	n-Paraffin	126	258	-57	-70	0.706	44.43	31.37	19,100	112,560	_
2,2,4- Trimethylpentane	C <sub>8</sub> H <sub>18</sub>	Isoparaffin	99.2	211	-107	-161	0.698	44.33	30.94	19,060	111,120	100
2,3,4- Trimethylpentane	C <sub>8</sub> H <sub>18</sub>	Isoparaffin	113	236	-109	-165	0.723	44.38	32.09	19,080	115,170	95.9
2,5- Dimethylhexane	C <sub>8</sub> H <sub>18</sub>	Isoparaffin	109	228	-91.1	-132	0.698	44.33	30.94	19,060	110,970	55.7
Nonane	C <sub>9</sub> H <sub>20</sub>	n-Paraffin	151	303	-53	-64	0.721	44.33	31.96	19,060	114,670	_
2,6- Dimethylheptane	C <sub>9</sub> H <sub>20</sub>	Isoparaffin	135	275	-103	-153	0.713	44.24	31.54	19,020	113,170	_

Source: ASTM DS 4B Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds.

#### Boiling Point, Density, and Freezing Point

Boiling point increases with carbon number for compounds in the same class. For a given carbon number, isoparaffins have the lowest boiling points, followed by normal paraffins, naphthenes, and aromatics. Density follows the same trend.

Freezing point also increases with carbon number for compounds in the same class but is strongly influenced by molecular shape. Molecules such as normal paraffins and unsubstituted aromatics freeze (crystallize) at much higher temperatures than other compounds with the same carbon number because they have a compact geometry that allows them to pack together easily into a crystalline structure.

#### Octane Number

Octane number varies widely with molecular structure. In general, octane number decreases with increasing carbon number for compounds in the same class and similar branching structures.

The octane number of isoparaffins depends on the number, location, and size of the alkyl substituents. Isoparaffins with several methyl side chains have the highest octane numbers.

Normal paraffins, which by definition have no alkyl substituents, have very low octane numbers for compounds with more than five carbon numbers.

Benzene and methyl-substituted benzenes generally have high octane numbers. As the substituent changes from methyl to higher carbon number alkyls, the octane number decreases.

Naphthenes have octane numbers intermediate between normal paraffins and aromatics. The octane numbers of alkyl-substituted naphthenes trend similarly to those of alkyl-substituted aromatics.

## **Energy Content**

For hydrocarbons with the same carbon number, energy content per unit weight increases in the order aromatic, naphthenic, paraffinic. On a volume basis, the order is reversed, with paraffins having the lowest energy content per unit volume and aromatics the highest.

# Sources of More Information

# Petroleum, General

"Petroleum Panorama." The Oil and Gas Journal, 57(5): 28 January 1959.

Dyroff, G.V., editor. *Manual on Significance of Tests for Petroleum Products*, 6th ed. West Conshohocken, Pa.: American Society for Testing and Materials. 1993.

# **Petroleum Refining**

Anderson, K.E.; Berger, B.D. Refinery Operation. Tulsa, Okla.: Petroleum Publishing. 1979.

Leffler, W.L. Petroleum Refining for the Nontechnical Person, 2nd ed. Tulsa, Okla.: PennWell. 1985.

#### **Aviation Fuel**

Smith, M. Aviation Fuels. Henley-on-Thames, Oxfordshire, U.K.: G.T. Foulis & Co LTD. 1970.

Goodger, E.; Vere, R. Aviation Fuels Technology. London, U.K.: Macmillan. 1985.

Coordinating Research Council. Handbook of Aviation Fuel Properties. 1983.

Heron, S.D.; Schlaifer, R. *Development of Aircraft Engines and Fuels*. Boston: Harvard University. 1950.

Gammon, J., editor. "Manual of Aviation Fuel Quality Control Procedures." ASTM Manual Series: MNL 5. West Conshohocken, Pa.: American Society for Testing and Materials. 2004.

Air Transport Association of America. "Standards For Jet Fuel Quality Control at Airports, ATA Specification 103." Washington, D.C. 2004.

# **Aviation Engines**

Heron, S.D. History of the Aircraft Piston Engine. Detroit, Mich.: Ethyl Corporation. 1961.

Smith, H. A History of Aircraft Piston Engines. Manhattan, Kan.: Sunflower University Press. 1981.

Brown, G.N.; Holt, M.J. *The Turbine Pilot's Flight Manual*. Ames, Iowa: Iowa State University Press. 1995.

"How Gas Turbine Engines Work", *How Stuff Works*. (http://www.howstuffworks.com) HowStuffWorks.com, Inc. 1999.

# **Questions?**

Contact Chevron Fuels Technical Service (510) 242-5357 fueltek@chevron.com

# **Abbreviations**

API American Petroleum Institute

ASTM American Society for Testing and Materials

ATA Air Transport Association of America

ATF Aviation Turbine Fuel

Btu British thermal unit

CIS Commonwealth of Independent States

CGSB Canadian General Standards Board

CRC Coordinating Research Council

CU conductivity unit

DEF STAN Defence Standard

EPA Environmental Protection Agency

FAA Federal Aviation Administration

FCC Fluid Catalytic Cracker

IATA International Air Transport Association

IP Institute of Petroleum

IRS Internal Revenue Service

JFTOT Jet Fuel Thermal Oxidation Tester

kPa kilo Pascal

MJ Megajoules

MOD Ministry of Defence

MSDS Material Safety Data Sheet

MSEP Micro Separometer

psi pounds per square inch

pS/m pico Siemens per meter

RVP Reid vapor pressure

SDA static dissipator additive

TEL tetra ethyl lead