

Investigation of Byproduct Application to Jet Fuel

Final Report

*J.E. Sinor Consultants Inc.
Niwot, Colorado*



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

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Operated by Midwest Research Institute • Battelle • Bechtel

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Introduction and Background

The National Renewable Energy Laboratory (NREL) has an on-going program for the conversion of biomass to ethanol. Such processes achieve less than 100% conversion, leaving a residual material consisting mostly of lignin. There is a need to find a way to convert this useless byproduct into a saleable product. Experiments have shown that it is possible to convert this material into a mixture of alkyl benzenes boiling at the high end of the gasoline boiling range. Such a material would have a high octane number and could be a useful additive to motor gasoline. It was not expected that an alkyl benzene product would also be useful as a jet fuel component. However, in order to ensure that no possibilities were overlooked, NREL asked J. E. Sinor Consultants Inc. to carry out a brief study of jet fuel characteristics and markets to determine whether any applications for an alkyl benzene product exist.

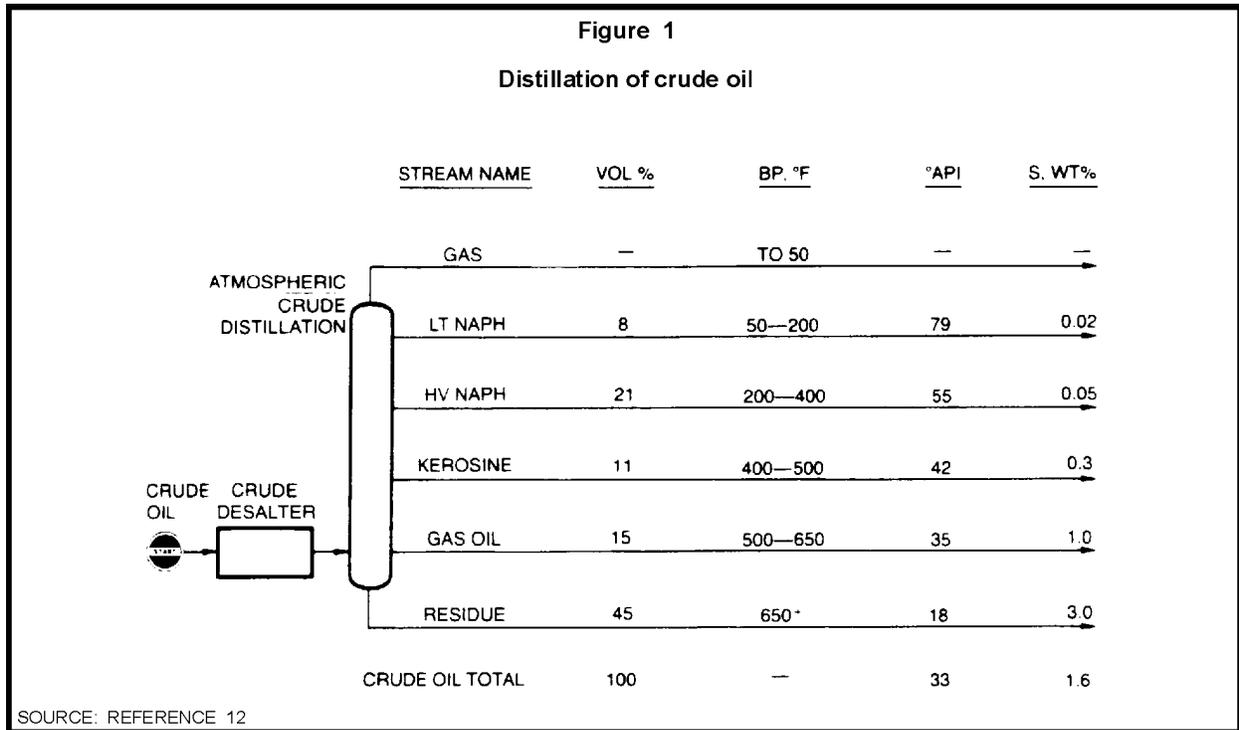
Definitions

Distillation of Crude Oil

When crude oil enters the refinery, it is first separated into various fractions by distillation. Primary distillation takes place at atmospheric pressure and the bottom temperature is limited to between 370°C and 400°C to prevent thermal cracking.

The lowest boiling fraction, taken from the top of the distillation column, is called naphtha (see Figure 1). It is mainly processed further to make motor gasoline. Next, kerosene and special solvents boil over, followed by the so-called “gas oil” or “middle distillate” fraction which includes diesel fuel, jet fuel, and heating oil. Finally, although the bottoms fractions or residual fraction can be used as heavy boiler fuel, it is usually vacuum distilled first to yield more high-value distillate.

The boiling point ranges shown in Figure 1 do not constitute strict boundaries. Jet fuel, kerosene, No. 1 fuel oil, No. 2 fuel oil, and diesel fuel are all popular distillate products coming from 200°C to 315°C fractions of crude oil. One grade of jet fuel uses the heavy naphtha fraction, but the kerosene fraction supplies the more popular, heavier grade of jet fuel.



Product Names

The distinction between refined products and petrochemicals is often a subtle one. In general, when the product is a fraction from crude oil that includes a fairly large group of hydrocarbons, the fraction is classified as a refined product. Examples of refined products are: gasoline, diesel fuel, heating oils, lubricants, waxes, asphalts, and petroleum coke.

Most refined products at the consumer level are blends of several refinery streams. Product specifications determine which streams are suitable for a specific blend. Part of the difficulty of refining literature lies in the industry's use of stream names that are different from the names of the consumer products.

In contrast, when the product from crude oil is limited to only one or two specific hydrocarbons of fairly high purity, the fraction is called a petrochemical. Examples of petrochemicals are: ethylene, propylene, benzene, toluene, and styrene—to name only a few.

Consider the listing in Table 1. The names in the last column are those used at the consumer level. Yet, within a refinery, these products will be blended from portions of crude oil fractions having the names shown in the first column. Furthermore, specifications and statistics for the industry are often reported under yet another set of names—those shown in the middle column of Table 1.

Petroleum naphtha is a generic term applied to refined, partly refined or unrefined petroleum products. Naphtha can also be a combination of product streams from several refinery processes. The main uses of petroleum naphtha fall in the general area of solvents.

Kerosene originated as a straight-run (distilled) petroleum fraction that boiled over the temperature range of 205°C to 260°C. In the early days of petroleum refining, some crude oils contained kerosene fractions of high quality, but other crude oils had to be thoroughly refined before a satisfactory kerosene fraction could be obtained. Kerosene is believed to be composed chiefly of hydrocarbons containing 12 to 15 carbon atoms per molecule (1). Low proportions of aromatic and unsaturated hydrocarbons are desirable to maintain the lowest possible level of smoke during burning.

Kerosene may be called coal oil to denote that it replaces stove oil (or range oil) once derived from coal. Kerosene's historical significance was first as illuminating oil for lamps that once burned sperm oil taken from whales. But today, kerosene fractions go mostly into transportation fuels such as jet fuel and high-quality No. 1 heating oil.

Jet Fuel Nomenclature

Commercial kerosene was used as a fuel in early developmental work on jet aircraft in the United States. The choice of kerosene over gasoline was based on its low volatility (to avoid occurrence of vapor lock) and on its availability as a commercial product with uniform characteristics. JP-1, the first military jet fuel, was highly refined kerosene having a low freezing point (-60°C). Kerosene from selected crudes high in naphtha was the only fuel having this low freezing point. As the demand for the fuel increased, the Military Petroleum Advisory Board recommended the development of a military jet fuel having greater availability in wartime than JP-1 (2). The second candidate jet fuel was JP-2, but it did not have the desired availability. JP-3 fuel was another possibility. It included the total boiling range of kerosene and gasoline. Testing demonstrated that the high vapor pressure of JP-3 (Reid Vapor Pressure [RVP] of 5 to 7 pounds per square inch [PSI]) resulted in vaporization of the fuel during climb to altitude.

Table 1

Names for Petroleum Products

| <u>Crude Oil Cuts</u> | <u>Refinery Blends</u> | <u>Consumer Products</u> |
|-----------------------|--|--|
| Gases | Still Gases Propane/Butane | Fuel Gas Liquefied Petroleum Gas |
| Light/Heavy Naphtha | Motor Fuel Aviation Turbine Fuel, Jet-B | Gasoline Jet Fuel (naphtha type) |
| Kerosene | Aviation Turbine Fuel, Jet-A No. 1 Fuel Oil | Jet Fuel (kerosene type) Kerosene (range oil) |
| Light Gas Oil | Diesel No. 2 Fuel Oil | Auto and Tractor Diesel Home Heating Oil |
| Heavy Gas Oil | No. 4 Fuel Oil No. 5 Fuel Oil Bright Stock | Commerical Heating Oil Industiral Heating Oil Lubricants |
| Residuals | No. 6 Fuel Oil Heavy Residual Coke | Bunker C Oil Asphalt Coke |

Source: 12

In addition, some times the fuel foamed excessively during vaporization so that large losses of liquid could occur along with the vented vapors.

To overcome the disadvantages of JP-3, JP-4 was developed in 1951, by reducing the RVP to 2 to 3 pounds. This fuel is a blend of 25% to 35% kerosene and 65% to 75% naphtha components and proved satisfactory for military requirements. During the Korean War, JP-5 fuel was developed for aircraft carriers. This is a special (60°C) flash point kerosene. Because of its low volatility, it can be stored safely in outer tanks of aircraft carriers.

Commercial airline jet fuels in the United States are classified as American Society for Testing and Materials (ASTM) Jet A, A-1 and B fuels. Jet A and A-1 are kerosene type fuels. Jet B corresponds to the military JP-4 fuel and is no longer used to any significant extent.

The operation of aircraft in long-duration flights at high altitude imposes a special requirement of good low-temperature flow behavior; this need established Jet A-1, which has a freezing point of -50°C (wax) as an international flight fuel. Jet A which has a freezing point of -40°C (wax) can serve shorter domestic routes.

JP-6 was the first fuel established by the Air Force for use in supersonic aircraft.

JP-7 is a highly refined, high thermal stability fuel developed in the 1960s to meet the high heat sink demands of the SR-71 reconnaissance aircraft (now retired). JP-7 was later designated as a high thermal stability fuel for use in a hydrocarbon-fueled Mach 4-8 missile (3).

The fuel is a complex mixture of hydrocarbons comprising mainly naphthenes, paraffins, and a maximum of 5% aromatics. It is thermally stable to 288°C.

In the 1990s, JP-8 became the standard jet fuel for the military services. For use on ships, the Navy still uses JP-5, but all other branches of the Army, Air Force, and Navy have standardized on JP-8. The only difference between JP-5 and JP-8 is that JP-5 has a minimum flash point of 140°F compared to 100°F for JP-8. JP-8 is virtually equivalent to today's commercial Jet A-1.

Jet fuel fulfills a dual purpose in aircraft. It provides the energy and also serves as a coolant for lubricating oil and other aircraft components. Exposure of the fuel to high temperatures may cause the formation of oxidation materials (gums) that reduce the efficiency of heat exchangers and clog filters and valves in aircraft fuel-handling systems. Thermal stability is the resistance to formation of gums at high temperature. The JP-4, JP-5, JP-8 and equivalent commercial fuels have satisfactory thermal stability for aircraft operating at speeds up to about Mach 2.0. Jet aircraft operating at higher speeds, e.g., Mach 3, may expose the fuel to greater thermal stresses and, therefore, may require a more stable fuel. The development of Mach 3-4 turbojets, Mach 6-plus ramjets, and rockets using hydrocarbon fuels will pose additional demands on fuel stability.

Fuel Properties

Average Properties

The average properties of current aircraft jet fuels are shown in Table 2. However, even fuels that fall within specification can vary widely from the averages. For example, the maximum allowable for aromatics content is 25%. For JP-8 purchased from 1990 to 1996 the range was from 25% to less than 9% aromatics, with a mean of 18.2% and a standard deviation of 3.1% (4).

Additives must be effective in all of these baseline fuels to qualify for sale.

Table 2
Typical Jet Fuel Properties

| <u>Property</u> | <u>JP-4</u> | <u>JP-5</u> | <u>JP-7</u> | <u>JP-8 (Jet A/A-1)</u> |
|---------------------------|----------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Approx. Formula | C _{8.5} H ₁₇ | C ₁₂ H ₂₂ | C ₁₂ H ₂₅ | C ₁₁ H ₂₁ |
| H/C Ratio | 2.00 | 1.92 | 2.07 | 1.91 |
| Boiling Range, F | 140-460 | 360-495 | 370-480 | 330-510 |
| Freeze Point, F | -80 | -57 | -47 | -60 JP-8/Jet A-1; -50 Jet A |
| Flash Point, F | -10 | 147 | 140 | 127 |
| Net Heating Value, BTU/lb | 18,700 | 18,500 | 18,875 | 18,550 |
| Specific Gravity 60F | 0.76 | 0.81 | 0.79 | 0.81 |
| Critical T, F | 620 | 750 | 750 | 770 |
| Critical P, psia | 450 | 290 | 305 | 340 |
| Average Composition | | | | |
| Aromatics, vol.% | 10 | 19 | 3 | 18 |
| Naphthenes | 29 | 34 | 32 | 20 |
| Paraffins | 59 | 45 | 65 | 60 |
| Olefins | 2 | 2 | | 2 |
| Sulfur, ppm | 370 | 470 | 60 | 490 |

Source: 4

Specification Properties

While all piston engine fuels have the same volatility but differ in combustion characteristics, jet fuels differ primarily in volatility and differences in their combustion qualities are minor. The volatility characteristics of several grades of jet fuel are shown in Table 3. For fuels in which the RVP is too low for accurate measurement, the flash point is given. This is the temperature to which a fuel must be heated to generate sufficient vapor to form a flammable mixture in air.

Table 3**Volatility Characteristics of Jet Fuels**

| <u>Jet Fuel Grade</u> | <u>Distillation Range, °F (°C)</u> | <u>RVP, psia (kPa, absolute)</u> | <u>Flash Point, °F (°C)</u> |
|-----------------------|------------------------------------|----------------------------------|-----------------------------|
| JP-1 | 325-450 (163-230) | -- | 120 (49) |
| JP-3 | 100-500 (38-260) | 6 (41) | -- |
| JP-4 | 150-500 (65-260) | 2.5 (17) | -- |
| JP-5 | 350-500 (177-260) | -- | 150 (65) |
| JP-6 | 300-500 (149-260) | -- | 100 (38) |
| Jet A | -- | -- | 100 (38) |
| Jet B | -- | -- | 100 |

Source: 13

Composition

Production of distillate turbine fuel uses about 8% of typical crude oil input to a refinery. This percentage could be increased at added incremental costs and with a concurrent reduction in the output of motor gasoline and diesel fuel. Turbine fuel contains aromatic hydrocarbons; limits are placed on this content because of concerns about smoke and coke formation. For military jet fuels, the limit on aromatics is 25% by volume, and for commercial fuel the limit is 20% (except by mutual agreement between supplier and purchaser, in which case the content may not exceed 20% for Jet A or 22% for Jet A-1 or Jet B).

There is also a limit on sulfur content: 0.3% by weight.

High-Temperature Stability

In subsonic jets, the fuel is used to cool the engine lubricant, and the temperature of the fuel can be raised by about 93°C. In supersonic jets, the fuel is used as a heat sink for the engine lubricant, for cabin air conditioning, and for cooling the hydraulic systems. For very-high-speed flight, the fuel may be used to cool additional engine components and critical air frame areas, such as the leading edges of wings. Therefore, depending on flight speeds and aircraft design, turbine fuels can be heated from 150°C to 260°C before they are burned. When they are heated to this degree, small amounts of solids may form, and foul the heat exchangers and clog the filters and fuel injectors. There are specifications (see Table 12) to indicate the temperature at which solids are first formed and the amount of solids formed with time.

Freezing Point

Turbine fuels must have low freezing points: -40°C for Jet A and -50°C for Jet A-1 and Jet B.

Heat of Combustion

The heat of combustion of all jet fuels is about 18,400 BTU per pound (42.8 MJ/kg). This is the net, or low heating value. A gallon of turbine fuel weighs about 6.7 pounds and thus has an energy content of about 123,000 BTU (1 liter weighs about 0.80 kilograms and has an energy content of about 34.4 MJ).

General Requirement

All jet fuels must meet the stringent performance requirements of aircraft turbine engines and fuel systems, which demand extreme cleanliness and freedom from oxidation deposits in high-temperature zones. Combustors require fuels that atomize and ignite at low temperatures, burn with adequate heat release and controlled radiation, and neither produce smoke nor attack hot turbine parts.

Static Charges

Fuels pumped through long multi-product pipelines or delivered by tanker are usually clay-filtered to ensure freedom from surfactants. Many stages of filters operate to ensure clean, dry product as the fuel moves into airport tanks, hydrant systems and finally aircraft. Because high-speed filtration can generate static electric charges, fuels may contain an electrical conductivity additive to ensure rapid dissipation of charge.

Research on Advanced Jet Fuels

Fuel Stability Requirements

The Air Force Research Laboratory at Wright-Patterson Air Force Base has established several target fuels of higher heat sink capacity than the Air Force's current fuel, JP-8. JP-8 is limited to a maximum temperature of about 325°F in current aircraft.

The thermal management requirements for hypersonic aircraft are well known. As shown in Figure 2, the required fuel heat sink increases dramatically with vehicle Mach number. From the figure, it can be seen that an engine for a Mach 8 vehicle would require a heat sink from the fuel of about 1,500 BTU per pound. This level of heat sink can only be obtained from endothermic fuels, where the sensible heat sink of the fuel ($C_p\Delta T$) is enhanced by heat-absorbing (endothermic) reactions in the bulk fuel.

JP-7 has a thermal stability temperature limit of 290°C, but costs about three times as much as JP-8 (4). Table 4 shows the fuel development targets. JP-8+100 has been demonstrated in the field in a considerable number of aircraft, while the development of JP-8+225 is just beginning (3,5).

Petroleum industry analysts expect that the thermal stability of jet fuels may decrease somewhat in the near future as regulations requiring dramatic reductions in sulfur contents of gasoline and diesel fuels go into effect (4).

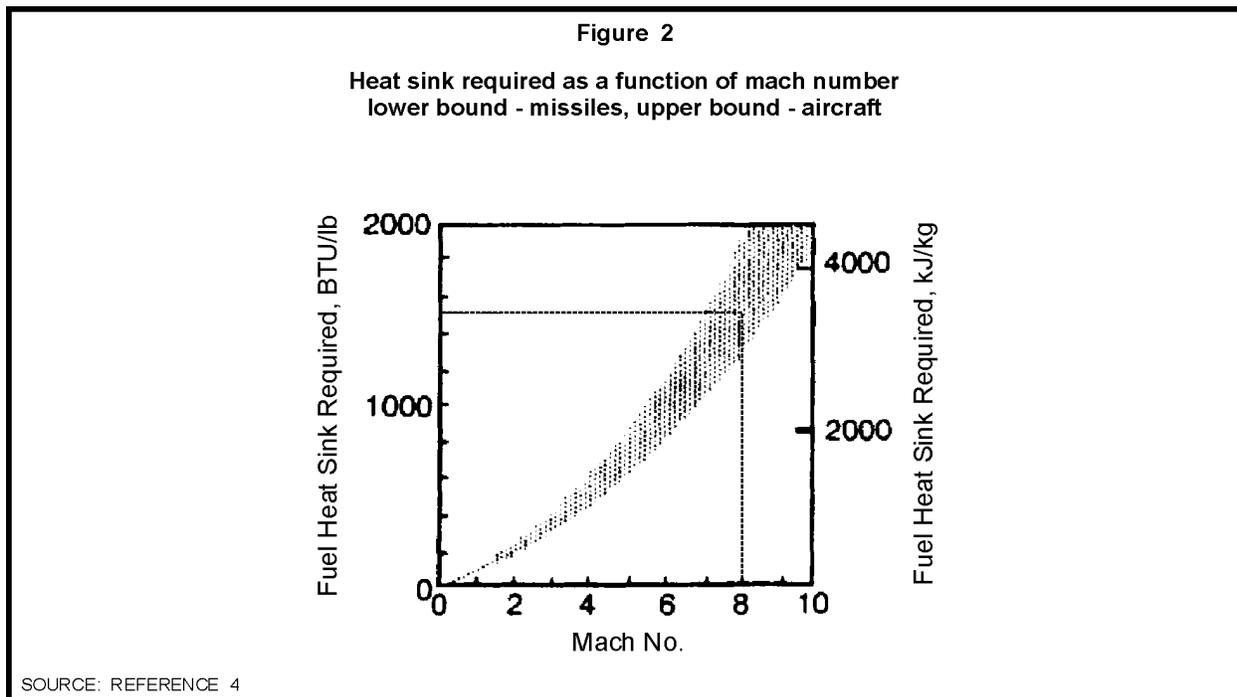


Table 4

High Heat Sink Fuel Goals

| <u>Fuel</u> | <u>Maximum Use T, F</u> | <u>Heat Sink (relative to JP-8)</u> |
|----------------|-------------------------|-------------------------------------|
| JP-8 | 325 | -- |
| JP-8+100 | 425 | 1.5X |
| JP-8+225 | 550 | 2.2X |
| JP-900 | 900 | 5X |
| Endothermic JP | n/a | 12X |

Source: 4

The Rationale for JP-900

The Air Force has a significant turbine engine development program, IHPTET, which has the overall goal of doubling the thrust-to-weight ratio of turbine engines. The IHPTET program studies ways to increase the engine cycle temperatures and pressures to achieve this increase in thrust-to-weight (along with component weight reduction goals). Ideally, this increase in cycle temperature would be achieved by developing more capable engine materials. However, a combination of improved materials and “cooled cooling air” may be required. In a cooled cooling air system, compressor bleed air is cooled with fuel or fan air and then used to maintain the engine materials within their temperature limits. In a recent study (6), a notional advanced engine with a turbine rotor inlet temperature of 2,100°C is described (compared to 1990s technology of less than 2,100°C). This notional engine uses materials expected to be available in 2010-2015 and assesses the benefits of cooled cooling air. Because of turbine cooling requirements, the baseline engine is limited to a compressor exit temperature of 760°C and pressure ratio of 32:1. The baseline system diverts almost 17% of the high-pressure air from the compressor to perform turbine cooling. With a cooled cooling air system, the cycle pressure ratio can be increased to 50, with a resulting increase in engine thrust-to-weight and decrease in specific fuel consumption. The best performing option in the study was to use the fuel as a heat sink so that the fuel temperature increased to 275°C. This option had an increase in thrust-to-weight of 11% and a decrease in specific fuel consumption of 3.3% over the baseline system.

Thermal management system layouts that take advantage of fuel heat sink show that a system employing a 900°F-capable (482°C) fuel would be optimum for land-based aircraft applications.

A JP-900 fuel will have to achieve both oxidative and pyrolytic stability, properties which seem to be inversely related (7). Oxidative instability is defined as deposit formation on engine surfaces shortly after the fuel reacts with its dissolved oxygen (usually between 180°C to 220°C). Pyrolytic instability, on the other hand, is an anaerobic deposit formation on engine surfaces that occurs at temperatures above 450°C.

The very chemical and structural characteristics that make hydrogen donors effective thermal stabilizers in the pyrolytic regime also accentuate the susceptibility to oxidation in the so-called autoxidation regime between 150°C to 300°C (8).

Recent work at the Pennsylvania State University (PSU) has shown that by understanding the mechanisms for the oxidative and thermal decomposition of jet fuels, it should be possible to rationally design additives that will achieve JP-900 (7).

Any additive (including antioxidants, anti-icers, metal deactivators, and detergents) that is susceptible to disintegration into free radicals in the pyrolytic regime can enhance degradation at temperatures above 400°C with potentially disastrous consequences. Classic antioxidants, such as, for example, the sterically hindered phenols that operate well in the autoxidation regime, actually promote free radical reactions in the pyrolytic regime. In other words, the additive introduced to prevent degradation of the fuel in storage and at moderately elevated temperatures can adversely affect the efficacy of the additive introduced to retard the formation of carbonaceous solids at high temperatures.

Such additives are most likely to be structurally simple and will not contain long aliphatic side groups or other moieties that can cleave and produce free radicals above 400°C (8). It is important that additives introduced to prevent the autoxidative degradation of the fuel also prevent degradation of the highly susceptible hydrogen donor stabilizers by suppressing the normal autoxidation pathway. Accordingly, when temperatures rise to those of the pyrolytic regime, the hydrogen donors will be free to suppress pyrolytic degradation via the usual H-transfer mechanism.

The PSU research has been focused on finding potential oxygen scavengers for use in jet fuels (8). The rationale is that if molecular oxygen is eliminated from the fuel, most of the problems are solved. The scavenger should protect both the fuel and the hydrogen donor in the autoxidative regime, and the reaction product between the scavenger molecule and oxygen should be reasonably stable and not generate free radicals in the pyrolytic regime. Potential oxygen scavengers include phosphines and like molecules.

Triphenylphosphine (TPP) appears to fulfill all the requirements, but test results were not encouraging.

However, dimethylphenylphosphine (DMPP) gave some encouraging results. Unfortunately, DMPP is a liquid with a strong stench and is unpleasant to handle.

This led PSU researchers to the alternative dialkylarylphosphine, dicyclohexylphenyl-phosphine (DCHPP).

DCHPP at a level of 200 ppm appears to protect fuel mixtures from oxidation at 250°C for periods of up to at least 12 hours. Moreover, at 425°C, carbonaceous deposits are not observed until after 6 hours. This is encouraging and warrants further investigation using JP-900 type jet fuels.

Intermediate Goals

The Air Force's JP-8+100 program increased the thermal stability of JP-8 by 100°F by developing an additive package. The JP-8+100 additive package consists of a dispersant, a metal deactivator and an antioxidant. The next intermediate goal, being worked on currently, is JP-8+225. This fuel would have a thermal stability of 225°F better than JP-8, which would allow operation at a temperature of up to 288°C (550°F). An additive approach is being pursued here also (5).

In other tests carried out at PSU four fuels were "stressed" in a reactor: JP-8, kerosene, dearomatized hydrotreated light cycle oil and Norpar-13. Norpar-13 is an industrial solvent manufactured by Exxon Chemical Company consisting of straight-chain alkanes ranging from C₁₁ to C₁₅. Norpar-13 was included as a model fuel.

Table 5 shows the composition of the four fuels before stressing. Kerosene, JP-8 and Norpar-3 all contain a high percentage of straight-chained alkanes. Kerosene and JP-8 also contain high percentages of branched-chain alkanes. In contrast, dearomatized hydrotreated light cycle oil has a high percentage of cyclic alkanes, which have been shown to be more thermally stable than straight-chain alkanes.

JP-8 exhibited the greatest carbon deposit formation, followed by Norpar-13. The dearomatized hydro-treated light cycle oil exhibited significantly less deposit formation than the other two fuels. The kerosene exhibited the least amount of deposit formation.

The fact that JP-8 produces significantly more deposit than the other three fuels studied is thought to be largely due to the high percentage of aromatic compounds present in the fuel. Alkyl aromatics have been shown to degrade easily. Additionally, JP-8 contains an additive package that is thought to decrease the thermal stability of the fuel.

Table 5
Composition of Unstressed Fuels
(Weight Percent)

| <u>Compounds</u> | <u>Kerosene</u> | <u>JP-8</u> | <u>DA/HT LCO</u> | <u>Norpar-13</u> |
|------------------|-----------------|-------------|------------------|------------------|
| n-Alkanes | 50% | 37% | 13% | >99.9% |
| iso-Alkanes | 15% | 42% | 16% | <0.1% |
| Alkenes | 5% | 7% | 5% | <0.1% |
| Cycloalkanes | 13% | 8% | 66% | <0.1% |
| Aromatics | 9% | 5% | <0.1% | <0.1% |
| Hydroaromatics | 8% | 1% | <0.1% | <0.1% |
| Other | <1% | <1% | <1% | <0.1% |

Source: 14

The compositions of the stressed fuels are shown in Table 6. The most notable change is an increase in the concentration of alkenes. Primary alkenes predominate, indicating that many of the alkenes are formed by β -scission decompositions. The fraction of n-alkanes and iso-alkanes drops upon stressing.

Dearomatized hydrotreated light cycle oil exhibits a drop in the concentration of cycloalkanes and a rise in the amount of hydroaromatics. Dearomatized hydrotreated light cycle oil contains a great deal of decalin, which can act as a hydrogen donor. As decalin undergoes dehydrogenation reactions, it forms tetralin and then naphthalene. This accounts for the increase in hydroaromatics. The drop in cycloalkanes may be attributed to cracking reactions that affect alkyl cycloalkanes, resulting in lighter cycloalkanes and light alkenes or alkanes.

Although dearomatized hydrotreated light cycle oil, which has a high content of cycloalkanes, was expected to be the most thermally stable fuel of those tested, kerosene was the most stable fuel under the conditions used. The kerosene employed contains a substantial percentage of hydroaromatic compounds, which have been shown to increase thermal stability in a deoxygenated environment.

Table 6
Composition of Stressed Fuel
(Weight Percent)

| <u>Compounds</u> | <u>Kerosene</u> | <u>JP-8</u> | <u>DA/HT LCO</u> | <u>Norpar-13</u> |
|------------------|-----------------|-------------|------------------|------------------|
| n-Alkanes | 42% | 29% | 9% | 72% |
| iso-Alkanes | 12% | 31% | 12% | 5% |
| Alkenes | 15% | 22% | 18% | 22% |
| Cycloalkanes | 13% | 7% | 56% | <1% |
| Aromatics | 9% | 8% | <0.1% | <1% |
| Hydroaromatics | 9% | 2% | 3% | <0.1% |
| Other | <1% | 1% | 2% | <1% |

Source: 14

Thermally Stable Jet Fuels From Coal

There are some unique compositional advantages to using coal-derived liquids for making advanced jet fuels, with respect to the high-temperature thermal stability. Compared to conventional petroleum-derived jet fuels, the coal-derived jet fuels display greater thermal stability at temperatures above 400°C in terms of much lower degree of decomposition and significantly fewer solid deposits. This is because coal-derived jet fuels are rich in cycloalkanes and the aromatic compounds in coal-derived jet fuels can be dominated by hydroaromatic structures (9). Cycloalkanes are more stable than the n-alkanes with the same or lower carbon number, and the stability of alkylated cycloalkanes decreases with increasing length or carbon number in the side chain. At temperatures above 400°C, decomposition of long-chain paraffins in jet fuels is dominated by radical-chain reactions. Hydroaromatic compounds such as tetralin are hydrogen donors that can serve as radical scavengers in pyrolytic reactions that inhibit the thermal decomposition of reactive hydrocarbons.

Coal-derived JP-8C fuel has been shown to be thermally stable at temperatures up to 482°C or 900°F (9).

Studies With Model Compounds

At PSU, the thermal stability of coal- and petroleum-derived jet fuels and the associated model compounds decahydronaphthalene and n-tetradecane was studied under both batch and flow conditions. Under batch reactor conditions, the decahydronaphthalene showed excellent thermal stability up to 500°C, whereas the n-tetradecane started its cracking process at around 450°C. Flow reactor studies mirrored the thermal decomposition of the model compounds, although the cracking appeared at higher bulk fuel temperatures. The thermal behavior of the experimental jet fuels also confirmed that the paraffinic portion of the fuels is the main reason for thermal fuel degradation.

The current jet fuels are petroleum-derived and consequently rich in linear alkanes, which are highly susceptible to pyrolytic cracking, resulting in coking. Therefore, the thermal stability of a jet fuel in the pyrolytic regime can be greatly enhanced by utilizing liquids rich in cycloalkanes.

An additional problem with jet fuels is the presence of dissolved oxygen from air, which reacts with the fuel during the autoxidative regime (150°C to 250°C) before the fuel and its oxygenated reaction products enter the pyrolytic regime (400° to 500°C). Accordingly, a recent study compares the thermal stability of coal- and petroleum-derived jet fuels and associated model compounds, as they go through the autoxidative and pyrolytic regime, both under batch and flow conditions (10). Differences in chemical reactivity between linear- and cyclo-alkane model compounds are related to the superior thermal stability of coal-derived jet fuels.

HIGH ENERGY DENSITY FUELS

At one time the military expended considerable effort on fuels with a high energy density. Of particular interest were the naphthenic (cycloparaffinic) fuels that can be produced from shale oil. However, almost all aircraft today are weight-limited on takeoff so a reduction in fuel volume is not of high value. Missile and rocket applications, such as cruise missiles, are volume constrained and could make use of high energy density, but these are limited applications in terms of the amount of fuel involved.

Demand, Production, and Prices for Jet Fuel

Demand for Jet Fuel

The historic demand for jet fuel in the United States is given in Table 7. As of 1999, jet fuel demand was 1.67 million barrels per day. This accounts for approximately 8.5% of total petroleum products demand.

Total military demand for jet fuel is about 228,000 barrels per day. This is nearly the same demand as existed in 1985 and is a little less than 14% of current total jet fuel demand, whereas in 1985 it was nearly 19% of total demand.

Demand Forecast

Summarized in Table 8 are various forecasts for jet fuel demand in the years 2010 and 2020. All show continuing increases in jet fuel demand through 2020. The forecast rate of growth to 2020 varies from 1.5% per year to 3.5% per year. For the period 2010-2020, all forecasts use a growth rate of about 3% per year.

Production of Jet Fuel

Production of jet fuel at United States refineries, by fuel type and by Petroleum Administration for Defense (PDA) district and by state is illustrated in Table 9. These data are for November 2000.

Prices for Jet Fuel

Historical fuel price statistics for Jet-A are given in Table 10. Sales for resale, that is, wholesale sales, are those made to purchasers who are other than ultimate consumers. Sales to end users are those made directly to the ultimate consumer, including bulk sales customer, such as agriculture, industry, and utilities, as well as residential and commercial customers.

Current prices for Jet-A used in private aircraft at various airports are listed in Table 11. These prices vary widely from airport to airport.

Table 7

**Jet Fuel and Total Petroleum
Products Supplied by Year**

| <u>Year</u> | <u>Jet Fuel</u> | <u>Total</u> |
|-------------|-----------------|--------------|
| 1950 | 0.00 | 6.46 |
| 1951 | 0.00 | 7.02 |
| 1952 | 0.05 | 7.27 |
| 1953 | 0.09 | 7.60 |
| 1954 | 0.13 | 7.76 |
| 1955 | 0.15 | 8.46 |
| 1956 | 0.20 | 8.78 |
| 1957 | 0.22 | 8.81 |
| 1958 | 0.27 | 9.12 |
| 1959 | 0.33 | 9.53 |
| 1960 | 0.37 | 9.80 |
| 1961 | 0.42 | 9.98 |
| 1962 | 0.49 | 10.40 |
| 1963 | 0.52 | 10.74 |
| 1964 | 0.56 | 11.02 |
| 1965 | 0.60 | 11.51 |
| 1966 | 0.67 | 12.08 |
| 1967 | 0.82 | 12.56 |
| 1968 | 0.95 | 13.39 |
| 1969 | 0.99 | 14.14 |
| 1970 | 0.97 | 14.70 |
| 1971 | 1.01 | 15.21 |
| 1972 | 1.02 | 16.37 |
| 1973 | 1.04 | 17.31 |
| 1974 | 0.98 | 16.65 |
| 1975 | 0.99 | 16.32 |
| 1976 | 0.98 | 17.46 |
| 1977 | 1.02 | 18.43 |
| 1978 | 1.04 | 18.85 |
| 1979 | 1.07 | 18.51 |
| 1980 | 1.06 | 17.06 |
| 1981 | 1.01 | 16.06 |
| 1982 | 1.01 | 15.30 |
| 1983 | 1.05 | 15.23 |
| 1984 | 1.18 | 15.73 |
| 1985 | 1.22 | 15.73 |
| 1986 | 1.31 | 16.28 |
| 1987 | 1.38 | 16.67 |
| 1988 | 1.45 | 17.28 |
| 1989 | 1.49 | 17.33 |
| 1990 | 1.52 | 16.99 |
| 1991 | 1.47 | 16.71 |
| 1992 | 1.45 | 17.03 |
| 1993 | 1.47 | 17.24 |
| 1994 | 1.53 | 17.72 |
| 1995 | 1.51 | 17.72 |
| 1996 | 1.58 | 18.31 |
| 1997 | 1.60 | 18.62 |
| 1998 | 1.62 | 18.92 |
| 1999 | 1.67 | 19.39 |

Source: 15

Table 8
Comparison of Jet Fuel Forecasts

| <u>Projection</u> | <u>Annual Energy Outlook 2001</u> | | | <u>Other Forecasts</u> | | |
|-------------------------------|-----------------------------------|----------------------------|-----------------------------|------------------------|------------|------------|
| | <u>Reference</u> | <u>Low World Oil Price</u> | <u>High World Oil Price</u> | <u>WEFA</u> | <u>GRI</u> | <u>DRI</u> |
| 2010 | | | | | | |
| World Oil Price (1999 \$/bbl) | 21.37 | 15.10 | 26.66 | 18.48 | 18.17 | 18.65 |
| Jet Fuel Demand, million bpd | 2.18 | 2.20 | 2.16 | 1.92 | 2.20 | 2.37 |
| 2020 | | | | | | |
| World Oil Price (1999 \$/bbl) | 22.41 | 15.10 | 28.42 | 20.41 | NA | 21.16 |
| Jet Fuel Demand, million bpd | 2.88 | 2.91 | 2.84 | 2.58 | NA | 3.16 |

Source: 16

Table 9

**Refinery Net Production of Jet Fuel by PAD and Refining District
(Data for Month of November 2000, Thousand Barrels)**

| | <u>Naphtha Type</u> | <u>Kerosene Type Military</u> | <u>Kerosene Type Commercial</u> |
|---------------------|-------------------------|-----------------------------------|-------------------------------------|
| PAD District I | | | |
| East Coast | 0 | 0 | 2,926 |
| Appalachian No. 1 | 0 | 11 | 39 |
| PAD District II | | | |
| IN, IL, KY | 0 | 189 | 5,289 |
| MN, WI, SD, ND | 0 | 45 | 902 |
| OK, KS, MO | 0 | 119 | 928 |
| PAD District III | | | |
| TX Inland | 0 | 307 | 1,326 |
| TX Coast | 0 | 1,447 | 10,737 |
| LA Coast | 0 | 363 | 10,851 |
| N. LA, AR | 0 | 43 | 218 |
| NM | 0 | 199 | 0 |
| PAD Districts IV, V | | | |
| Rocky Mountain | 0 | 153 | 711 |
| West Coast | 1 | 1,247 | 10,552 |

Source: 17

Table 10

**Refiner Sales Prices and Refiner Margins
For Jet Fuel
(Cents per Gallon)**

| <u>Year</u> | <u>Sales Price to Resellers</u> | <u>Sales Price to End Users</u> | <u>Refiner Margin</u> |
|-------------|-------------------------------------|-------------------------------------|---------------------------|
| 1983 | 85.4 | 87.8 | 16.4 |
| 1984 | 83.0 | 84.2 | 14.9 |
| 1985 | 79.4 | 79.6 | 15.8 |
| 1986 | 49.5 | 52.9 | 14.9 |
| 1987 | 53.6 | 54.3 | 11.2 |
| 1988 | 49.5 | 51.3 | 14.6 |
| 1989 | 58.3 | 59.2 | 15.5 |
| 1990 | 77.3 | 76.6 | 24.4 |
| 1991 | 65.0 | 65.2 | 19.6 |
| 1992 | 60.5 | 61.0 | 16.5 |
| 1993 | 57.7 | 58.0 | 18.6 |
| 1994 | 53.4 | 53.4 | 16.3 |
| 1995 | 53.9 | 54.0 | 12.9 |
| 1996 | 64.6 | 65.1 | 15.3 |
| 1997 | 61.3 | 61.3 | 16.0 |
| 1998 | 45.0 | 45.2 | 15.2 |
| 1999 | 53.8 | 53.8 | 12.2 |

Source: 18

Table 11

**National Fuel Price Statistics
(Dollars per Gallon, March 27, 2001)**

| <u>Region</u> | <u>High</u> | <u>Average</u> | <u>Low</u> | <u>Difference</u> |
|------------------|-------------|----------------|------------|-------------------|
| USA -- 48 States | 3.60 | 2.42 | 1.48 | 2.12 |
| Northwest Region | 2.99 | 2.42 | 1.76 | 1.23 |
| Southwest Region | 3.29 | 2.46 | 1.59 | 1.70 |
| N Central Region | 2.99 | 2.36 | 1.48 | 1.51 |
| S Central Region | 3.11 | 2.30 | 1.57 | 1.54 |
| E Central Region | 3.31 | 2.44 | 1.72 | 1.59 |
| Northeast Region | 3.60 | 2.52 | 1.75 | 1.85 |
| Southeast Region | 3.33 | 2.46 | 1.52 | 1.81 |

Source: 19



Chemical and Physical Properties Needed for Jet Fuel

Specifications

Specifications for Jet-A are published in ASTM D1655 (11). Specifications for JP-8 are contained in MIL-T-83133E. Summaries of the two are given in Tables 12 and 13, respectively.

The chief differences between the two are in the additives package used.

Mil Spec 83133 covers three variations of JP-8 according to the additives used (Table 14).

Limits on Aromatics

Although made up of many different hydrocarbons, jet fuels consist essentially of four general types of compounds: paraffins (including isoparaffins), cycloparaffins or naphthenes, aromatics, and olefins. The proportion of each compound type varies with the different types of crude oils and the processing needed to produce the fuel. A typical fuel will contain hundreds of different compounds. In general, paraffin hydrocarbons offer the most desirable combustion cleanliness characteristics for jet fuels. Naphthenes are the next most desirable hydrocarbons for this use.

Although olefins generally have good combustion characteristics, their poor gum stability usually limits their use in aircraft turbine fuels to about 1% by volume or less. Aromatics generally have the least desirable combustion characteristics for aircraft turbine fuel. In aircraft turbines they tend to burn with a smoky flame and release a greater proportion of their chemical energy as undesirable thermal radiation than the other hydrocarbons. Naphthalenes or bicyclic aromatics produce more soot, smoke, and thermal radiation than monocyclic aromatics and are, therefore, the least desirable hydrocarbon class for aircraft jet fuel use. Thus, Jet A is limited to 20% maximum aromatics and JP-8 is limited to 25% by volume. Naphthalene content is limited to 3% for the same reason.

Except for the restrictions on aromatics, the proportions of hydrocarbon types are not directly controlled. In fact, not even the source of the feedstock is constrained, other than that it must be from petroleum, tar sands, oil shale or mixtures thereof. The requirements for density, energy content, freeze point and hydrogen content favor paraffinic- or isoparaffinic-based fuel. The hydrocarbon constituents of most jet fuels are primarily normal or isoparaffins (50% to 70% by volume) and cycloparaffins (20% to 40% by volume). See Table 3.

Fuels From Non-Conventional Sources

Jet fuels containing synthetic hydrocarbons have been previously allowed under ASTM Specification D 1655. However, the fraction of synthetic hydrocarbons was not limited, and there were no requirements or restrictions placed on either these hydrocarbons or the final blend. It has been recognized that synthetic blends represent a potential departure from experience and from key assumptions on which the fuel property requirements defined in Table 12 have been based.

Table 12

Specifications for Domestic Aviation Turbine Fuels

| Property | Jet A or Jet A-1 | Jet B |
|--|---------------------------------------|--------------------|
| Composition | | |
| Acidity, total mg KOH/g, max | 0.10 | -- |
| Aromatics, vol.%, max | 25 | 25 |
| Sulfur, mercaptan, wt.%, max | 0.003 | 0.003 |
| Sulfur, total wt.%, max | 0.30 | 0.3 |
| Volatility | | |
| Distillation Temp., °C | | |
| 10% Recovered, temp., max | 205 | -- |
| 20% Recovered, temp., max | -- | 145 |
| 50% Recovered, temp., max | report | 190 |
| 90% Recovered, temp., max | report | 245 |
| Final Boiling Point, temp., max | 300 | -- |
| Distillation Residue, %, max | 1.5 | 1.5 |
| Distillation Loss, %, max | 1.5 | 1.5 |
| Flash Point, °C, min | 38 | -- |
| Density at 15°C, kg/m ³ | 775 - 840 | 751 - 802 |
| Vapor Pressure, 38°C, kPa, max | -- | 21 |
| Fluidity | | |
| Freezing Point, °C, max | -40 Jet A* -47 Jet A-1* | -50* |
| Viscosity -20°C, mm ² /s, max | 8.0 | |
| Combustion | | |
| Net Heat of Combustion, MJ/kg, min | 42.8 | 42.8 |
| One of the Following Requirements Shall be Met: | | |
| Luminometer Number, min | 45 | 45 |
| Smoke Point, mm, min | 25 | 25 |
| Smoke Point, mm and | 18 | 18 |
| Naphthalenes, vol.%, max | 3.0 | 3.0 |
| Corrosion | | |
| Copper Strip, 2 h at 100°C | No. 1 | No. 1 |
| Thermal Stability JFTOT (2.5 h at control temp. of 260°C min) | | |
| Filter Pressure Drop, mm Hg, max | 25 | 25 |
| Tube Deposits Less Than | 3 | 3 |
| | No Peacock or Abnormal Color Deposits | |
| Contaminants | | |
| Existent Gum, mg/100 mL, max | 7 | 7 |
| Water Reaction: Interface Rating, max | 1b | 1b |
| Additives | | |
| Electrical Conductivity, pS/m | see Table 14 ** | see Table 14 ** |

*Other freezing points may be agreed upon between supplier and purchaser.

**If electrical conductivity additive is used, the conductivity shall not exceed 450 pS/m at the point of use of the fuel.

Source: 11

Table 13

Military Aviation Fuel Specification

| <u>Property</u> | <u>Min.</u> | <u>Max.</u> |
|--|-------------|-----------------|
| Color Saybolt | | a |
| Total Acid Number, mg KOH/gm | | 0.015 |
| Aromatics, vol.% | | 25.0 |
| Sulfur, total, mass % | | 0.30 |
| Sulfur Mercaptan, mass % OR | | 0.002 |
| Doctor Test | | negative |
| Distillation Temp., °C | | |
| Initial Boiling Point | | a |
| 10% Recovered | | 205 |
| 20% Recovered | | a |
| 50% Recovered | | a |
| 90% Recovered | | a |
| End Point | | 300 |
| Residue, vol.% | | 1.5 |
| Loss, vol.% | | 1.5 |
| Flash Point, °C | 38 | |
| Density or Gravity | | |
| Density, kg/L at 15°C OR | 0.775 | 0.840 |
| Gravity, API at 60°F | 37.0 | 51.0 |
| Freezing Point, °C | | -47 |
| Viscosity, at -20°C, mm ² /s | | 8.0 |
| Net Heat of Combustion, MJ/kg | 42.8 | |
| Hydrogen Content, mass% | 13.4 | |
| Smoke Point, mm, OR | 25.0 | |
| Smoke Point, mm, AND | 19.0 | |
| Naphthalene, vol.% | | 3.0 |
| Calculated Cetane Index | | a |
| Copper Strip Corrosion, 2hr at 100°C (212°F) | | No. 1 |
| Thermal Stability | | |
| Change in Pressure Drop, mm Hg | | 25 |
| Heater Tube Deposit, visual rating | | <3 ^b |
| Existent Gum, mg/100 ml | | 7.0 |
| Particulate Matter, mg/L | | 1.0 |
| Filtration Time, minutes | | 15 |
| Water Reaction Interface Rating | | 1b |
| Water Separation Index | d | |
| Fuel System Icing Inhibitor, vol.% | 0.10 | 0.15 |
| Fuel Electrical Conductivity, pS/m | c | c |

^aTo be reported, not limited

^bPeacock or abnormal color deposits result in failure

^cThe conductivity must be between 150 and 450 pS/m for F-34 (JP-8) and between 50 and 450 pS/m for F-35, at ambient temperature. In the case of JP-8+100, the conductivity limit must be between 150 and 700 pS/m at ambient temperature.

^dThe minimum microseparator rating using a Micro-Separator (MSEP) shall be as follows:

| <u>JP-8 Additives</u> | <u>MSEP Rating, min.</u> |
|---|--------------------------|
| Antioxidant (AO), Metal Deactivator (MDA) | 90 |
| AO, MDA, and Fuel System Icing Inhibitor (FSII) | 85 |
| AO, MDA, and Corrosion Inhibitor/Lubricity Improver (CI/LI) | 80 |
| AO, MDA, FSII and CI/LI | 70 |

Source: 20

Table 14

Military Jet Fuels

| <u>NATO Code No./Grade</u> | <u>Description</u> |
|----------------------------|--|
| F-35 | Kerosene type turbine fuel which will contain a static dissipator additive, may contain antioxidant, corrosion inhibitor/lubricity improver, and metal deactivator but will not contain fuel system icing inhibitor. |
| F-34 (JP-8) | Kerosene type turbine fuel which will contain a static dissipator additive, corrosion inhibitor/lubricity improver, and fuel system icing inhibitor, and may contain antioxidant and metal deactivator. |
| JP-8+100 | F-34 (JP-8) type kerosene turbine fuel which contains a thermal stability improver additive. |

Source: 20

The longer-term strategy is to revise Specification D 1655 to fully encompass fuels from non-conventional sources, but this has yet to be defined. As an interim solution, ASTM has deemed necessary to recognize, on an individual basis, fuels from non-conventional sources whose performance complies with the intent of this specification.

The Sasol semi-synthetic fuel, a blend of conventionally produced kerosene and a synthetic kerosene is recognized as meeting the requirements of Specification D 1655.

Additive Requirements

For JP-8, the following additives are allowed or required.

Antioxidants

Immediately after processing and before the fuel is exposed to the atmosphere (i.e., during rundown into feed/batch tankage), an antioxidant is added in order to prevent the formation of gums and peroxides after manufacture. The concentration of antioxidant added must be not less than 17.2 mg nor more than 24.0 mg of active ingredient per liter of fuel. The following antioxidant formulations are approved:

- 2,6-di-*tert*-butyl-4-methylphenol
- 6-*tert*-butyl-2,4-dimethylphenol
- 2,6-di-*tert*-butylphenol

- 75% minimum 2,6-di-*tert*-butylphenol
25% maximum *tert*-butylphenols and tri-*tert*-butylphenols
- 72% minimum 6-*tert*-butyl-2,4-dimethylphenol
28% maximum *tert*-butyl-methylphenols and *tert*-butyl-dimethylphenols
- 55% minimum 2,4-dimethyl-6-*tert*-butylphenol and
15% minimum 2,6-di-*tert*-butyl-4-methylphenol and
30% maximum mixed methyl and dimethyl *tert*-butylphenols

Metal Deactivator

A metal deactivator, N,N'-disalicylidene-1,2-propanediamine, may be blended into the fuel. The concentration of active material used on initial batching of the fuel at the refinery must not exceed 2.0 mg/L. Cumulative addition of metal deactivator when redoping the fuel, must not exceed 5.7 mg/L.

Static Dissipater Additive

An additive is blended into the fuel in sufficient concentration to increase the conductivity of the fuel to within the range specified in Table 13 at the point of injection. The following electrical conductivity additive is approved: Stadis 450 marketed by Octel America Inc.

Corrosion Inhibitor

A corrosion inhibitor conforming to *MIL-PRF-25017* shall be blended into the F-34 (JP-8) grade fuel by the contractor. The corrosion inhibitor additive is optional for F-35.

The conductivity of the fuel must be between 150 and 450 pS/m for F-34 (JP-8) and between 50 and 450 pS/m for F-35, at ambient temperature. In the case of JP-8+100, the conductivity limit must be between 150 and 700 pS/m at ambient temperature.

Fuel System Icing Inhibitor

The use of a fuel system icing inhibitor is mandatory for NATO F-34 (JP-8) and shall conform to *MIL-DTL-85470*.

Thermal Stability Improver Additive

Personnel at the operating location must request written approval from the cognizant authority if they wish to add a thermal stability improver additive to the fuel.

Qualified thermal stability improver additives are SPEC AID 8Q462, and AeroShell Performance Additive 101.

Fuel Lubricity

Aircraft/engine fuel system components and fuel control units rely on the fuel to lubricate their moving parts. The effectiveness of a jet fuel as a lubricant in such equipment is referred to as its lubricity. Differences in fuel system component design and materials result in varying degrees of equipment sensitivity to fuel lubricity. Similarly, jet fuels vary in their level of lubricity. In-service problems experienced due to low lubricity have ranged in severity from reductions in pump flow to unexpected mechanical failure leading to in-flight engine shutdown.

Severe hydroprocessing removes trace components, resulting in fuels that tend to have lower lubricity than straight-run or wet-treated fuels. Certain additives, for example, corrosion inhibitors, can improve the lubricity and are widely used in military fuels. They have been used occasionally in civil jet fuel to overcome aircraft problems but only as a temporary remedy while improvements to the fuel system components or changes to fuel were achieved. Because of their polar nature, these additives can have adverse effects on ground base filtration systems and on fuel water separation characteristics.

Some modern aircraft fuel system components have been designed to operate on low lubricity fuel. Problems are more likely to occur when aircraft operations are confined to a single refinery source where fuel is severely hydroprocessed and where there is no co-mingling with fuels from other sources during distribution between refinery and aircraft.

Conclusion

A brief examination of jet fuel specifications shows that aromatic compounds are generally undesirable components of jet fuel. The major reason is their unfavorable combustion behavior in aircraft turbine engines. Aromatic fuels result in smoke in the exhaust along with coke formation and overheating in the combustor. Therefore, jet fuel specifications limit the amount of aromatics allowed in both military and civilian jet fuels.

Military research directed toward jet fuels of the future has focused on high energy density fuels and on fuels with high temperature stability. Only the latter is currently being pursued in a significant way. Although alkyl benzenes might have a reasonably high energy density and good temperature stability, the unfavorable combustion characteristics completely bar their use as a bulk fuel.

Even if use as a bulk fuel is not allowable, it is possible that small amounts could be employed as an additive. Useful changes in fuel properties would have to result. A review of currently used additives and their chemical composition did not reveal any applications for alkyl benzenes.

We therefore conclude that there is no potential market for alkyl benzenes as jet fuel components or additives.

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