JOURNAL OF PROPULSION AND POWER
Vol. 19, No. 6, November–December 2003

Liquid Fuels and Propellants for Aerospace Propulsion: 1903–2003

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Introduction

MAJOR increases in liquid-fueled propulsion performance have occurred in the past 100 years. The Wright brothers first flew on 14 December 1903 with an engine that generated slightly more than 130 lb of thrust for flights that ranged from 120 to 850 ft (Ref. 1). Contrast that with current aircraft such as the Boeing 777, which can fly 8000 n miles, equipped with engines from the GE90 and PW4000 series that generate over 100,000 lb of thrust. The Wright brothers probably consumed less than a gallon of gasoline in that first day of flight tests. In 1997, airlines consumed an average of 177 million gal/day of jet fuel worldwide.[2*] Robert Goddard's first flight of a liquid rocket on 16 March 1926 reached an altitude of 41 ft and landed 184 ft from the launch point (see Ref. 3). Again, the contrast with current vehicles such as the space shuttle, which can lift over 50,000 lb to 200+ miles into low Earth orbit,[4] is dramatic. The intent of this paper is to describe the evolution of liquid fuels for aircraft and rockets as the engines and vehicles they fuel have undergone these significant increases in performance.

Engine Figures of Merit

To understand the evolution of fuels and propellants, it is helpful to introduce the fuel properties that drive engine performance. For reciprocating, for example, Otto cycle, engines, the key engine parameters are horsepower/weight ratio (primarily driven by compression ratio) and specific fuel consumption (fuel mass flow divided by engine thrust or horsepower). As described later, the maximum compression ratio is typically limited by the tendency of aviation gasoline to autoignite prematurely, as characterized by octane number. For gas turbine (Brayton cycle) engines, the most important engine parameters are thrust/weight ratio and specific fuel consumption. The fuel parameters most relevant to gas turbine engine and vehicle performance are the heat of combustion on a mass basis in air and the density. Through the well-known Breguet range equation, these two parameters directly affect the range of the aircraft. For aircraft today, the cost of the fuel is also a key parameter. There are many other fuel parameters that are important to reliable engine operation relating to fuel composition, volatility, combustion performance, stability, and contaminants. The role of these properties in gas turbine engine performance is a key part of the historical discussion to follow.

For liquid propellant rockets, the key propellant-related parameters are specific impulse I_{sp} (thrust divided by propellant mass flow rate) and propellant density. Of course the key difference between aircraft engines and rocket engines is the rocket requirement to carry an oxidizer onboard the vehicle. The propellant-driven parts of the I_{sp} parameter are the propellant (fuel plus oxidizer) heats of formation and the propellant stoichiometry.[5,6] In general, I_{sp} is proportional to the square root of the ratio of the flame temperature to the combustion-product molecular weight, so that I_{sp} is maximized by high flame temperatures and low-molecular weight combustion products. A key parameter for both rockets and airbreathing missiles is the propellant density. For a given application, the figure of merit for the propellants is $I_{sp} \times \text{density}^a$, where a is an exponent that varies for different applications, but is typically between 0.2 and 1 (Ref. 7). In general, density is most important for the first stage of multistage vehicles. Although the cost of the propellants is a small fraction of the launch cost, the operations cost and ease of handling of propellants is a key concern, particularly for cryogenic and toxic storable propellants. For ballistic missile applications (where the rocket must remain fueled for long-periods of time), noncryogenic (storable) propellants are used to avoid the difficulties of long-term storage of cryogenic propellants.

Brief Note on Terminology

Fuels based on petroleum distillates have incorporated a host of somewhat nebulous terms based in the terminology of the early refining industry. Early petroleum refineries were primarily distilleries, with products (fractions) differentiated by boiling point. Thus, a reader may come across unfamiliar terms such as kerosene, naphtha, gas oil, heavy or light fraction, sweet or sour crude, straight-run, hydrotreated, etc. Table 1 is an attempt to list the common terms for petroleum fractions.[2,8–11] There is considerable overlap between categories, as well as considerable disagreement about the definition of a particular generic category. For example, one reference gives a definition of kerosene as "a refined petroleum distillate that has a flash point of 25 C (77 F),"[11] in contrast to the boiling range definitions in Table 1. In general, as the boiling temperature increases, the molecular weight and density increase and the vapor pressure decreases. Thus, one might describe the upper boiling range of a fraction as the heavy or residual end of the fraction.

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Received 17 April 2003; revision received 15 August 2003; accepted for publication 29 August 2003.

[*] Data also available at http://www.chevron.com/prodserv/fuels/bulletin/.

Table 1 Petroleum distillate terminology [2,8–11]

Fractions	Approximate boiling range, °C	Typical average carbon number	Most prevalent carbon number
Generic terms			
Gasoline	<200		
Naphtha	150–250		
Kerosene	200–300		
Fuel oil/gas oil	>275		
Specific products			
Avgas	45–145	C_7	C_8
Motor gasoline (mogas)	30–200	C_7	C_5
Auto diesel	200–350	C_{16}	C_{16}
Jet fuel	150–265	C_{11}	C_{11}

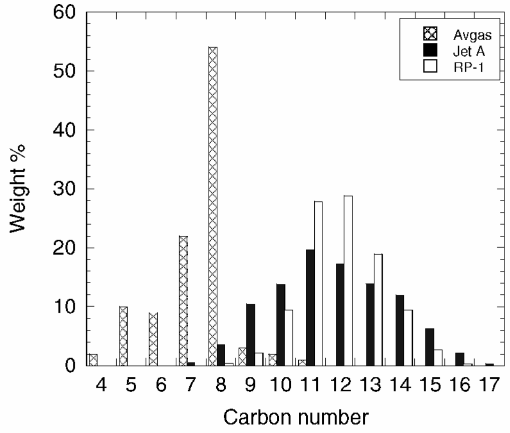


Fig. 1 Carbon number distribution for various hydrocarbon fuels and propellants.

Low- (mercaptan) sulfur-content products are described as sweet (in contrast to high-sulfur products being described as sour). A fuel that is created primarily by distillation is straight run, whereas a fuel subjected to the two most common treatments to reduce sulfur and other impurities would be called either hydrotreated or Merox treated. The original product of the petroleum refining industry was lamp fuel; hence, Whittle's use of illuminating kerosene in his gas turbine engine. Aviation gasoline obviously falls in the generic gasoline fraction, whereas most jet fuels and liquid hydrocarbon propellants can be described generically as kerosene. These definitions are shown in Fig. 1, where the carbon number distribution for aviation gasoline (avgas), jet fuel (Jet A), and rocket fuel (RP-1) is illustrated. The carbon number distribution in Fig. 1 is interpreted as, for example, avgas consisting of over 50% (by weight) molecules that contain 8 carbon atoms. Auto diesel fuel falls mostly into the kerosene range, whereas some heavier, for example, marine, diesel fuels can be described as gas/fuel oil or residual fuel. Currently, the United States consumes roughly twice as much gasoline as diesel and jet fuel combined, whereas other parts of the world have a more even distribution.

Airbreathing Aviation Fuels

This discussion on aviation fuels relies very heavily on several significant references.[12–16] The interested reader is strongly encouraged to seek out these excellent documents, and the references cited therein, for additional details that are beyond the scope of this paper.

Aviation gasoline (avgas)

In 1903, the Wright brothers flew, quite naturally, on motor gasoline. They built their own engine, one of many innovations in their aircraft. Their four-cylinder water-cooled engine weighed 180 lb (83 kg) and developed 12 hp (9 kW). They used "several cans of Standard Oil motor gasoline from a nearby boatyard."[12] This engine was quite an advance over the steam engines used by some of their competitors. As subsequent aircraft engines evolved, the tendency of the gasoline to autoignite ahead of the spark (preignition) or before the arrival of the flame front (knocking, pinging) was a key limiting factor in aircraft engine performance. This is the same knocking that occurs in automobile engines today, but it is much more destructive and dangerous in aircraft engines. During the World War I period, various researchers (notably Ricardo's group in England) identified this autoignition phenomenon and began to identify the fuel's characteristics that controlled it. The hydrocarbon constituents of fuels can be divided into five classes of compounds (Fig. 2): paraffins, isoparaffins, cycloparaffins (naphthenes), olefins, and aromatics. It was found that aromatics such as benzene (benzol in older literature was a crude mixture of aromatics consisting primarily of benzene) were less prone to knocking and thus, avgas produced from crude oils rich in aromatics were better performers than fuels that were primarily paraffinic. These differences became evident as the United States entered World War I and began supplying gasolines from quite different sources than typically encountered in Europe. The more-paraffinic U.S. gasolines performed relatively poorly in the advanced European engines such as the French Gnome. A key development in understanding avgas performance came in the 1920s with the standardization of test methods and engines to determine a the tendency of a fuel to knock. This standardization work was led by the Cooperative Fuel Research (CFR) committee in the United States, composed of representatives from the engine and petroleum refining industries. The tendency of a fuel to knock was characterized by its octane rating, developed by Edgar, which compared the tendency of a given gasoline to knock to that of a reference fuel composed of a mixture of n-heptane (octane number = 0) and isooctane (octane number = 100). On this scale, the Wright brother's 1903 fuel has been estimated to be 38 octane,[13,17] with their 1910 fuel estimated as 58 octane (Ref. 18). By 1932, industry had generally adopted a standardized method for knock rating, using an engine designed by H. L. Horning of the Waukesha Motor Company for the CFR committee, and Edgar's fuel standards. Note that the octane scale ranks fuels quite differently than the cetane scale for fuels for diesel engine applications. In a compression-ignition engine such as a diesel, fuels that ignite easily are desirable. Thus, cetane (hexadecane, $C_{16}H_{34}$) has a cetane number of 100, whereas the isoparaffin heptamethylnonane has a cetane rating of 15. Note the inversion of the scales: Aromatics and isoparaffins rank high on the octane scale and low on the cetane scale, whereas the reverse is true of *n* paraffins.

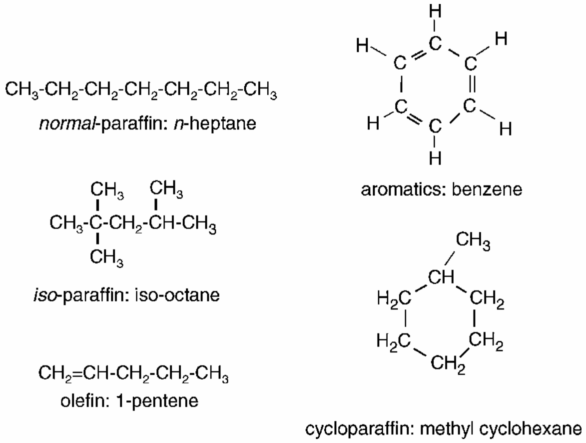


Fig. 2 Classes and examples of hydrocarbons found in hydrocarbon fuels; research octane numbers: isooctane = 100, n-heptane = 0, 1-pentene = 77, methyl cyclohexane (MCH) = 71, and benzene = 123.

In a reciprocating spark-ignition engine, the fuel and air are mixed, injected into a cylinder, compressed, and then ignited. The development of higher octane avgas was driven by the engine performance increases obtainable via turbocharging/supercharging and increased compression ratios.[2,4] Turbocharging is accomplished by compressing engine inlet air using a turbine driven by hot engine exhaust gas. Supercharging is the same air compression accomplished by a shaft-mounted turbine. Turbocharging/supercharging dramatically increase the maximum speed and altitude that can be achieved, when compared to an engine where the intake air is at ambient pressure. The compression ratio is the ratio of the combustion chamber volume at bottom dead center (maximum) and top dead center (minimum). Higher compression ratios enable smaller engines for a given power output, in other words, increased engine power/volume ratios. The maximum compression ratio and maximum amount of inlet air pressurization are both limited by knocking/fuel autoignition. A tremendous advance in fuel performance came from the investigations of Midgeley and Boyd, working for Charles Kettering in the Dayton Engineering Laboratory (Delco) in Dayton, Ohio. From an exhaustive study of knock promoters and preventers emerged the remarkable additive tetraethyl lead (TEL) in December 1921. This additive enabled the production of large quantities of higher octane avgas. It was found that the sensitivity of avgas to lead varied widely, with aromatic avgas less sensitive to knock retardation by lead (as compared to more paraffinic gasolines). The problem of deposition of solid lead oxides on exhaust valves was solved by the addition of ethylene dibromide (EDB) with the TEL. The EDB reacted with the lead in the combustion chamber, forming volatile lead bromide compounds.

Fuel refiners and engine manufacturers engaged in a game of technological leap frog in the late 1920s and 1930s, as improvements in engines led to requirements for improved fuels (and vice versa). The first avgas specification that included octane number performance requirements was issued by the U.S. Army for 87 octane in 1930.[12,14] A significant milestone came in 1934, when the Powerplant Branch of the U.S. Army Air Corps at McCook (later Wright) Field in Dayton issued the specification X3575 for 100/130 octane avgas. This specification came about from the work at McCook Field (Dayton, Ohio) led by Heron, which demonstrated the significant gains in performance from higher octane fuels. The first number in the specification is the lean octane rating and the second is the rich (high-power) rating. Octane ratings above 100 were characterized by performance numbers, with the reference fuels being mixtures of isooctane and TEL. For example, 3–cm^3 TEL/gal of isooctane yields a rich performance number (PN) of 145. The PN scale is roughly linearly related to maximum engine output power; in other words, a fuel with a 145 PN will yield 45% more knock-limited output power than a 100 PN (=100 octane) fuel. Alternatively, an engine rated at 1500 hp on 145 PN avgas may only develop 600 hp on 80 octane avgas.[16] The 100/130 octane specification (AN-F-28 in 1942) allowed up to 3-cm^3 of TEL/gal, but still required high octane base gasoline. The production of this fuel challenged refiners for the next 10 years and lead to the development of alkylation and catalytic cracking processes. The availability of 100 octane avgas from the United States is widely acknowledged as one of the key contributors to the British victory in the Battle of Britain against a numerically superior foe during World War II. The production of avgas increased from 54 million gal/year in 1932 to more than 25 million gal/day at the end of World War II. The unprecedented industry/government cooperation needed to surmount the challenges posed by this enormous expansion in refining capacity has been described by Heron.[14] The quest for more powerful engines led to 108/135 and 115/145 avgas specifications in the 1940s. The rather chaotic pace of gasoline and engine development led to the creation of 12 separate grades of gasoline by 1945, often distinguished by dye.[19] In that year, the American Society for Testing and Materials (ASTM) codified the grades of avgas in specification D 615: 80/87 (red) with 0.5-cm^3 TEL/gal, 91/96 (blue, 4.6-cm^3/gal), 100/130 (green, 4-cm^3/gal), and 115/145 (purple, 4.6-cm^3/gal).

As gas turbine-powered aircraft became predominant following World War II, the 100/130 and 80/87 octane specifications became the primary ones used. Civilian airlines had generally resisted the use of 100 octane fuel before the war because of cost factors. However, improvements in fuels and engines enabled greater altitudes of operation, which had many operational benefits. The availability of improved fuels has been credited as the biggest contribution of World War II to the commercial airline industry.[20] Once the airline industry adopted the gas turbine engine in the late 1950s,[21] the use of aviation gasoline was confined to the relatively small general aviation market. An illustration of these market changes can be seen in the fuel consumption numbers in Fig. 3.[2,22]

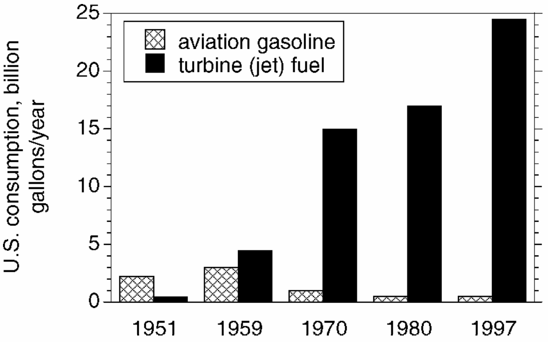


Fig. 3 Trends in U.S. aviation fuel consumption.[2,22]

By the 1980s, various forces had reduced the available grades of avgas to essentially one: 100LL (low lead), currently specified under (ASTM) specification D 910 as containing a maximum of 0.56 g/l TEL maximum. Type certification can be obtained from the aircraft manufacturer for the use of unleaded motor gasoline. The use of (unleaded) automotive gasoline in aircraft is controversial.[22,23] Aside from the lead issue, there are differences in volatility, additives and blending components (especially oxygenates), and quality control.

Thus, the development of high-performance avgas in many ways paced the development of reciprocating aircraft engines. The relationship between jet fuels and gas turbine engines was not as close, however. Even in 1949, it was anticipated that improvements in gas turbine engine performance would be much less sensitive to improvements in fuel.[14]

Turbine Engine Fuels

The early pioneers in gas turbine development, Whittle in England and Von Ohain in Germany, faced a wide variety of options in choosing a fuel for gas turbines. Whittle had considered diesel fuel, but ended up choosing illuminating kerosene because of an expected requirement for a lower freeze point than that available with diesel (see Ref. 15). In contrast, Von Ohain originally demonstrated his turbine engine with hydrogen, but vehicle considerations led to a switch to liquid fuel (see Refs. 12 and 21). The world's first turbojet-powered flight was made on 27 August 1939 in a Heinkel 178 aircraft burning avgas. The first flight of the Whittle engine occurred on 15 May 1941 in a Gloster Meteor aircraft using kerosene as the fuel. Despite their head start in turbojet engine development, Germany did not decide until 1943 to produce jet-powered aircraft. One of the arguments for development at that time was Germany's shortage of high octane fuel and that the jet engine could run on diesel fuel.[12]

Most of the jet engines developed before the end of World War II utilized conventional kerosene as a fuel. The first jet fuel specification was directorate of engine research and development (DERD 2482), published in England in 1947.[19] As engines and specifications developed, it became apparent that several fuel properties were key to bounding the envelope of jet fuel characteristics. High-altitude operation meant fuel freeze point required attention. However, the lower the freeze point, the lower the fraction of crude oil that was suitable, so that freeze point had to be balanced against availability. Higher fuel volatility/vapor pressure aided vaporization-controlled engine performance requirements such as altitude relight, which had to be traded against boiloff and entrainment losses from fuel tanks at altitude (as well as safety concerns from explosive mixtures in tank vapor spaces).[24] In the United States, JP-1, JP-2, and JP-3 were unsuccessful attempts to balance the conflicting requirements of volatility, freeze point, and availability/cost.[15] Two fuels emerged in the late 1940s and early 1950s from this chaotic situation: a wide-cut naphtha/kerosene mixture called JP-4 in the United States (MIL-F-5624 in 1950) and a kerosene fuel with a −50°C (−58°F) freeze point (DERD-2494 in England and Jet A-1 in ASTM D-1655 in the United States). This freeze point was arrived at through a significant research effort. ASTM D-1655 also specified Jet A with a −40°C (−40°F) freeze point. The Jet A-1 freeze point was changed to −47°C in the late 1970s to increase availability.[19] Civil aviation currently uses Jet A-1 (or its equivalent) throughout the world, except for domestic carriers in the United States, who use Jet A. Military aircraft used JP-4 until converting to JP-8 in the 1980s. JP-8 (MIL-T-83133) is essentially Jet A-1 with three military-specified additives (as described later). The conversion to JP-8 occurred primarily to improve the safety of aircraft, although the single fuel for the battlefield concept (and the similarity of jet fuel to diesel fuel) is centered on the use of aviation kerosene in all U.S. Air Force and U.S. Army aircraft and ground vehicles. A similar process is occurring in the U.S. Navy, where the large variety of liquid fuels have compressed down to just two, JP-5 (for aircraft) and F-76 diesel for all other liquid fuel requirements.

The history of the evolution of conventional, widely available jet fuels from the late 1950s to the present is mainly the story of the evolution of test methods and fuel additives to maintain the integrity of the jet fuel supply and to improve safety and correct operational problems. Because their importance, specifications/test methods and additives are discussed separately later.

Specialty fuels were developed for various applications throughout the second-half of the 20th century. In the early 1950s, JP-5 (included in MIL-F-5624) was developed. JP-5 is a high-flash-point (60°C/140°F) aviation kerosene used onboard U.S. Navy ships to enhance safety. The development of higher Mach aircraft led to several specialty fuels. As flight velocity increases, aerodynamic heating leads to larger amounts of heat being rejected to the fuel, both in the tanks and in the engine, leading to vapor pressure and thermal stability concerns. The cutoff point between the use of conventional Jet A-1/JP-8 fuels and specially produced fuels is between Mach 2.2 and 3. Thus, the Mach 2.2 Concorde uses Jet A-1, whereas the Mach 2-3 XB-70 and SR-71 used specialty fuels. JP-6 (MIL-F-25656) was a low-volatility kerosene developed for the Mach 2+ XB-70.[25] The Mach 3 SR-71 required JP-7 (MIL-T-38219), a low-volatility/high thermal stability, highly processed (low sulfur and aromatics) kerosene.[15,24] The U-2 high-altitude reconnaissance aircraft required both improved thermal stability and lower freeze point in its fuel (JP-TS, MIL-T-25524) because of its high-altitude, long-duration cruise. These specialty fuels gave higher performance than conventional aviation kerosenes, at the expense of higher fuel and logistical costs (JP-7 and JP-TS are roughly three times the cost of JP-8 and Jet A-1). The accepted operational temperature limits of these various fuels are approximately 163°C (325°F) for Jet A/Jet A-1/JP-8/JP-5, 219°C (425°F) for JP-TS, and 288°C (550°F) for JP-7 (Ref. 26).

Russian jet fuels underwent a parallel evolution throughout this period.[27,28] In most areas, current Russian fuels TS-1 and RT and Russian specifications (GOST 10227) are interchangeable with Jet A-1/JP-8. The main difference between fuels TS-1 and RT is in the area of thermal stability: TS-1 is a straight-run fuel, whereas RT is hydrotreated. By comparison with Jet A-1/JP-8, TS-1 and RT are lighter (have a lower initial boiling point and 10% recovery point in distillation) and have a correspondingly lower flash point and freeze point. Thus, worldwide there are three major specifications in civil use: ASTM D 1655, British Defence Standard (Def Stan) 91-91 (successor to DERD 2494), and GOST 10227. International oil companies have created the Joint Check List to standardize jet fuel deliveries worldwide under Jet A-1/Def Stan 91-91. The International Air Transport Association has also issued guidance material for its members codifying the Jet A/Jet A-1/TS-1 specifications.

Pustyrev discusses two specialty Russian fuels specified in GOST 12308: T-8V, a higher density/higher flash-point kerosene and T-6, a high-density kerosene (specific gravity 0.84 vs 0.8 for Jet A-1/JP-8), which has no commercial or military counterpart in Europe or the United States.[28] U.S. Air Force programs in the 1980s demonstrated the production of fuels similar to T-6 (Refs. 29 and 30), but no specification was published in the absence of user requirements.

Beyond Mach 5, flight speeds are considered hypersonic (vs supersonic). The high-heat loads encountered by vehicles in hypersonic flight leads inevitably to regenerative cooling of (at least) the combustor. The heat loads and fuel flows are such that high levels of fuel heat sink are required. This heat sink can be obtained from sensible heating of high-heat capacity fuels such as liquid hydrogen or the use of endothermic (hydrocarbon) fuels. For many applications, hydrocarbon fuels are preferred due to their greater density[31] and ease of handling. Endothermic fuels achieve heat sink by deliberate reactions of the bulk fuel, such as dehydrogenation or cracking.[32–35] Engine concepts for hypersonic aircraft are currently under development in several programs. Potential future developments in this area will be discussed in the Future Trends section.

The petroleum shortages of the 1970s led to the search for domestic sources of liquid transportation fuels. Large United States reserves of coal and oil shale (and Canadian reserves of tar sands) spurred the development of conversion processes to produce fuels from these non-petroleum sources. In the 1980s, programs were initiated to demonstrate the suitability of fuel derived from shale,[36–38] coal,[39] and tar sands.[40] Engine testing and flight demonstrations of shale-derived JP-4 indicated no deleterious effects resulting from the use of shale-derived fuel. The success of this program indicated that the JP-4 specification was restrictive enough to provide adequate fuel, regardless of the hydrocarbon source. Jet fuels produced from synthesis gas ($CO + H_2$) via Fischer–Tropsch (F–T) technology are currently being studied for their suitability for aircraft (see Refs. 41 and 42). The synthesis gas can be produced from coal, natural gas, or other carbon-containing materials. A 50/50 mixture of petroleum-derived Jet A-1 and isoparaffinic kerosene derived from coal is being delivered to aircraft in South Africa. A thorough study by Southwest Research Institute demonstrated that the 50/50 mixture properties fell well within the Jet A-1 specification range and should have no impact on engine operation.[41,42] The composition differences between the two fuels are shown in Figs. 4 and 5. Lubricity and elastomer compatibility issues for use of the pure F–T fuel are currently being addressed.

World-wide jet fuel consumption was 177 million gal/day in 1997, with about 40% of the consumption in the United States.[2] U.S. jet fuel consumption is predominately (~90%) by commercial aircraft.

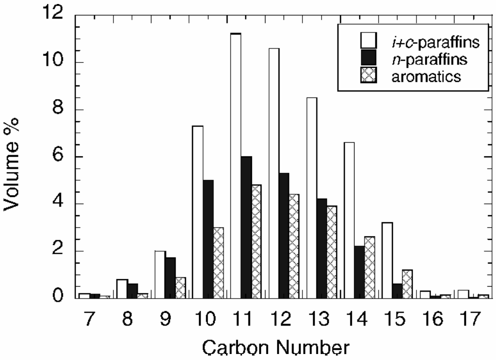


Fig. 4 Composition distribution for South African petroleum-derived Jet A-1 (Ref. 41).

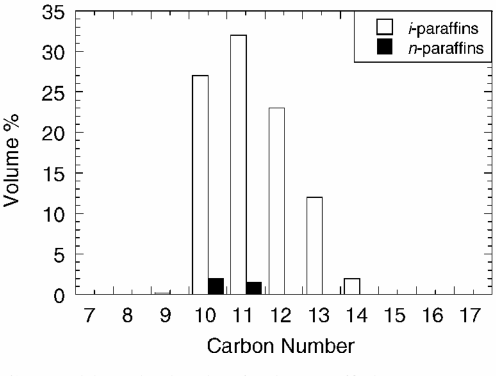


Fig. 5 Composition distribution for isoparaffinic kerosene produced from coal-derived synthesis gas by F–T process.[41]

Fuel Specification Requirements and Test Methods

Fuel specifications and testing have been an integral part of the development of aviation fuels. Fuel specifications are performance specifications in general and are written to allow any particular combination of hydrocarbons that meets the specified performance. Properties are allowed to vary to the extent that the variations will have no deleterious effect on the performance of the fuel in aircraft. The tighter (smaller variations in properties allowed) the specification is written, the higher is the cost of the fuel in general. The first U.S. Government specification was issued in 1907 for the purchase of gasoline (U.S. Navy specification 24 G.5), and required only that the fuel be of a certain specific gravity (density) and that it not be contaminated with materials that would leave a residue after fuel evaporation.[12] As fuel demand grew and problems in service became apparent, limitations on chemical composition and more performance requirements were added. By 1922 there were standard tests established for color (Saybolt number), corrosion and gums (copper dish test), and sulfur content (Doctor test), as well as others.[15,19] As already described, octane number became an important specification requirement in 1930. Higher altitude operation led to a requirement for maximum freeze point. ASTM has been a key force in the development and standardization of test methods for fuel specification testing.

Current aviation fuel specification requirements can be broken into three categories: chemical composition, physical properties, and miscellaneous requirements. Composition requirements include tests to determine the hydrocarbon types in the fuel, to evaluate the sulfur content, and to quantify the organic and inorganic acids in the fuel. Physical properties specified include density (or specific gravity), volatility, vapor pressure, flash point, viscosity, and freeze point. Miscellaneous requirements include determination of heat of combustion, burning quality, corrosivity, cleanliness, particulates, thermal stability, color, existent gum, and electrical conductivity. The requirements table from the JP-8 specification is presented in Table 2. The Jet A/Jet A-1 specification (ASTM D1655, Def Stan 91-91) is very similar. Note the significant number of test methods employed in certifying JP-8, most driven by operational problems. More detailed discussions can be found in Refs. 15 and 19.

A summary of jet fuel properties is given in Table 3.[20,43–46] An example of the variations in delivered JP-8 aromatic concentration over several years is shown in Fig. 6, illustrating the variability in composition permitted within the specification.

Additives[15,19]

Fuel additives are chemicals that are added to fuels to impart specific properties, or to counteract the effects of fuel contaminants that are not easily removed. The selection of additives is subject to many constraints. Additives intended to enhance performance of the fuel in one aspect can have deleterious effects on other fuel properties. A major concern is the compatibility of additives with the materials in the fuel system and in the engine hot section. A large number of fuel additives have been developed and investigated over the years. The following paragraphs contain brief discussions of the various additives currently in use. Many of these additives are shown in Fig. 7.

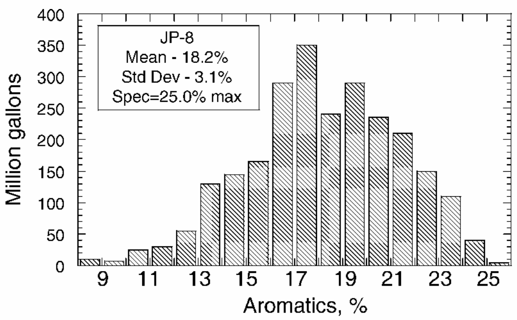


Fig. 6 Distribution of JP-8 aromatics for 1990–1996 fuel purchases.[44]

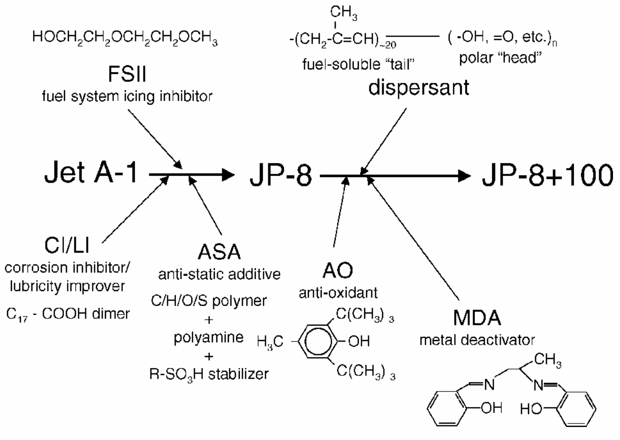


Fig. 7 Jet fuel additives.

In 1954, the U.S. Government began using commercial pipelines to transport aircraft fuel to U.S. Air Force facilities. To combat the excessive corrosion in the ground fuel systems, and to reduce the carryover of corrosion products into aircraft fuel systems, corrosion inhibitor additive requirements were added to specifications for both avgas and turbine engine fuels. A specification (MIL-I-25017) was issued in 1954 for corrosion inhibitor additives. These additives also act to improve fuel lubricity (lubricating capability) and are typically added at approximately 20 ppm.

Water contamination in aviation fuels has always been a serious problem. In liquid form, water can cause temporary flameout in the engine, but in solid form (ice), it can block filters and fuel lines and completely stop the flow of fuel to the engine. In the 1940s and 1950s, free, undissolved water in fuel was suspected as the cause of many in-flight incidents and accidents. A major research and development program was initiated to solve the water-in-fuel problem as a result of a B-52 crash in 1958. One objective was the development of a fuel system icing inhibitor (FSII). The FSII was to be added to the fuel, but would preferentially migrate to any free water present and act as an antifreeze. The current icing inhibitor used is diethylene glycol monomethyl ether at a maximum concentration of 0.15 vol%. The FSII also acts as a biocide.

Because of their low electrical conductivity, aviation fuels can build up a static electrical charge, especially during fueling. Discharge of this builtup charge in areas where flammable fuel/air mixtures exist, for example, fuel tanks, has been a problem. A solution is use of static dissipator additives (SDA) in the fuel. Octel Stadis 450 is the only currently approved SDA for turbine engine fuels.[15] Typical concentrations of 0.5–2.0 mg/l increase the fuel conductivity to between 200 and 600 pS/m. As shown in Table 2, the minimum conductivity allowed in JP-8 is 150 pS/m. The main difference between commercial Jet A-1 fuel and military JP-8 fuel is the specified presence of corrosion inhibitor, FSII, and SDA.

Antioxidant additives are added to turbine engine fuels and other petroleum products to prevent the formation of gums and peroxides during storage by reducing the formation of free radicals in the fuel. Peroxides are deleterious to thermal oxidative stability, possibly being precursors to the formation of deposits. Peroxides also attack fuel tank polysulfide sealants and other fuel system elastomers. The most common antioxidants are hindered phenols, exemplified by 2,6–di–tert–butyl–4–methylphenol[butylatedhydroxy–toluene (BHT), also used in food]. Normal antioxidant concentrations in turbine engine fuels range up to 14 mg/l.

Metal deactivator additives (MDAs) were initially added to gasolines that had been treated using the copper sweetening process (a method to convert mercaptan sulfur compounds to less noxious sulfur compounds). Copper is known to catalyze oxidation reactions that form gums, and so MDA was used to deactivate any traces of copper left in the fuel. MDAs function by forming a chelate with the metal. The chelate effectively isolates the metal from the fuel. MDAs are optional additives in military turbine engine fuels. MDAs are approved for use in military turbine engine fuels at concentrations up to 6 mg/l.

Table 2 JP-8 specification chemical and physical requirements, MIL-DTL-83133E

Property	Minimum	Maximum	Test methods ASTM standards
Color, Saybolt		——[a]	D156[b] or D6045
Total acid number, mg KOH/gm		0.015	D3242
Aromatics, vol%		25.0	D1319
Sulfur, total, mass %		0.30	D129, D1266, D2622, D3120, D4294[b] or D5453
Sulfur mercaptan, mass % or		0.002	D3227
Doctor test		Negative	D4952
Distillation temperature, °C[c]			D86,[b] D2887
(D2887 limits given in parentheses)		——[a]	
Initial boiling point		205 (186)	
10% recovered		——[a]	
20% recovered		——[a]	
50% recovered		——[a]	
90% recovered		——[a]	
Endpoint		300 (330)	
Residue, vol%		1.5	
Loss, vol%		1.5	
Flash point, °C	38	——[d,e]	D56, D93[b] or D3828[d]
Density or gravity			
Density, kg/L at 15°C or	0.775	0.840	D1298 or D4052[b]
Gravity, API at 60°F	37.0	51.0	D1298
Freezing point, °C		−47	D 2386,[b] D 5901, or D5972
Viscosity, at -20°C, mm^2/s		8.0	D445
Net heat of combustion, MJ/kg	42.8		D3338[c] or D4809[b]
Hydrogen content, mass %	13.4		D3701,[b] D3343
Smoke point, mm, or	25.0		D1322
Smoke point, mm, and	19.0		D1322
Naphthalene, vol %		3.0	D1840
Calculated cetane index		——[a]	D976[f]
Copper strip corrosion, 2 h at 100°C (212°F)		No. 1	D130
Thermal stability			D3241[g]
Change in pressure drop, mm Hg		25	
Heater tube deposit, visual rating		< 3[h]	
Existent gum, mg/100 ml		7.0	D381
Particulate matter, mg/L		1.0	D2276[i] or D5452[b]
Filtration time, minutes		15	——[i]
Water reaction interface rating		1 b	D1094
Water separation index	——[j]		D3948
Fuel system icing inhibitor, vol %	0.10	0.15	D5006[k]
Fuel electrical conductivity, ps/m	——[l]	——[l]	D2624

[a] To be reported, not limited.

[b] Referee test method.

[c] Condenser temperature of 0–4°C (32–40°F) shall be used for the distillation by ASTM D86.

[d] ASTM D56 may give results up to 1°C (2°F) below the ASTM D93 results. ASTM D3828 may give results up to 1.7°C (3°F) below the ASTM D93 results. Method IP170 is also permitted.

[e] When the fuel distillation test is performed using ASTM D2887, the average distillation temperature, for use in ASTM D3338 shall be calculated as $V = (10\% + 50\% + 95\%)/3$.

[f] Midboiling temperature may be obtained by either ASTM D86 or ASTM D2887 to perform the cetane index calculation. ASTM D86 values should be corrected to standard barometric pressure.

[g] See MIL-DTL-83133E for ASTM D3241 test conditions and test limitations.

[h] Peacock or abnormal color deposits result in a failure.

[i] A minimum sample size of 3.79 liters (1 gal) shall be filtered. Filtration time will be determined in accordance with procedure in Appendix A. This procedure may also be used for the determination of particulate matter as an alternate to ASTM D2276 or ASTM D5452.

[j] Water separation index limits dependent upon additives present in fuel as described in MIL-DTL-83133E.

[k] Test shall be performed in accordance with ASTM D5006 using the diethylene glycol monomethyl ether (DiEGME) scale of the refractometer.

[l] The 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 or 29.4°C (85°F), whichever is lower, unless otherwise directed by the procuring activity. In the case of JP-8 + 100, JP-8 with the thermal stability improver additive (see 3.3.6), the conductivity limit must be between 150 to 700 pS/m at ambient temperature or 29.4°C (85°F), whichever is lower, unless otherwise directed by the procuring activity.

Thermal stability[47] is another fuel property than can be improved by additives. Jet fuel picks up a significant amount of waste heat in aircraft fuel systems through the cooling of components and other fluids (such as engine oil). Thermal instability of the fuel results in deposit formation in fuel system passages, in controls, and on filters. Currently, the specification test device for thermal stability is the jet fuel thermal oxidation tester, as described in ASTM D3241. The JP-8+100 research program was initiated by the U.S. Air Force, in cooperation with other government agencies, industry, and universities, in 1989.[48] The main goal of the program was to increase the heat sink capability of JP-8 fuel by 50%, by increasing the fuel operating temperature limit by 100°F (56°C), from 325 to 425°F (163–219°C). This was to be accomplished by developing additives to blend with the fuel at a cost of one dollar or less per 1000 gal (3.785 m^3) of fuel. It was felt that fuel additive development was the best compromise to balance the engine performance requirements (technology needs), fuel cost (economic factors), and fuel availability (strategic factors). JP-8+100 is designed to alleviate the need for development of expensive specialty fuels such as JP-7 and JP-TS for future advanced aircraft and will decrease maintenance costs for current

Table 3 Typical aviation fuel properties[15,17,20,35,44–46]

Property	Avgas	JP-4	JP-5	JP-7	JP-8 (Jet A/A-1)	RP-1
Approximate formula[a]	C_7H_{15}	$C_{8.5}H_{17}$	$C_{12}H_{22}$	$C_{12}H_{25}$	$C_{11}H_{21}$	$C_{12}H_{23}$
H/C ratio	2.09	2.00	1.92	2.07	1.91	1.95
Boiling range, °F (°C)	115–295 (46–145)	140–460 (60–240)	360–495 (180–260)	370–480 (190–250)	330–510 (165–265)	350–525 (175–275)
Freeze point, °F (°C)[b]		−80 (−62)	−57 (−49)	−47 (−44)	JP-8/Jet A-1: −60 (−51); Jet A: −50 (−45)	−55 (−48)
Flash point, °F (°C)		−10 (−23)	147 (64)	140 (60)	127 (53)	134 (57)
Net heating value, Btu/lb (kJ/kg)		18,700 (43,490)	18,500 (43,025)	18,875 (43,895)	18,550 (43,140)	18,650 (43,370)
Specific gravity, 16°C (60°F)	0.72	0.76	0.81	0.79	0.81	0.81
Critical temperature, °F (°C)		620 (325)	750 (400)	750 (400)	770 (410)	770 (410)
Critical pressure, psia (atm)		450 (30.5)	290 (19.5)	305 (20.5)	340 (23)	315 (21.5)
Average composition						
Aromatics, vol%	25	10	19	3	18	3
Naphthenes		29	34	32	35	58
Paraffins		59	45	65	45	39
Olefins	10	2	2		2	
Sulfur, ppm		370	470	2	490	20

[a] For illustration of average carbon number, not designed to give accurate H/C ratios.
[b] Typical.

inventory aircraft. The JP-8+100 program led to a number of other advancements, including new test techniques, improved fuel/water separation technology, and a better understanding of fuel thermal-oxidative stability. The initial JP-8+100 additive package is based on a detergent/dispersant, packaged with an anti-oxidant and MDA (as shown in Fig. 7) at a concentration of 256 mg/l. The JP-8+100 additive has been shown to produce 50–95% reductions in deposits in more than 10 thermal stability test rigs with a wide variety of JP-8/Jet A fuels.[49–57] Several base-level trials have quantified significant reductions in fuel-related engine maintenance during use of the additive. Further discussion on the topic of thermal stability appears in the Future Trends section. Over 300 additive combinations were screened in this program.

Missile Fuels

Missiles impose quite different constraints from reusable aircraft on their fuels. Because of the expendable nature of missiles (and, thus, their relatively short life requirement and small fuel consumption), the cost of missile fuels is usually not a significant driver for missile system cost. Missiles are typically volume limited, rather than weight limited, as are most aircraft, so that fuel volumetric energy is a key parameter. Storage stability is key because missiles may be stored fueled for periods on the order of 10 years. Low-temperature and low-pressure performance are key drivers for air-launched missiles, which may be cold-soaked at very low ambient temperatures. For example, the U.S. Air Force requires a −54°C (−65°F) freeze point for missile fuels, significantly lower than the freeze point of the fuel for the aircraft carrying the missile.

Before the 1960s, the only fuels available for missiles were JP-4 and JP-5. RJ-4 was developed for the ramjet-powered Talos missile in the early 1960s.[15,58] As shown in Fig. 8, RJ-4 is a mixture of the isomers of *exo*-tetrahydrodi(methyl cyclopentadiene). Also known as TH dimer and H-MCPD, the need for a nonchemical name is obvious. Joint U.S. Air Force/Navy research in higher density missile fuels for turbine-engine-powered cruise missiles culminated in the creation of JP-10 in the mid-1970s.[15,58] JP-10 is *exo*-tetrahydrodicyclopentadiene (Fig. 8) and is the only airbreathing-missile fuel in operational use by the United States at the present time. JP-10 has the impressively low freeze point of −79°C (−110°F). Higher density missile fuels have been developed, for example, RJ-5, perhydrodi(norbornadiene), but cost and freeze-point limitations prevented field use. The potential for extending the range of missiles beyond what is possible with conventional high-density missile fuels prompted interest in slurry fuels that contain additives, such as boron, carbon, or aluminum in suspension in a gelled form. Such slurry fuels can provide a very high heating value per unit volume. The result of the many years of slurry fuel work demonstrated that formulation of stabilized slurry fuels is possible, but to make such fuels a viable option for turbine-engine-powered cruise missiles, a substantial amount of additional fuel system and propulsion engineering would be required.

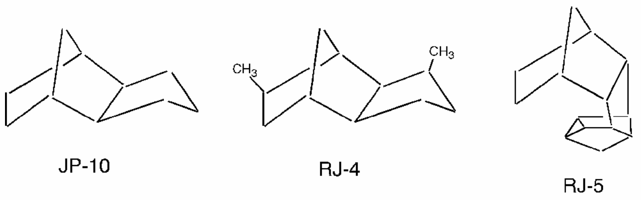


Fig. 8 Missile fuel structures.

Liquid Rocket Propellants

This discussion on rocket propellants can only give a flavor of the innumerable propellant combinations that have been tested/flown since Goddard's first flight. Interested readers can consult the many references that follow, for example, Forbes and Van Splinter,[59] or consult the many web-sites devoted to space travel, for example, www.astronautix.com. A brief introduction to propellant development from the perspective of notable rockets is followed by a more detailed discussion of the various classes of propellants.

Brief History of Liquid Rockets and Their Propellants

Early pioneers in the study and assessment of liquid rockets include Konstantin Tsiolkovsky, Hermann Oberth, and Robert Goddard (see Ref. 3). In the early 1900s they pioneered the analysis of propulsion concepts to get into space, often inspired by Jules Verne and other fiction writers' concepts for visiting other planets. These analyses concluded that only liquid propellants (vs solid propellants or gases) had the necessary properties to achieve access to space. Tsiolkovsky pointed out the advantages of liquid hydrogen (LH_2) and liquid oxygen (LOX) very early. In fact, 2003 could be described as the centennial of rocket regenerative cooling, first postulated by Tsiolkovsky in 1903 (see Ref. 60). Many private clubs and government organizations supported early tests of rocket concepts. Robert Goddard is credited with the first flight of a liquid propellant rocket in March 1926. His choice of propellants was gasoline as the fuel and LOX as the oxidizer. LOX and noncryogenic nitric acid were common oxidizers in this early period, but many fuels were used. Throughout the 1930s, many groups in Europe and the United States tested larger and larger rockets, although none came close to getting to space. The advent of World War II accelerated the development of rockets, especially in Germany, with the most noticeable development being the A-4 rocket (popularly known as

Table 4 Major operational liquid propellant families

Family	Example	Stoichiometry	I_{sp}, s[a] (Ref. 63)	Attributes
Cryogenic	LH_2/LOX	$2H_2 + O_2 \rightarrow 2H_2O$	391	High performance
Kerosene (cryogenic)	RP-1/LOX	$CH_2 + 1.5O_2 \rightarrow CO_2 + H_2O$	300	Higher density, cheaper handling
Storable	Nitrogen tetroxide/hydrazine	$2N_2H_4 + N_2O_4 \rightarrow 3N_2 + 4H_2O$	292	Storable, hypergolic
Storable nontoxic	Kerosene/peroxide	$CH_2 + 3H_2O_2 \rightarrow CO_2 + 4H_2O$	273	Storable, relatively nontoxic
Mono-propellant	Hydrazine	$2N_2H_4 \rightarrow 2NH_3 + H_2 + N_2$	230[66]	Decomposition over catalyst eliminates need for separate fuel plus oxidizer

[a] Equilibrium 1000-psia (1-atm) expansion.

the V-2). The A-4 flight on 3 October 1942 was the first rocket flight that demonstrated the potential of achieving orbit, returning to Earth 120 miles from the launch site. The propellants used on the A-4 were a 75% ethyl alcohol/water mixture as the fuel and LOX as the oxidizer. At first glance, the use of an alcohol/water mixture seems rather odd because many other fuels give higher performance (as described later). However, the use of the alcohol/water mixture had the advantage of a lower flame temperature, which helped the A-4's fuel-cooled combustor to survive the relatively long burn time. Other authors credit the scarcity of gasoline and diesel fuel for the choice of ethyl alcohol as the V-2 fuel. Many other rockets were developed for other military applications during the 1940s, such as rocket-assisted takeoff and liquid-fueled missiles. These types of applications required storable, that is, noncryogenic, propellants for ease of use and readiness.[61] The most common storable oxidizer in this period was nitric acid. Various hydrocarbons were used as storable fuels (gasoline, jet fuel, etc.), but rockets using the hydrocarbon/nitric acid combination were plagued with destructive hard starts and other combustion problems. These problems were largely solved by the use of fuels that were hypergolic with nitric acid, such as aniline and hydrazine. Hypergolic propellants ignite on contact, which simplifies the ignition process dramatically and eliminates most of the combustion problems such as hard starts. In the 1950s, nitric acid was largely supplanted by nitrogen tetroxide as the storable oxidizer of choice, usually paired with one of the various types of hydrazine. Storable propellant development during the 1940s and 1950s was a very large research effort, devoted to optimizing propellant properties, material compatibility, storage stability, and combustion performance. After World War II, long-range rocket development in the United States and the Soviet Union was the most vigorous, based in large part on the German A-4 (and its developers). The Soviet Union achieved the most notable successes in the late 1950s, orbiting the first satellite and the first human. The rocket used was the multistage R-7, with kerosene and LOX as the propellants. In the early 1960s, the X-15 explored the limits of winged flight, reaching Mach 6.7 in 1967. The X-15 was powered by a liquid ammonia/LOX rocket.

The difficulty of summarizing rocket propellants is illustrated by the Saturn V. In 1969, the United States reached Earth's moon propelled by the Saturn V/Apollo, which utilized engines ranging in thrust from 100 lb (445 N) (attitude control systems) to 1.5 × 10^6 lb (6.7 kN) (the first-stage booster engines). These engines used five different propellants in three combinations. The first-stage booster engine propellants were RP-1 kerosene and LOX. The second- and third-stage booster engines were LH_2/LOX. The Apollo command module and the lunar descent and ascent engines, as well as the attitude control thrusters, utilized nitrogen tetroxide oxidizer and several types of hydrazine fuels. Spacecraft during this period generally used this storable propellant combination for control. An alternative propellant for these applications was hydrazine as a monopropellant, utilizing a catalyst to aid in the decomposition. A departure in design, if not in propellants, occurred with the U.S. space shuttle, first flown in 1981. The space shuttle uses a reusable LH_2/LOX main engine, with a detachable external propellant tank and solid rocket boosters, to reach orbit. The space shuttle orbital manuevering engine uses storable propellants (hydrazine/nitrogen tetroxide). The auxiliary power unit uses hydrazine monopropellant. Major expendable launch systems at the close of the 20th century utilized either LOX/LH_2, for example, some Ariane stages, Titan 4; LOX/kerosene, for example, Sea Launch, Atlas, Delta 3; or storables, for example, Chinese Long March, some Ariane stages.[62] Some properties and attributes of these propellant families are presented in Table 4. In closing, note that the propellants currently in use were all in use or active development in the 1950s (if not earlier); recent increases in vehicle performance have come more from improvements in hardware than from improvements in chemical propellants. New propellants have not had a good record of making it into operational vehicles, especially launch vehicles, in the past several decades.

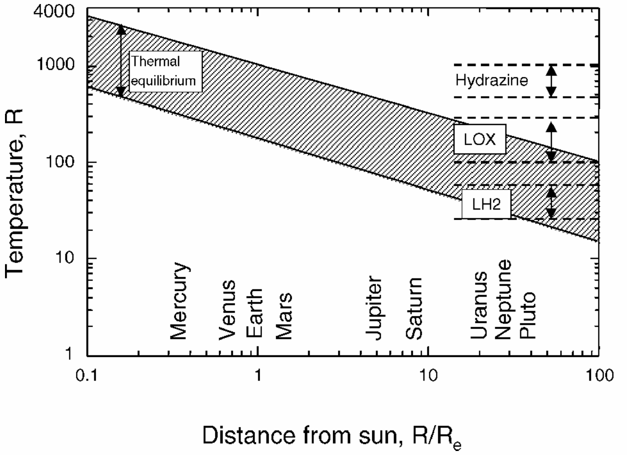


Fig. 9 Equilibrium temperature in space;[71] limits of thermal equilibrium depend on insulation, absorptivity/emissivity, etc.

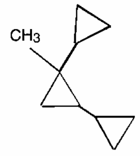
Summary of Operational Propellants

This section gives some summary details on the various operational propellant families. More detail may be found in Refs. 6, 7, 59, 61, and 63–71. Note that some oxidizers and fuels can also be used as monopropellants (such as hydrogen peroxide and hydrazine). Note also that the term storable is confusing unless a storage location is given. For example, Fig. 9 shows that LH_2 would be space storable in orbit around Pluto, whereas LOX is space storable throughout much of the solar system.[71] Typically, storable is meant to refer to the Earth's surface conditions for launch vehicles and strategic missiles.

Cryogenics (LOX/LH_2, LOX/Kerosene)

For the properties of LOX/LH_2, LOX/Kerosene, and kerosene propellants, see Table 5.[5,45,59,72–74] Oxygen/hydrogen is the highest performing operational propellant family. Of course, the low temperatures and explosion hazards of hydrogen impose significant launch cost penalties. The low density of liquid hydrogen is also a drawback. For these reasons, Russian launch vehicles and many U.S. vehicles have used various types of liquid hydrocarbons as a fuel. Although Goddard's initial flight test used gasoline, operational hydrocarbon-fueled rockets since then have typically used kerosene. As discussed earlier, the term kerosene is used to describe a distillate fraction of petroleum boiling between (roughly) 200 and 300°C (390 and 570°F). Jet fuels, as described earlier, are kerosenes; naturally, jet fuels such as JP-4 were the initial kerosenes used in rocket tests (although JP-4 does not strictly fit the definition of a kerosene because of its low initial boiling point). However, it was found that jet fuel did not have tight enough specification properties to serve as an effective propellant. The Rocketdyne Rocket Engine Advancement

Table 5 Properties of LOX, LH_2, and kerosene propellants[5,45,59,72–74]

Propellant	Formula	Relative density (specific gravity)	Heat of formation, cal/g (298 K)	Comments
LOX	O_2	1.14 (90 K)	−95	
LH_2	H_2	0.071 (20 K)	−950	
RP-1	Approximate $C_{11.7}H_{22.8}$	0.806 (22°C)	−400[a]	See Table 1; H/C∼1.952
RG-1	$C_{12.3}H_{23.9}$	0.832 (22°C)	−433	75–85% naphthenes; H/C∼1.946
Syntin	$C_{10}H_{16}$	0.85[77]	+234	

[a] Significant variations in Literature: −423 (Ref. 73), −389 to −606 (Ref. 74), −400 (calculation from heat of combustion),[74] −444 (Ref. 59), and −389 (Ref. 5). RG-1 value calculated from heat of combustion using method in (Ref. 74).

Table 6 Properties of storable propellants[5,59,63,65,66,67]

Propellant	Formula	Oxidizer, fuel, and/or monopropellant	Heat of formation, cal/g	Freezing point, K	Relative density (293 K)
WFNA	HNO_3	O	−660	231	1.50
Nitrogen tetroxide	N_2O_4	O	−45.5[a]	262	1.43
Hydrazine	N_2H_4	F, M	+376	275	1.01
MMH	$CH_3N_2H_3$	F	+285	221	0.88
UDMH	$(CH_3)_2N_2H_2$	F	+205	216	0.79
Aniline	C_6H_5-NH_2	F	+79	267	1.01
Furfuryl alcohol	$C_4H_3OCH_2OH$	F	−674	240	1.13
Hydrogen peroxide (98%)	H_2O_2	O, M	−1320	273	1.45

[a] Value from (Ref. 5) other values: −50.8 (Ref. 65), −50.9 (Ref. 59), −73.9 (Ref. 63), and +25.0 (Ref. 67).

Program is usually credited with eliminating the shortcomings of jet fuels as propellants by developing rocket propellant 1 (RP-1, MIL-P-25576) in the mid-1950s. In comparison to jet fuel, RP-1 has a much narrower allowable density range and lower limits on fuel components that were thought to cause deposits during regenerative cooling, such as sulfur, olefins, and aromatics.[6] Typical properties are shown in Table 3. Deposit formation (coking) led to a maximum fuel-wetted surface temperature limit that ranges from 290 (550) (Ref. 75), to 450°C (850°F) (Ref. 76). The variability of this limit is discussed further later in the Future Trends section. The amount of coking is very dependent upon the fuel-wetted surface, with copper causing more deposition than steel. Russian kerosene (RG-1, naphthyl) is somewhat different from RP-1, notably with a higher density/specific gravity (0.832 vs 0.806 at 22°C) (Ref. 45). RG-1 has been chilled before use to increase its density (and, thus, the mass of propellant that can be loaded onto the rocket). Engine applications include the RD-180, RD-170, and NK-33. Russian aircraft fuel T-6 has been used in engine tests in place of RG-1 because of its similar physical properties. Some upper stages of the Russian Proton launch vehicles used a synthetic (nondistillate) hydrocarbon syntin (or sintin) to increase payload over that obtainable with RG-1 (Ref. 77). These synthetic hydrocarbons produce higher I_{sp} than RG-1/RP-1 (at the same H/C ratio) by adding strain energy to the molecule and increasing its heat of formation. Syntin production apparently ceased in 1996 after the break-up of the Soviet Union.[78] The structure and heat of formation for syntin in Table 5 are inferred from a report of the structure and are unconfirmed. The structure is consistent with Russian descriptions of the fuel as "a synthetic hydrocarbon of the cyclopropane row."[77] There is significant current interest in cryogenic liquid methane, which has a higher I_{sp} but lower density than kerosene.[79]

Storables

The properties of storable propellants are given in Table 6.[5,59,63–67] Earth-storable fuels and oxidizers were often used in early rockets, and their development accelerated during World War II.[61] The most common storable oxidizer was nitric acid, which came in several forms. White fuming nitric acid (WFNA) is essentially pure nitric acid. Red fuming nitric acid contains a significant amount of nitrogen dioxide. Nitric acid caused high corrosion rates in materials, but the addition of a small amount of hydrofluoric acid (HF) acted as a corrosion inhibitor, forming inhibited red fuming nitric acid (IRFNA). Gasoline and nitric acid were an early storable combination, but the combination had combustion instability problems. Aniline and nitric acid were found to ignite on contact (hypergolic), which eliminated the combustion instability problem. Aniline is an example of a nitrogen-containing amine molecule, many of which were found to be hypergolic with nitric acid. Jet fuels could be made hypergolic with nitric acid by the addition of amines, for example, JP-X and the various mixed amine fuels (MAFs). Amines can be classified as primary (R-NH_2) (where R is a nitrogen or carbon atom), secondary (R_2NH), or tertiary (R_3-N). Tertiary amines were the most hypergolic with nitric acid, but other properties then came into play in determining the most-desirable fuel. For example, the already-mentioned aniline had a relatively high freeze point (−6°C, 21°F). A eutectic (roughly 50/50) mixture of furfuryl alcohol and aniline was found to have a freeze point of −42°C (−44°F) and remained hypergolic with nitric acid. N-ethyl aniline ($C_6H_5NHC_2H_5$) had a freeze point of −63°C (−81°F) and also remained hypergolic. Rocket-assisted-takeoff units for aircraft and surface-to-air missiles used late in World War II used N-ethyl aniline and nitric acid. The surface-to-surface Corporal missile used the nitric acid/furfuryl alcohol/aniline combination.

Throughout the late 1940s and early 1950s, a large number of storable fuels and oxidizers were tried in various combinations. The most successful were the hydrazines, including monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH). Hydrazine (N_2H_4) has a relatively high freeze point, is only partially miscible with hydrocarbons, and is shock sensitive. Thus, MMH and UDMH, alone or in mixtures with hydrazine, are often used for improved handling properties, despite a somewhat lower I_{sp} than pure hydrazine. For example, the Titan 2 uses Aerozine 50, a 50/50 hydrazine/UDMH mixture as the fuel. As MMH became more available, it was often used in place of Aerozine 50. Russian vehicles typically used UDMH. Addition of hydrazines to hydrocarbons created hypergolic mixtures with nitric acid; thus, the Nike

Ajax missile fuel was 17% UDMH in JP-4. The UDMH/IRFNA mixture was used in the Lance missile and the Bell Agena rocket motor. For oxidizers, N_2O_4 gives higher performance than nitric acid and is the most common storable oxidizer in current use, but has a higher freeze point. Strategic missiles fired from silos and launch vehicles, (for example, Titan 2) used hydrazine/N_2O_4 propellants.

Hydrogen peroxide (90%) has a similar freeze point to N_2O_4 (-12°C, 11°F) and somewhat lower performance, but has the advantages of being less corrosive and less toxic than either nitric acid or N_2O_4 (Refs. 80 and 81). Peroxide/kerosene engines are under consideration for storable applications where the toxicity of the propellants is a concern. Interest in peroxide as an oxidizer is increasing, with applications to new engines such as rocket-based combined cycle.[82] The ability of a catalyst to decompose peroxide (key to its use as a monopropellant as described later) allows some flexibility in combustion system design unavailable with other oxidizers. One difficulty with peroxide is the incompatibility between the decomposition catalyst and peroxide additives used to improve storage life.[81]

Monopropellants

Various monopropellants (see Table 6) have been studied throughout the years, including hydrazine, hydrogen peroxide (used as a gas generator on the German A-4), and various nitrates. A monopropellant is passed over a catalyst to generate hot gas, which can be used for propulsion, attitude control, or turbomachinery drive gas. The first monopropellant in common use was peroxide (H_2O_2) passed over a catalyst (typically silver was the active metal). For safety (detonability) and performance, hydrazine is essentially the only monopropellant in current use.[66] A milestone in monopropellant development occurred in 1964, when the first ambient temperature catalyst for hydrazine (Shell 405) was developed.[69] When passed over this iridium-based catalyst, hydrazine rapidly and reproducibly breaks down to a mixture of ammonia, nitrogen, and hydrogen. Although the I_{sp} is relatively low compared to bipropellants, the simplicity of the single propellant and ease of ignition and reliable performance have led to widespread use of hydrazine as a monopropellant. However, the toxicity of hydrazine has led to a renewal of interest in peroxide, despite its lower performance.[80] Higher performing alternatives are also being examined, such as mixtures based on hydroxyl ammonium nitrate [(HAN), discussed in more detail in the next section].

Future Trends in Fuels and Propellants

Several drivers for changes to fuels and propellants seem apparent. Commercial and military kerosene jet fuels are becoming more similar and interchangeable. Logistical and cost considerations lead to the expectation that this trend will continue. Ever-tighter emissions regulations seem certain to decrease the sulfur levels in aviation fuel in the next few years, probably to levels consistent with diesel and gasoline (low tens of parts per million). This level of sulfur may create lubricity problems for pumps and other fuel-lubricated components. As the production of oil begins to decline, the use of fuels derived from nonpetroleum sources (coal, natural gas, etc.) is expected to increase. If these fuels are produced from synthesis gas (F–T), then the lack of aromatics in the fuel may cause problems with seals and pumps, as described earlier.[41,42] In balance, however, low-sulfur/low-aromatics fuels are expected to reduce emissions relative to current fuels. Because of the significant number of existing engines, it is anticipated that the general kerosene character of jet fuels will continue for many years, whatever the original source of the hydrocarbons in the fuel.

Lowering the cost of access to space is a big driver for all launch customers. Improved propellants for both single-stage-to-orbit and two-stage-to-orbit vehicles are being sought. The use of airbreathing engines for all or parts of these vehicle's missions is being considered. An area of high impact in this search for better propellants is increasing the density of hydrogen (and kerosene) propellants through various means, including decreasing temperature (subcooling), gelling, and adding metals.[83,84] In contrast, one alternative to achieving lower launch costs has been called the big dumb booster approach.[4] In this approach, minimum cost is achieved through the deliberate use of lower cost/lower performance systems, such as the use of pressure-fed engines and LOX/hydrocarbon or peroxide/hydrocarbon propellants. An example of this approach (although not fully demonstrated) was Beal Aerospace's jet fuel/peroxide booster, the second stage of which was tested in 2000. One drawback of this approach is the wide variation in jet fuel density and heat of formation permitted by current specifications. The use of combined cycle engines raises the interesting option of using the same fuel for both cycles to save on fuel system weight and volume. That raises the question of the most appropriate fuel for the combined cycle engine. For example, in a rocket-based combined cycle engine, should you use rocket fuel in the scramjet, or scramjet fuel in the rocket?

Because of the toxicity of hydrazine, alternatives are actively being sought for both bipropellant and monopropellant applications[85,86] (in addition to peroxide as discussed earlier). Current alternatives being researched include HAN and dimethyl-2-azidoethylamine (DMAZ). One drawback to the alternatives for monopropellant applications is the higher temperatures achieved and the impact of these high temperatures on catalyst materials.[87] Another drawback for bipropellant applications is the difficulty achieving the low ignition delay values of the hydrazine-fueled systems.

Modeling and simulation of complex kerosene fuels has been receiving a lot of attention. Because kerosene fuels consist of a mixture of hundreds (if not thousands) of hydrocarbons that vary from refinery to refinery (and day to day in a given refinery depending on crude source), simplifications are inevitable. One approach is the use of fuel surrogates, where a much smaller set of hydrocarbons is used to simulate the kerosene fuel, either in modeling or testing. The size of the set of surrogate hydrocarbons depends on the property being simulated.[72] For modeling some simple flame behavior, a one- or two-component surrogate may be adequate. For combustion testing that focuses on an aspect of fuel combustion that is dependent on many aspects of fuel composition (such as boiling range and chemical composition), a more complex surrogate might be necessary.[46]

Two areas of future development with significant current interest will be discussed in detail: 1) increased heat sink capability of advanced hydrocarbon fuels/propellants for high-pressure rockets and advanced aircraft and 2) hydrocarbon fuels for airbreathing hypersonic vehicles. A common feature of these two areas is the difficult struggle to increase hydrocarbon fuel thermal performance while minimizing fuel system deposit formation.

Increased Heat Sink for Advanced Hydrocarbon Fuels and Propellants

The key challenge for hydrocarbon fuels and propellants is the difficulty of extending the cooling capability of the fuel to higher heat fluxes and temperatures without having the vehicle's life limited by carbonaceous deposition formation (coking, fouling) due to fuel thermal instability. For aircraft, higher engine cycle pressures and temperatures (driven by desired increases in engine performance) and higher subsystem cooling requirements are increasing the heat load being absorbed by the fuel. This is especially true for supersonic aircraft, where ram air loses much of its cooling capability. For rockets, higher chamber pressures are desirable for increased engine thrust/weight, but increase the heat flux into the regeneratively cooled structure.

Jet fuel thermal stability already has been briefly described in the jet fuel additive section. An excellent review of jet fuel thermal stability has been published.[47] As discussed earlier, in current aircraft the rule of thumb is to maintain JP-8/JP-5/Jet A/Jet A-1 temperatures below 150–163°C (300–325°F) to prevent deposits on fuel system controls, valves, screens, heat exchangers, and other components. As the fuel temperature increases above this level, fuel thermal-oxidative degradation begins to lead to deposits. As shown in Fig. 10 (for a situation where fuel temperature increases linearly while flowing from left-to-right), the roughly 70 ppm (Ref. 57) of dissolved oxygen in fuel exposed to air reacts with the hydrocarbons to form peroxides and eventually deposits. Oxidative deposition ceases on complete consumption of the dissolved oxygen. Further increases in temperature lead to thermal cracking of the fuel and a reinitiation of deposition. An overall outline of the thermal-oxidative deposition process has been presented by Taylor (see Refs. 47 and 173) and is reproduced in Fig. 11. Jones and Balster have quantitatively assessed the formation soluble and insoluble gums and solids and shown the relationship between fuel oxidation and the formation of deposit precursors.[88] Much of the complexity of this process comes from the involvement of trace heteroatomic species, for example, organic sulfur compounds, and dissolved metals. The average sulfur content is JP-8 is roughly 500 ppm (Refs. 44 and 89). In addition, the deposits themselves are a trace component of the fuel, accounting for much less than 1 ppm of the fuel flow through a component. Yet, over the multithousandhour life of typical aircraft fuel systems, even below parts per million levels of deposition may be intolerable. The JP-8+100 thermal stability additive package discussed earlier appears to reduce deposition by reducing particle agglomeration and subsequent deposition.[90] The effect of the additive on the fuel oxidation reactions is fairly minor, although a delay in oxidation is certainly seen.[91] A further complication is the use of fuel recirculation onboard aircraft, which can accelerate the deposition process.[92]

Moving beyond the ~200°C (400°F) capability provided by a detergent/dispersant package such as +100 will require control of the fuel autooxidation chain mechanism. Oxygen is consumed rapidly as temperature increases, due to (roughly) Arrhenius kinetics.[47,93] For example, at 150°C (300°F), a typical jet fuel might require a residence (reaction) time of 1 h to consume the 70 ppm of dissolved oxygen present in air-saturated fuel. At 260°C (500°F), complete oxygen consumption requires on the order of 1 s. Under complete oxygen consumption conditions, the oxidative deposition (scaled by the fuel flow) is relatively insensitive to flow velocity/residence time.[49,94] However, under conditions of incomplete oxygen consumption, the relationship between oxygen consumption and deposition can be complex.[95] As shown in Fig. 12,[96] this complex process offers several opportunities for interrupting the chain. Current models of the oxidation process include up to 19 reactions and more may be added to account for differences in oxidation behavior between the aliphatic and aromatic fractions of the fuel. The current models lump heteroatom-containing species into one or two classes of compounds for purposes of modeling the effect of nonhydrocarbon species on oxidation and deposition.[97,98] These heteroatomic species act as natural antioxidants[99] with relatively nonlinear effects on deposition when good and poor fuels are mixed.[100] It may be necessary to separate these deposit precursors into different subclasses based on a physical property such as polarity[101] rather than heteroatom content. An alternative is to separate reactive species into different chemical classes (such as sulfur being split into sulfides/disulfides and thiophenes[102]), recognizing the differing impact on thermal stability: Thiophenes are relatively unreactive, whereas sulfides and disulfides are recognized for decreasing thermal stability. Then, the challenge for predicting fuel system life would be to estimate the appropriate heteroatom contents to represent the average fuel that an engine would encounter over its life, or the appropriate fuel quality distribution. It is conceivable that an engine's (deposition-limited) life may be dominated by the occasional marginal fuel it encounters, rather than long periods of operation with typical fuels.

It has long been known that removal of dissolved oxygen in the fuel, typically by sparging with oxygen-free helium or nitrogen, results in a tremendous increase in thermal stability.[47,103] Recently a

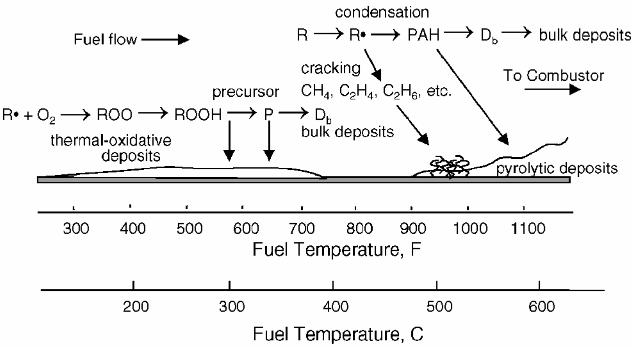


Fig. 10 Fuel deposition regimes.

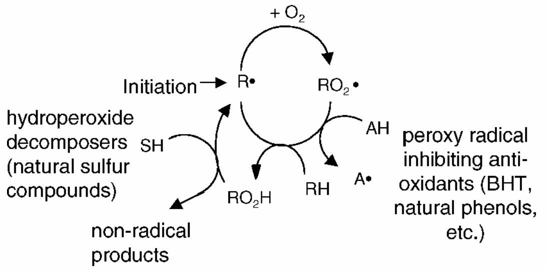
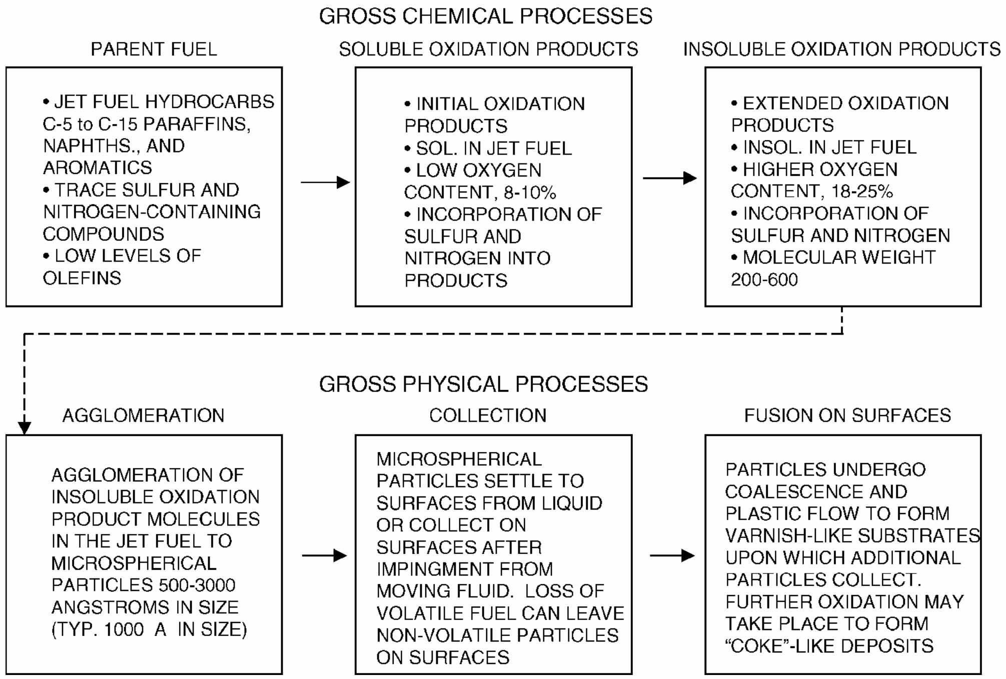


Fig. 12 Details of fuel autooxidation mechanism.[96]


GROSS CHEMICAL PROCESSES

PARENT FUEL

- JET FUEL HYDROCARBS C-5 to C-15 PARAFFINS, NAPHTHS., AND AROMATICS
- TRACE SULFUR AND NITROGEN-CONTAINING COMPOUNDS
- LOW LEVELS OF OLEFINS

SOLUBLE OXIDATION PRODUCTS

- INITIAL OXIDATION PRODUCTS
- SOL. IN JET FUEL
- LOW OXYGEN CONTENT, 8-10%
- INCORPORATION OF SULFUR AND NITROGEN INTO PRODUCTS

INSOLUBLE OXIDATION PRODUCTS

- EXTENDED OXIDATION PRODUCTS
- INSOL. IN JET FUEL
- HIGHER OXYGEN CONTENT, 18-25%
- INCORPORATION OF SULFUR AND NITROGEN
- MOLECULAR WEIGHT 200-600

GROSS PHYSICAL PROCESSES

AGGLOMERATION

AGGLOMERATION OF INSOLUBLE OXIDATION PRODUCT MOLECULES IN THE JET FUEL TO MICROSPHERICAL PARTICLES 500-3000 ANGSTROMS IN SIZE (TYP. 1000 A IN SIZE)

COLLECTION

MICROSPHERICAL PARTICLES SETTLE TO SURFACES FROM LIQUID OR COLLECT ON SURFACES AFTER IMPINGMENT FROM MOVING FLUID. LOSS OF VOLATILE FUEL CAN LEAVE NON-VOLATILE PARTICLES ON SURFACES

FUSION ON SURFACES

PARTICLES UNDERGO COALESCENCE AND PLASTIC FLOW TO FORM VARNISH-LIKE SUBSTRATES UPON WHICH ADDITIONAL PARTICLES COLLECT. FURTHER OXIDATION MAY TAKE PLACE TO FORM "COKE"-LIKE DEPOSITS

Fig. 11 Taylor mechanism for fuel thermal-oxidative instability (see Ref. 47).

program has been initiated to develop an onboard fuel deoxygenation (degassing) system based on membrane separation.[104] Chemical deoxygenation is also under current investigation,[105,106] but the difficulties involved with ensuring that the oxygen scavenging occurs at the desired point in the fuel system and only scavenges dissolved oxygen (and not other reactive heteroatoms) have not been overcome. It is desirable that oxygen scavenging occur not in the fuel tank (with its unlimited supply of atmospheric oxygen because most tanks are vented) but elsewhere in the fuel system, where the presence of the dissolved oxygen could lead to deposit formation. Thus, a scavenger additive that only becomes active at temperatures above (notionally) 93°C (200°F) would be the most effective. An alternative approach involves the addition of peroxide decomposers to interrupt the chain at the peroxide step in Fig. 12. Triphenyl phosphine (TPP) and sulfur compounds have been studied for this purpose, with some success in slowing oxidation and reducing deposition.[107] TPP by itself is not as effective as the JP-8+100 additive package in reducing deposition from JP-8, but the combination together is better than either additive separately.

The effect of surfaces on thermal-oxidative deposition is complex and still poorly understood.[47] Smoother surfaces appear to inhibit deposition, or (more precisely) to lengthen the induction time, the initial period of low deposition rate often seen on clean surfaces. Recent results indicate that inert surfaces based on silica also inhibit deposition in a complex manner depending on location along the fuel oxidation reaction pathway.[108,109] It is to be expected that a surface coating would lose its effectiveness after accumulation of deposits effectively isolates the surface from the fuel deposition process. An example of the result of using the best available additive (+100), best available surface coating (Silcosteel®), and deoxygenation is shown in Fig. 13 for an extended test at 370°C (700°F) fuel temperatures. This indicates that progress is indeed being made toward the goal of a conventional jet fuel stable throughout the thermal-oxidative regime. Deposition-resistant heat exchanger designs have also been investigated.[110]

Note that the basis of most of the current research is based on the premise that the approach to improved fuels is limited to methods of improving current jet fuels, for example, JP-8, Jet A, without including refining changes. This approach is driven by fuel cost: The fuel cost is a significant fraction of aircraft operating cost, so that changes in fuel that change the baseline fuel itself are considered to be cost prohibitive. The added logistics burden of handling specialty fuels is also significant. There may be niche applications where this is not the case and specialty fuels are preferable. If one is willing to consider higher cost fuels and/or specialty chemicals, there are a wide variety of fuels that have higher thermal stability than conventional kerosene jet fuels, as shown in Table 7 (Refs. 49, 111) and Fig. 13 for JP-7. The relatively poor thermal stability of methyl cyclohexane (MCH) has been observed by several investigators and has yet to be adequately explained.

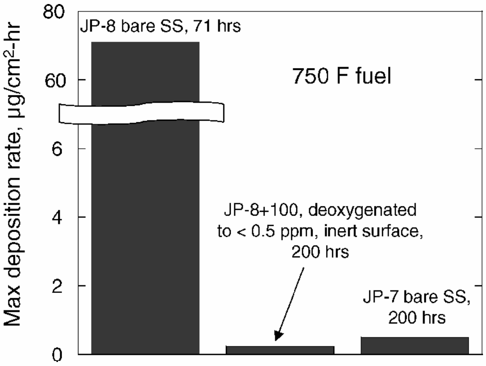


Fig. 13 Comparison of deposition reduction approaches in single-tube heat exchanger (described in Ref. 109); conditions: 1-gal/h fuel flow rate, 0.085-in.-i.d. (2.15-mm) tubing, and 750°F (400°C) fuel outlet temperature.

Table 7 Thermal-oxidative surface deposition rates (complete oxygen consumption)[49,111]

Fuel	Total surface deposition rate, ppm
JP-8 (Jet A)	0.8–1.6
JP-8+100	0.08–0.2
JPTS	0.12
JP-7	0.07
MCH	~0.5
JP-10	~0.1
Decalin	~0.08

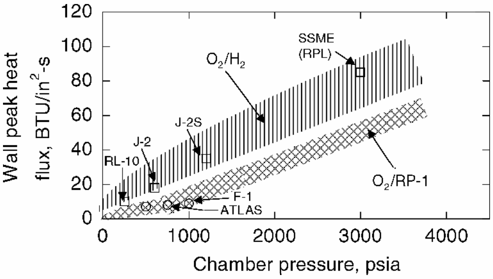


Fig. 14 Effect of chamber pressure on nozzle heat flux.[113]

The desire for increased rocket thrust/weight is driving the pressure of hydrocarbon-fueled thrust chambers higher.[84] The current issue is how (or if) regenerative cooling limits for hydrocarbons might be extended for high-pressure engines. (Cooling limits for nonhydrocarbons are also available.[76,112]) The final developmental F-1 LOX/RP-1 engines for the Saturn 5 approached 70 atm (1000 psia) in chamber pressure in the late 1960s. The current state of the art in hydrocarbon engines, as exemplified by the RD-180, utilizes chamber pressures in excess of 250 atm (3675 psia). This increased pressure helps enable an increased I_{sp} (311 s (sea level) for the RD-180 vs 265 s for the F-1). As discussed later, engine heat flux is roughly proportional to chamber pressure, so that this increased engine pressure comes at the expense of increased combustion heat flux delivered to the chamber wall and the fuel. An example of this is shown in Fig. 14,[113] where the throat heat flux increases from 10 Btu/in.$^2 \cdot$ s (F-1) to about 70 Btu/in.$^2 \cdot$ s at 3750 psia. This increased heat flux may require augmentation of the regenerative cooling by film or transpiration cooling.[114] However, film cooling can result in performance losses, so that the desired approach is to extend the regenerative cooling limits of the propellant used to cool the thrust chamber and nozzle.

At first glance, it would seem that regeneratively cooled thrust chambers would share many similarities with fuel-cooled aircraft components. However, as touched on in the cryogenic propellant section, the thermal stability requirements for rockets are much more stringent than those for conventional aircraft, despite the much shorter lifetime of the rocket. This is due to the much higher heat fluxes encountered in the rocket. At these high heat fluxes, the thermal resistance from deposits in the cooling channel can very rapidly cause structural temperatures to rise past the point of failure (a burnthrough). The aircraft and rocket conditions are contrasted in Table 8. The rocket thermal stability problem has received much less attention than the aircraft case. It is instructive to go into a bit more detail on the rocket case to illustrate future research directions (and past research head scratchers).

As shown in Fig. 15, regenerative cooling is best expressed as a series of heat transfer processes. Combustion (hot-side) heat flux is calculated as

$$q \sim h_g(T_g - T_{wg})$$

where q is the heat flux for example, in British thermal units per squre inch per second, h_g is the combustion-side heat transfer coefficient, and the temperatures are approximately as shown.[114,115] Combustion-side heat transfer is beyond the scope of this paper, but a few comments are relevant.

1) Heat transfer coefficient $h_g \sim P^{0.8}$, so that the trend of increasing chamber heat pressure increases wall heat flux.[113]

Table 8 Comparison of aircraft and rocket cooling conditions for notional advanced missions

Cooling conditions	Aircraft heat exchangers/fuel nozzles	Rocket regen cooling channels
Typical maximum heat flux, Btu/in.^{2} · s	1	100
Required lifetime	2000 h (minimum)	300 s/mission[a] × 50
Materials	Superalloys, perhaps coated	Cu alloys
Incompatible materials	Cu, Cd, Zn, Pb	Cu incompatibility with S in fuel[75]
Effect of dissolved oxygen	Oxygen removal below 1 ppm (from typical 70 ppm) dramatically reduces deposition[47]	Little effect?[123]
Maximum deposition rates	JP-8:JP-7∼140:1	JP-8:RP-1:JP-7∼1:1:1 (Ref. 117)
Maximum allowable deposit thickness	0.001 in. (10% flow reduction in typical 0.020 in.-i.d. passage)	1 × 10^{-6} in. (estimate) to avoid burnthrough in Cu at 100 Btu/in.^{2} · s
Deposition mechanism	150–315°C (300–600°F), molecular growth through hydroperoxide chain mechanism with acceleration by polar heteroatomic impurities; >480°C (900°F), pyrolytic fuel cracking leads to molecular growth through radical chain reactions	On Cu surfaces, sulfur-enhanced corrosion of the surface[75]; on non-Cu surfaces, mechanism is unclear.
Specification thermal stability limits?	Yes, ASTM D3241	No

[a]Missions = 4 h.

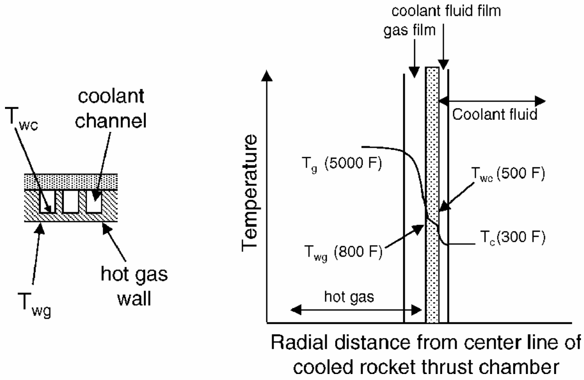


Fig. 15 Regenerative cooling schematic.[114,115]

2) The heat flux absorbed by the propellant also increases as $P^{0.8}$, but the propellant mass flow increases as $P^{1.0}$, so that the overall temperature rise in the propellant may decrease with pressure. In other words T_{wc} increases with pressure, but T_c at the coolant jacket exit may decrease as thrust chamber pressure increases.

3) Carbon (soot) deposition on hot-side (combustion) chamber walls acts as a thermal resistance and thus reduces heat flux.[116]

On the coolant side, heat flux is a strong function of propellant velocity through the Reynolds number (which is directly proportional to flow velocity),

$$q = h_c(T_{wc} - T_c)$$

where $h_c \sim Re^a Pr^b$, with the exponent a typically ranging from 0.8 to 0.9 (Refs. 117 and 118).

Fuel heat flux capability is increased by increasing flow velocity and/or careful cooling channel design. Flow velocities can exceed 200 ft/s, which can cause fluid hydraulic problems.[76] High heat fluxes can be absorbed by fluids undergoing nucleate boiling,[119] but current engine designs for hydrocarbons employ pressures well in excess of the critical pressure [∼310 psia(21 atm) for RP-1], so that this type of heat transfer augmentation is not an option. Note that any thermal resistance on the coolant side of the thrust chamber acts to increase T_{wc} for a given heat flux, which can lead to chamber failure (burnthrough) if material temperature limits are exceeded. Carbon deposition is the limiting factor for hydrocarbon propellant heat flux capability.[113,120] As shown in Table 9, the excellent insulating properties of coke deposits are evident. The temperature rise due to coking is proportional to the heat flux, and so rockets can tolerate much smaller thicknesses of deposition than aircraft. At the high velocities in regenerative cooling channels (which can exceed 100 ft/s), carbon deposition can also create increased fuel system pressure drop and result in injection problems. Significant research efforts in the last 20 years or so have been reported by Aerojet,[75,121] United Technologies Research Center (UTRC),[122,123] Rocketdyne,[124] and NASA John H. Glenn Research Center at Lewis Field (GRC).[117,125,126]

Table 9 Thermal conductivities of various materials relevant to regenerative cooling

Material	k, Btu/h · ft · °F (W/m · K)
Copper	210 (360)
Alumina	3.5 (6)
Superalloy	13 (22.5)
Coke deposit[a]	0.07 (0.12)

[a]Data from Hazlett.[47]

Table 10 RP-1 coking wall temperature limit, T_{wc}

Reference	Upper temperature limit, °F (°C)
Ziebland and Parkinson, 1971 (Ref. 112)	800 (425)
Van Huff, 1972 (Ref. 76)	850 (450)
Wagner and Shoji, 1975 (Ref. 113)	650–700 (340–370)
Wheeler, 1977 (Ref. 127)	600 (315)
Rosenberg and Gage, 1991 (Ref. 75)	580 (305)
Cook and Quentmeyer, 1980 (Ref. 120)	600 (315)
Michel, 1983 (Ref. 128)	550 (290)

Deposition is avoided by keeping the fuel temperature within a coke limit, which is usually specified as a maximum coolant-side wall temperature (T_{wc} in Fig. 15). However, this limiting T_{wc} is not universally agreed on or well characterized in terms of its relationship to coolant velocity, system life, etc. As shown in Table 10, published values for RP-1 vary from 288 to 455°C (550 to 850°F) (Refs. 75,76,112,113,120,127 and 128). Typically, propane is found to have similar limiting temperatures, whereas methane's limit is often cited as several hundred degrees Fahrenheit higher.[118,120] The interaction of the fuel sulfur with copper (the preferred thrust chamber material) is a key driver for hydrocarbon propellant deposition.[75,121] As described in Table 8, copper is avoided in aircraft fuel systems because below part per million levels of dissolved copper in jet fuels can have deleterious effects on thermal stability.[47] Under rocket conditions, gold[121] and nickel[122,123] coatings on copper surfaces have been found to be very effective in reducing sulfur-related corrosion.

The carbon deposition rate is often approximated as in Arrhenius form,

$$\text{deposition rate} \sim \exp(-E/RT_{wc})$$

yielding plots such as that shown in Fig. 16.[75] Such a strong temperature dependence would be difficult to overcome to increase regenerative cooling capability of hydrocarbons by increasing T_{wc}. Note also the presence of a velocity dependence of deposition. As coolant velocity increases at a constant T_{wc}, the boundary layer next to the

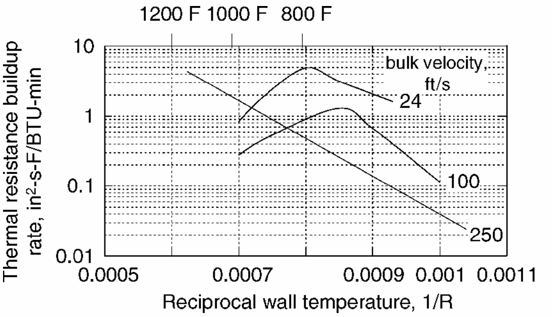


Fig. 16 **Typical deposition (thermal resistance) behavior as a function of temperature.**[75]

wall thins and the coolant residence time decreases. Note the nonlinear behavior shown at lower velocities. This is similar to the behavior of kerosene fuels in aircraft heat exchangers and fuel nozzles as described earlier, where deposition peaks at about 260°C (500°F) and then decreases as the limited amount of dissolved oxygen in the fuel (the deposit precursor) is consumed.[47,129] Deposition after this point is low, until fuel thermal cracking commences at about 480°C (900°F) (as shown in Fig. 10). The very high velocities (and resulting low residence times) in the rocket lead to some significant differences between the aircraft and rocket cases. For example, in most rocket situations, the dissolved oxygen is only partially consumed, whereas aircraft fuels at the same temperatures would have completely consumed the dissolved oxygen. This high-velocity/short-residence time has produced some incongruous results, when viewed from an aircraft perspective. For example, UTRC tests of deoxygenated fuels showed little improvement in fuel thermal stability[123] in dramatic contrast to the results shown in Fig. 13 under aircraft conditions. Aerojet tests with pure, very low sulfur hydrocarbons also showed no apparent improvement over RP-1, in contrast to expectations.[75] Note that current RP-1 has very low sulfur levels, on the order of 20 ppm, much lower than the specification limit (500 ppm). It remains to be demonstrated that reducing sulfur levels below 20 ppm provides any benefit to hydrocarbon fuel regenerative cooling of rockets.

Several types of hydrocarbons are being examined as possible enhancements/alternatives to RP-1 (Ref. 84). Alternative kerosenes tend to focus on higher density, although lower H/C ratios often mitigate any net vehicle benefits.[130] Cryogenic hydrocarbons, for example, propane, methane, offer increased I_{sp} at the expense of reduced density.[79] High-energy (strained ring) hydrocarbons offer high I_{sp} and potentially increased density, but are relatively uncharacterized and may have toxicity and cost concerns. Note, however, that RP-1 costs for current expendable launch vehicles (Atlas, Delta) are roughly 0.05% of the $50 million plus launch cost. A key limitation of this assessment of alternative propellants is the lack of understanding of the relationship between propellant composition and deposition levels. An effort is currently underway to collect more data in this area, using both existing and newly constructed high-heat-flux test rigs.[131] The need for this new data becomes more evident as one looks at the differences between the behavior of jet fuels under aircraft conditions and rocket propellants under high-heat-flux conditions. For example, recent NASA GRC data shows roughly equivalent thermal stability for JP-8, JP-8+100, RP-1, JP-7, and JP-10 (Ref. 117), as shown in Fig. 17. These results are for stainless-steel surfaces: On copper, the high sulfur JP-8 and JP-8+100 give much larger deposition rates than the other fuels, as expected. The contrast with the deposition levels for these same fuels under aircraft conditions (lower velocity/heat flux) on stainless steel, as shown in Fig. 13 and Table 7, is dramatic. Current efforts are assessing the thermal stability under rocket conditions for subcooled cryogenic hydrocarbons, improved kerosenes, for example, very low sulfur, higher density, and prospective high-energy, strained ring hydrocarbons.[84]

Based on the preceding discussion, one might expect that roughly 480°C (900°F) would be an upper (wetted-wall) limit for hydrocarbon propellants. However, significantly higher temperatures than that are routinely encountered in current hypersonic (scramjet) engines. The reason for that lies in the great need for fuel heat sink in scramjet engines.

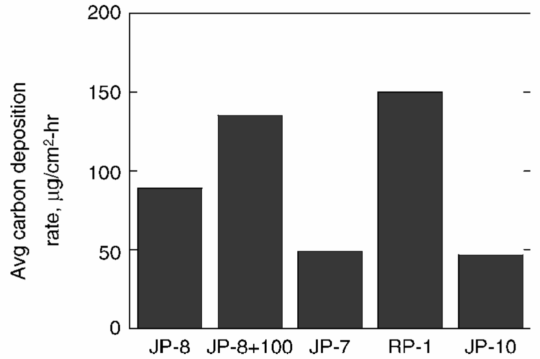


Fig. 17 **Average deposition rates of various fuel under rocket regenerative cooling conditions**[117] **(75 ft/s, 1000 F wall).**

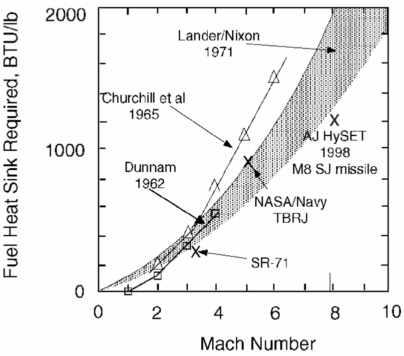


Fig. 18 **Heat sink required as a function of Mach number**[33,134–137] **[turboramjet (TBRJ)].**

Hydrocarbon Fuels for Hypersonics

For combined cycle engines used in the first (airbreathing) stage of a two-stage-to-orbit system, as well as for hypersonic cruise vehicles and hypersonic weapons, the scramjet part of the cycle appears to be the driver for improved fuels. As described in references on the subject,[32–35,132] scramjet operation at Mach 6 and above places serious demands on the heat sink capacity of fuel used to cool the engine regeneratively (especially for hydrocarbon fuels). As in the rocket first-stage booster case, the low density of hydrogen makes liquid hydrocarbons competitive as fuels.[31] At Mach 8, uncooled scramjet combustor structures can exceed 5000°F, well in excess of the temperature capability of known materials, demonstrating the need for fuel cooling.[133] Although the amount of fuel heat sink required is obviously aircraft and mission dependent, some general trends are evident in Figs. 18 (Refs. 32, 134–137) and 19.[138,139] As shown in Fig. 18, heat load is roughly proportional to Mach^2, as might be expected from the proportionality of air stagnation temperature to Mach^2. As shown in Fig. 19, airframe (external surface) heating at higher Mach numbers can eliminate many popular lightweight materials choices, for example, aluminum, as well as creating significant fuel tank heating, which can decrease the ultimate heat sink capability of the fuel (coolant). High fuel tank temperatures can also drive a fuel volatility limit to avoid fuel boiling in the tanks, as was required with JP-7 in the SR-71. Achieving these heat sink levels can drive significant sensible heating of the fuel, $C_p\Delta T$. Under typical fuel system conditions, when the fuel temperature exceeds about 480°C (900°F), the hydrocarbons in the fuel begin to thermally react. Several of these reactions can absorb significant amounts of heat; hence, the term endothermic fuel is used when the fuel reactions are deliberate. This is shown schematically in Fig. 20, which indicates the large enhancement of fuel heat sink capability possible with endothermic reactions, although the heat sink capability still falls far short of hydrogen on a gravimetric basis. However, the ratio of fuel

Table 11 Chemical heat sink values for various endothermic fuels[a]

Endothermic reaction	Reaction types	Theoretical chemical heat sink, unreacted fuel, kJ/kg	Calc. heat of combustion of endothermic products, unreacted fuel, kJ/kg
C_7H_{14} (MCH) $\rightarrow C_7H_8$ (toluene) $+ 3H_2$	Dehydrogenation	2190	45,800
$C_{12}H_{24}$ (kerosene) $\rightarrow C_2H_4$ (ideal)	Cracking	3560	47,200
$C_{12}H_{24} \rightarrow CH_4, C_2H_4, C_2H_6$, etc., (actual)	Cracking	$\ll$3500	
$C_{12}H_{24} + 6H_2O \rightarrow 9CH_4 + 3CO_2$ (AJAX stage 1)	Steam reforming	net: (stage 1 + 2)	Net: (stage 1 + 2)
$CH_4 + H_2O \rightarrow CO + 3H_2$ (AJAX stage 2)	Steam reforming		
Net: $C_{12}H_{24} + 15H_2O \rightarrow 9CO + 3CO_2 + 27H_2$	Steam reforming	5490[b]	21,240
$2NH_3 \rightarrow N_2 + 3H_2$	Dehydrogenation	2720	19,280
$CH_3OH \rightarrow CO + 2H_2$	Dehydrogenation	4000	20,420
Decalin ($C_{10}H_{18}$) $\rightarrow$ naphthalene ($C_{10}H_8$) $+ 5H_2$	Dehydrogenation	2210	40,700

[a] Heat sink for kerosene calculated using dodecane heat of formation as an approximation.

[b] Heat sink for steam reforming based on total propellant mass (fuel plus water).

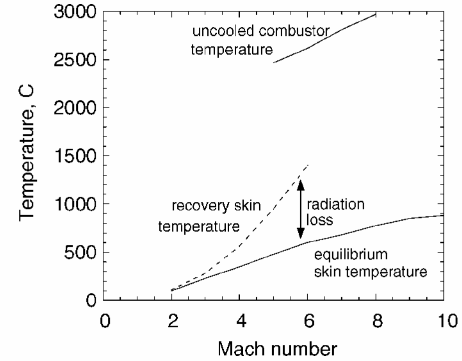


Fig. 19 Uncooled surface temperatures as a function of Mach number.[138,139]

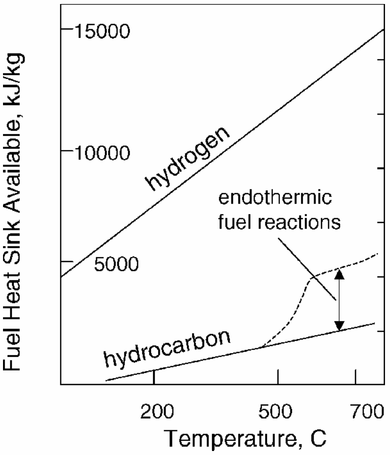


Fig. 20 Comparison of heat sink capability of LH_2 and hydrocarbons.

heat sink to fuel heat of combustion is comparable for hydrogen and endothermic hydrocarbon fuels.

There are several types of heat-absorbing (endothermic) reactions possible during regenerative cooling, as given in Table 11. These endothermic reactions can be purely thermal, catalytically enhanced, and/or require the presence of another component. An example of an added component is the use of steam reforming of the fuel in the notional AJAX vehicle.[140,141] The additional heat sink obtained from the reactions of the water must, of course, be balanced against the vehicle range decrease due to the weight of the inert nature of this propellant. Ground engine demonstrations have been performed utilizing the two major types of endothermic reactions, dehydrogenation and cracking. Thermal/catalytic cracking has been the focus of most recent endothermic fuels research in Russia and the United States.

Note that the thermodynamically favored (equilibrium) fuel reaction products under these conditions are methane and solid carbon, a net exothermic reaction. Thus, a key challenge for endothermic hydrocarbon fuels is to maximize the endothermic products and minimize the formation of methane and carbon. Some carbon formation is inevitable: Thermal reactions of the bulk fuel eventually lead to carbonaceous deposit formation on surfaces and suspended in the fuel. Because this same type of hydrocarbon cracking process is used to create billions of pounds of ethylene each year, a large body of literature exists on pyrolytic carbon formation or coking, for example, Crynes and Albright.[142] A generic coking mechanism amalgamated from the industrial hydrocarbon pyrolysis literature is shown in Fig. 21 (an expansion of the mechanism shown in Fig. 10). However, hypersonic aircraft fuels at high temperatures experience a number of environmental conditions that are significantly different than typical industrial fuel applications. Industrial cracking typically occurs at near-atmospheric pressure with steam-diluted hydrocarbons in large [>2.5-cm (1-in.) i.d.] tubes. In contrast, typical aircraft fuel system pressures are 35–70 atm (500–1000 psia), the fuel is undiluted (except in the steam reforming case), and the passage size is much smaller, on the order of millimeters (Refs. 143 and 144). Thus, it might be anticipated that high-temperature aircraft fuels might show some differences in behavior from industrial experience. In particular, coking rates might be expected to be much higher in aircraft fuel systems because of the higher hydrocarbon concentrations and the larger surface–volume ratios. However, there is some evidence that supercritical pressures can reduce coking under catalytic cracking conditions.[145] Even so, endothermic fuel system life at temperatures above 700°C (1300°F) can be measured in minutes, rather than hours.[146]

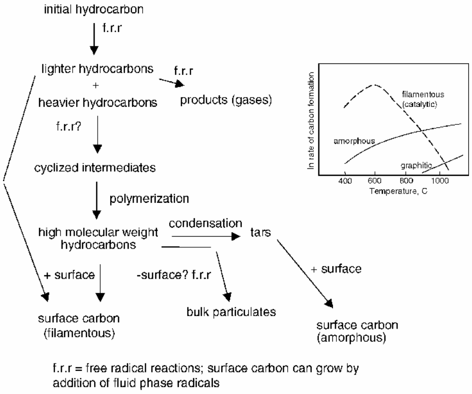


Fig. 21 Pyrolytic deposition mechanisms, where f.r.r. is free radical reactions; surface carbon can grow by addition of fluid-phase radicals.

As shown in Fig. 21, three distinct types of pyrolytic deposits have been identified in the literature based on their morphology: filamentous, amorphous, and graphitic.[147–152] All types have been identified under high-pressure fuel system conditions.[153–155] It remains desirable to identify the high-pressure conditions that control the formation of the various types of coke deposits. Filamentous carbon is the most deleterious form of coke because it involves the removal of small pieces of structural metals, weakening the material and reducing ductility. Iron-, nickel-, and cobalt-containing alloys are most susceptible to attack, whereas other materials (such as rhenium) are resistant. This type of coking is predominant at 920 K (1200°F) under steam-cracking conditions, which involve run times of months in superalloy furnace tubes.[149] By contrast, in 2-h tests (relevant to an expendable aircraft) with 1030 K (1400°F) fuel tube surface temperatures, it was found that very little filamentous carbon was formed from high-pressure jet fuels on typical superalloys.[156] No weakening of the thin [0.4-mm (0.015-in.) wall thickness] superalloy tubes was found. Hence, superalloys may be acceptable for short fuel system lifetimes, although significant differences have been seen between the various superalloys, based primarily on trace element concentrations.[154] Filamentous carbon formation in endothermic fuels systems appears to be controllable with careful material selection and/or the use of inert surface coatings, for example, silica.[35,154] Additives have also found to inhibit filamentous carbon formation through a similar surface modification process.[157] Electrolytic/plasma processing of surfaces is also reported to be very effective at reducing pyrolytic deposition.[35]

The other types of pyrolytic coking (amorphous, graphitic) appear to be directly related to molecular growth of the thermal cracking products.[158–161] This process is analogous to soot formation in some respects.[159] The cracking rates of different hydrocarbons vary depending on their structure, with paraffins and isoparaffins being the least stable to cracking, followed by cycloparaffins (naphthenes) and aromatics (although endothermic initiators can be added to the fuel to initiate endothermic reactions at somewhat lower temperatures[162]). In addition to the propensity to crack, some fuel structures are more prone to pyrolytic deposition than others. Thus, the coking potential of various fuels at a given temperature consists of two parameters: 1) the amount of cracking of the fuel and 2) the tendency of a fuel to form deposits once cracking has occurred. It is easy to imagine a situation where a fuel that is stable to cracking might form significant deposits once it does begin to crack. This fuel should then be limited to conditions where cracking does not occur. For example, JP-7 and JP-8 fuels are mostly paraffinic and crack much more readily at a given temperature than decalin or JP-10, which are naphthenes. However, in flowing tests, decalin and JP-10 tend to form more pyrolytic deposits than JP-7 and JP-8 at a given temperature, despite the lower amount of cracking.[94,163] Thus, decalin could have a lower use temperature than JP-7 or 8, despite its greater stability toward cracking. Recent endothermic tests with JP-7, JP-8, n octane, and JP-10 have indicated that the pyrolytic coking ranking under catalytic conditions is JP-10>n octane> JP-8>JP-7 (Ref. 146).

This result is somewhat surprising given the lower quality of the JP-8 in terms of trace heteroatomic impurities, as described in the discussion of thermal-oxidative fouling earlier. There is some evidence that naphthenic species, although consisting of cyclic species that might be considered to be precursors to multiring aromatic deposit-forming species, can act as hydrogen donors to stabilize the paraffinic fraction of the fuel.[164–166] Other efforts have been made to introduce species/additives to interrupt the molecular growth process, with notable results seen at the 1% additive level.[167] Fuel deoxygenation, so effective in the reduction of thermal-oxidative fouling, can actually increase pyrolytic deposition.[153,168] Thus, it appears that the oxidation products act as a deposit suppresser, at least for pure hydrocarbons. Alternatively, some pyrolytic deposit-promoting species may be consumed by oxidation reactions. The control of pyrolytic coking will require a significant effort to better understand the chemistry and physics of the process under endothermic fuel conditions. For a given fuel at a given flow rate (or given residence time), the level of deposition is roughly exponential in temperature and linear in time,[32,94,168–170] indicating a significant barrier to increasing current heat sink levels while maintaining significant system life. Additional approaches, such as the identification of coking-resistant heat exchanger geometries[110] will also be required. System thermal limits can also be extended by the identification of low-heat-rejection structures. For example, the use of ceramic combustion structures capable of operating at higher temperatures has been shown theoretically to reduce the heat load into the fuel.[134] It seems clear that pyrolytic deposition is the primary barrier to the use of endothermic hydrocarbon fuels in aircraft. As current endothermic fuel models evolve,[171,172] pyrolytic deposition will need to be integrated into the models to create a predictive tool.

Summary

The first half-century of powered flight witnessed significant research and development in fuels and propellants, driven by a dynamically changing array of aircraft and launch vehicles. As aircraft flight (in particular) has become routine, the pace of jet fuel development has been significantly reduced because fuel has become a commodity, traded more on price than performance. Note that the fastest aircraft of flight's second half-century, the SR-71, has been retired due to high operating cost, rather than technical obsolescence. There is some evidence that the rocket industry is following the same path, with low product and logistics costs driving propellant selection, rather than performance. It is a measure of the success of the aerospace industry that flight in all of its forms is viewed as somewhat routine by the public, although the recent TWA 800 and Columbia tragedies demonstrates that perception is flawed: Reliable access to air and space is a tremendously difficult technical accomplishment dependent on the labors of many thousands of people. Their dedicated efforts have not received the recognition they deserve.

Acknowledgments

The author gratefully acknowledges research support from the U.S. Air Force Research Laboratory/Propulsion Directorate and from the Air Force Office of Scientific Research. Unpublished summaries of jet fuel development by M. Brian Bergsten and missile fuel development by James R. McCoy provided valuable information for this paper.

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