Aviation Fuels Technology

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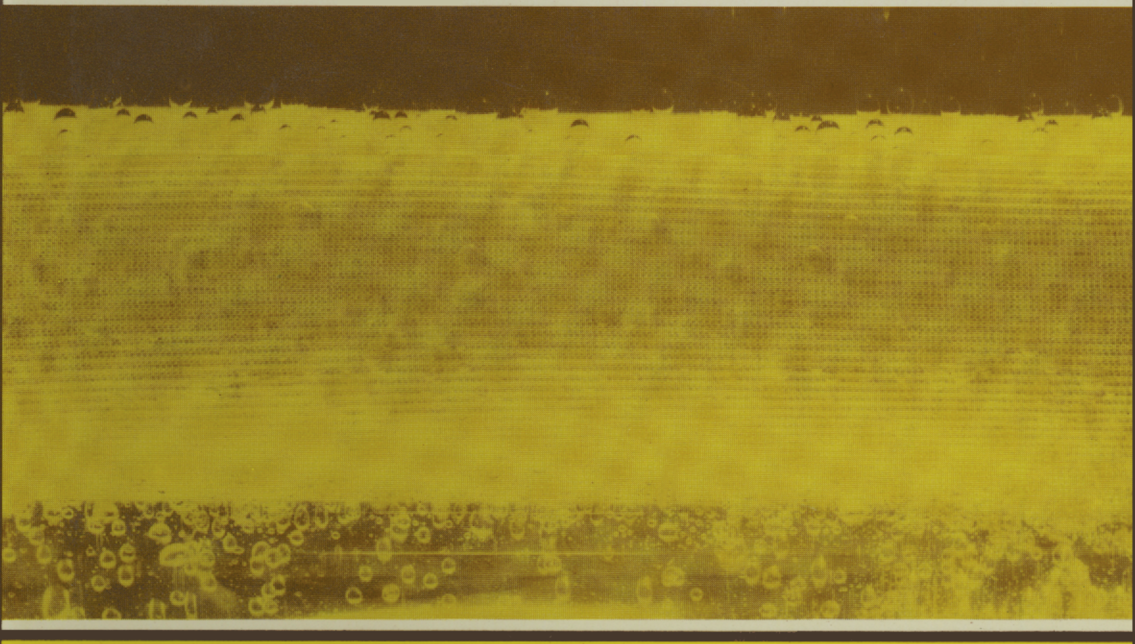

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‘. . .aviation fuel is a small factor in a field of large and powerful forces. Its future is at the mercy of various developments: political, sociological, economic and technical.’

Charles L. Blake
Federal Aviation Administration
U.S.A.
1982

Contents

Preface

The pace of development in the technology of aviation fuels is characterised by continual striving towards distant targets, set initially for improved power, latterly for greater economy, and constantly for reliability and safety. Following the passage of a full decade since shock waves were generated by the first oil crisis, it is now timely to review the role of fuel in the aviation sphere, and to make some assessment of the future.

As in all branches of technology, the pressures of economics and policies are dominant, and many a product of undoubted ingenuity has foundered through lack of financial support or market matching. Nevertheless, from a scientific standpoint, these factors are ephemeral, and can change drastically almost overnight. These present studies, therefore, comment only marginally on prices, and are concerned largely with such durable features as the properties of fuels, together with the constantly growing quantity of data on fuel combustion performance and handling characteristics. The implications of the degradation in crude oil quality, which is already reflected in product quality, and the inevitable demise of petroleum resources some few decades ahead, are noted in various places throughout the book, together with a limited range of potential alternatives. In summary, with continuation of research, development and good fuel housekeeping and management practices, a cautious optimism appears to be justified for sustained international aviation based on liquid fuels.

The aviation fuel picture presented here is largely from a British viewpoint, with some reference to differences in the United States and elsewhere, and is supported by brief indications of the historical roots, and of subsequent routes to present and possible future practices.

The background knowledge for this enterprise has been gained by one of us (R.A.V.) from a full career within the oil industry as a chemist engaged in aviation fuels technology in the refinery, the distribution system and the research laboratory, with service on governmental committees involving many investigations into user problems, and field experience with airline operators and engine and component manufacturers. The other one of us (E.M.G.) embarked on aeronautical engineering before embracing fuel technology, and has been involved for a similar period of time on the more academic side of research and teaching in fuel property-performance relationships, with emphasis latterly on the potential of alternative fuels. We jointly express our gratitude to our parent organisations for their assistance in our studies, and to the many reference authors, colleagues and students who have helped us in numerous ways.

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Eric Goodger
Cranfield
1985

Ray Vere
Barton on Sea

1 Introduction

Aviation has become firmly established internationally both as a prime mover of passengers and a significant handler of freight. Journey times benefit from the characteristically high flight speeds, and also from direct routeing unimpeded by coastlines or mountain ranges. The high operating altitudes, while imposing their own problems of atmospheric conditions, minimise the costly and uncomfortable effects of weather. Since the vehicle has to be supported as well as propelled, the energies involved in aviation are high in comparison with slower forms of transport, with values of payload-range per fuel litre reaching only 0.06 and less than 0.01 respectively of the corresponding values for buses and supertanker ships. The impact of recent turbulences within the oil world has underlined the key role of the fuel element in airline technical accounting, and in effective military operations. In civil aircraft, for example, the (fuel/direct operating) cost ratios have increased from 0.25 in the early 1970s to about 0.60 today. The cost effectiveness of aviation fuels is therefore a key factor in the future viability of aviation in general, and the airline industry in particular.

By the nature of the operational role of aircraft, and of fuel transfer to and within their tankage systems, energetic fuels in the liquid phase are virtually essential and, as outlined in this text, the types and qualities of the conventional aviation fuels have been developed to a generally satisfactory stage. Usage of aviation fuels is expected to reflect the continuing growth in air transport, with a 50 per cent increase in annual consumption by the end of this century; nevertheless this *quantity* will still not exceed about 6 per cent of the total petroleum market. However, since an aircraft in difficulties cannot pull into a lay-by or drop anchor, in-flight reliability is paramount, hence aviation fuel *quality* is vital, yet this must be achieved and maintained with economic viability. This has always been so since aviation became of age, with aeronautical engineering considered as a particularly demanding discipline, and the aero engine as the athlete of the species. Consequently, the requirements for quality will continue to be the more precisely and thoroughly specified, on the lines shown broadly in table 1.1, in view of the essential standards of reliability and the wide ranges of operating conditions.

Studies of aviation fuels are therefore concerned primarily with both quantity and quality as they affect availability, handling, performance and overall

Table 1.1 Quantities and Qualities of Petroleum Fuels in the U.K., 1982

Fuel type	Annual consumption		Typical number of properties specified
	Mtonne	per cent	
Avgas	0.027		14
Avtag/Avtur/Avcat	4.477		21
	4.504	6.0	
Mogas	19.247		9
Derv	5.731		11
	24.978	33.0	
Marine gas oil/ diesel fuel/fuel oil	2.761	3.7	13
LPG	1.449	1.9	10
Other middle distillates	16.355	21.6	11
Industrial fuel oils	16.191	21.4	13
Other products + refinery fuel	9.362	12.4	–
Totals	75.600	100.0	–
Total (world)	2818.8		

economy in terms of both energy and costs. In consequence, this book explores the technology involved with aviation fuels in their progress through refining, distribution, storage, metering to the engine, combustion and subsequent emission to the environment. It complements this with discussion of the specification data, and of the operational experience which helps to determine them. The quantities of fuel involved with some individual aircraft covering representative ranges of size and performance are shown in table 1.2.

Conventional aviation fuels are invariably derived from petroleum, and this dwindling fossil resource is expected to continue in use for as long as is practicable. Fuel quality may tend to deteriorate to some extent, however, owing to the inevitable restrictions in crude oil selection at the refinery, demanding greater tolerance from fuel systems and engines. Concern over this demise of petroleum thus raises questions regarding the continuation of supply of fuels of suitable types and qualities. Longer-term trends in aviation fuels are therefore explored in later chapters, based on supplementation with conventional-type fuels from alternative sources, and eventual substitution with alternative fuels of widely different properties. Several alternatives are seen to be feasible, but the possibility also arises of the preferential reservation of petroleum fractions for aviation on the basis that other types of fuel could be used by some other consumers. Whether aviation can expect such favour remains to be seen but, in any case, there is reason to believe that most types of aircraft can foresee fuelling well

Table 1.2 Fuel capacity of representative aircraft
(Derived from *Jane's "All the World's Aircraft, 1980–81"*, Jane's Publishing Co. Ltd, London, 1980)

Aircraft	Max. T.O. mass (kg)	Fuel mass (kg)	(F/T.O.) mass (per cent)	Propulsive thrust (kN) or power (kW)	Engine type	Max. cruise speed (km/h)	Range (km)	Ceiling (km)
Beechcraft Bonanza V35B	1 542	200	13	213 kW	P	338	1326	5.45
Jetstream 31	6 400	1 400	22	1342 kW	T/P	488	778	9.63
BAe Hawk	7 750	1 365	18	25.4 kN	T/F	1038	2433	15.24
Cessna Citation III	8 845	2 826	32	32.5 kN	T/F	869	4400	15.55
HS 125	11 566	3 700	32	33 kN	T/F	592	4482	12.50
BAe One Eleven	47 400	11 220	24	112 kN	T/F	871	3484	10.67
Airbus A 300	142 000	47 500	33	445 kN	T/F	911	3334	10.68
Concorde	185 065	95 830	52	677 kN	T/J	2179	6580	18.29
Lockheed Tristar	195 045	72 112	37	560 kN	T/F	964	8080	12.80
Boeing 747	371 945	146 700	40	890 kN	T/F	969	8710	13.72

Note: Values are approximate only since many aircraft are available in different configurations, with choice of power plant, drop tanks, loading etc.

P = Piston engine. T/P = Turboprop. T/F = Turbofan. T/J = Turbojet.

into the future, and that any technical and many economic problems that arise are likely to be resolved by continuing development, as in the past. Nevertheless, prudence entails close and continuing attention to the question of fuel supply and usage.

In conclusion, the special fuels required for ultra-high performance aircraft are examined, together with an indication of reactants used for rocket propulsion. Simplified treatments of some basic fuel chemistry and fluid dynamics are covered in the appendixes.

This book therefore attempts to review and prospect all the above features in order to aid both understanding of the present situation, and decision making for the future.

2 Current Aero Engine Types

Propulsion within a fluid environment is generally achieved by the thrust created as a reaction to the rearward acceleration of a fluid jet. Fluid acceleration can arise either by driving a system of rotating vanes, or by releasing heat directly into the fluid flow within a duct coupled with change in cross-sectional area along the axis of the duct. The former method is employed with the combination of aero piston engine and propeller, and the latter with the various types of ramjet and rocket engine. Turbopropeller, turbofan and turbojet engines, in that order, represent gradation from the former to the latter method. Although a claim for being 'first' with any development in aeronautics can lead to controversy, since it depends largely on the definitions of 'flight' (height reached, distance covered, time airborne, speed attained etc.), the following years mark notable early uses of the different aero propulsion engine types:

1232	Rockets, Kai Feng, China
1903	Piston engine in Wright Flyer, U.S.A.
1939	Turbojet (von Ohain) in Heinkel He 178, Germany
1942	Pulsejet (Schmidt-Argus) in V1 weapon, Germany
1945	Turboprop (Derwent 2) in converted Gloster Meteor, U.K.
1947	Ramjet (Leduc 0-10), France

2.1 Engine Concept Development

The aero piston engine derives its power from combustion within closed cylinders, the resulting increase in pressure acting on pistons which rotate a crankshaft, and drive through a reduction gear to the propeller. Combustion is spark-ignited, and the pressure-volume events approximate to those of the theoretical Otto 'constant volume' cycle. Engines based on the potentially more efficient Diesel 'constant pressure' cycle have rarely been used in aviation since the need for compression ignition entails very high compression ratios, and consequently heavy engines of lower power/weight ratios.

Because of the fall in atmospheric air density with increase in altitude, the power output of the normally aspirated aero piston engine operating at a fixed throttle position shows a similar fall. Augmentation of power at altitude thus requires a boost to the inlet pressure, and this was formerly achieved by means of a rotary engine-driven supercharger which, coupled with an automatic boost selector, maintained constant the inlet manifold pressure by progressively opening the throttle butterfly plate. Since the back pressure at the exhaust ports also falls with atmospheric pressure, this technique results in a slight rise in power as the aircraft climbs, although some power must be provided to the supercharger itself. Eventually, a 'full-throttle height' is reached at which the butterfly plate is fully opened, the engine power then falling with further increase in altitude just as in a normally aspirated engine. This is illustrated in figure 2.1, where it is noted that plotting against altitude density, rather than altitude itself, gives straight lines.

The next step was to change gear and drive the supercharger at a higher rotational speed, which drew more power from the engine but extended the full throttle height, gear change being effected at the 'trough height'. Clearly, the optimal arrangement would be an infinitely variable speed drive so that full

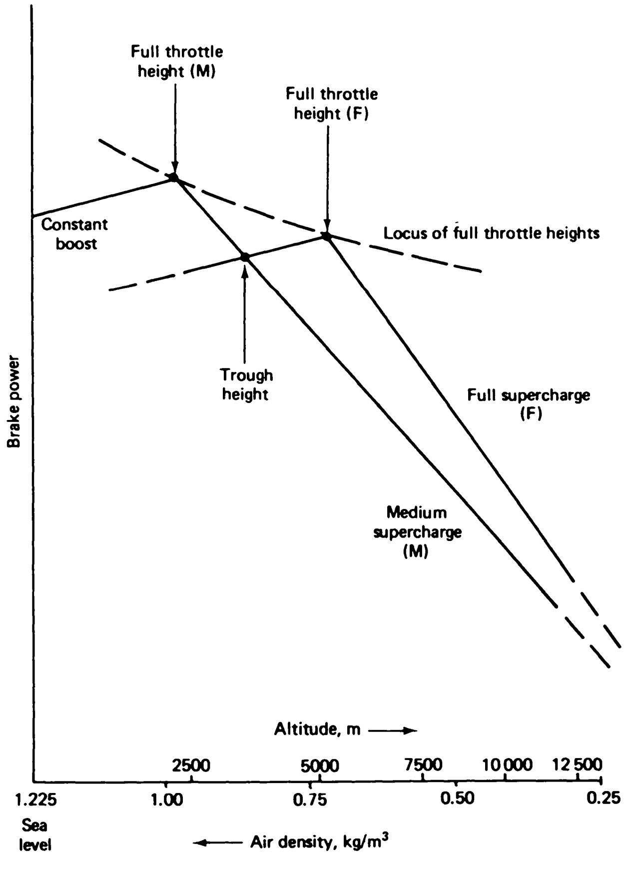

Figure 2.1 Altitude power variation for aero piston engine with two-speed supercharger

throttle is just reached at every altitude above the initial power peak, giving operation along the locus of the former full-throttle power peaks. This optimum can be approached closely by means of a supercharger powered by an exhaust-driven turbine, coupled with a waste gate to give precise control over supercharger speed. The energy remaining in the exhaust gases can make a contribution to thrust by being ejected rearwards. (In fact, it is reported that the Hurricane aircraft, using a mechanically driven supercharger, achieved half its propulsive thrust at altitude by exhaust ejection.) As well as multi-speed, the supercharger developed into a multi-stage unit in order to permit intercooling for control of temperature, and thus density, of the compressed air. Eventually, the turbocompressor unit became so significant that the piston engine itself, with its inherent complexities, became secondary, and was replaced by the much more simple design of a fixed combustion chamber operating at the constant outlet pressure of the compressor (figure 2.2).

The concept of the turbocharged piston engine thus evolved into the gas turbine engine in which, as before, energy is extracted from the combustion products to drive the turbocompressor unit, with some proportion of energy remaining in the products to provide propulsion by rearwards ejection. In the turboprop version of the gas turbine engine, most of the remaining energy is extracted from the gas stream by means of the turbine, commonly using an additional disc, and transmitted through shafting to a conventional propeller, with a relatively minor contribution to thrust from the final jet. The overall result is thrust achieved by a high mass flow rate of gas at relatively low velocity, which promotes a high propulsive efficiency at low flight speeds, but less so above Mach numbers of about 0.5 because of the loss in propeller efficiency. Furthermore, additional weight and mechanical complexity is involved with the extra turbine, reduction gear and the variable pitch mechanism for the propeller. In the case of the turboshaft engine for helicopters, the energy from the additional turbine is taken to the rotor.

The decay in propeller efficiency at high flight speed led to the development of the turbofan engine in which some of the engine air is bypassed through a ducted fan mounted either upstream of the compressor, or on the periphery of one of the turbine discs. The pitch of the fan blades can be made variable, and can serve in reverse for braking. Current development centres on a high-efficiency propeller comprising thin highly swept blades, termed a propfan, together with the hybrid turbofan-prop engine comprising a turbofan engine with one of these advanced propellers. The turbojet engine is used for higher flight speeds where the energy remaining in the gas downstream of the compressor turbine is applied direct to the propelling nozzle for conversion to thrust. Since the conversion efficiency is greater when fluid momentum is achieved with a high level of mass flow, rather than velocity, in some designs a portion of the air bypasses the combustor and turbine units to mix with the main efflux immediately upstream of the propelling jet, resulting in a bypass turbojet engine.

With further increase in flight speed, the ram effect of the entry air is such that the resulting pressure approaches the levels required for efficient combustion

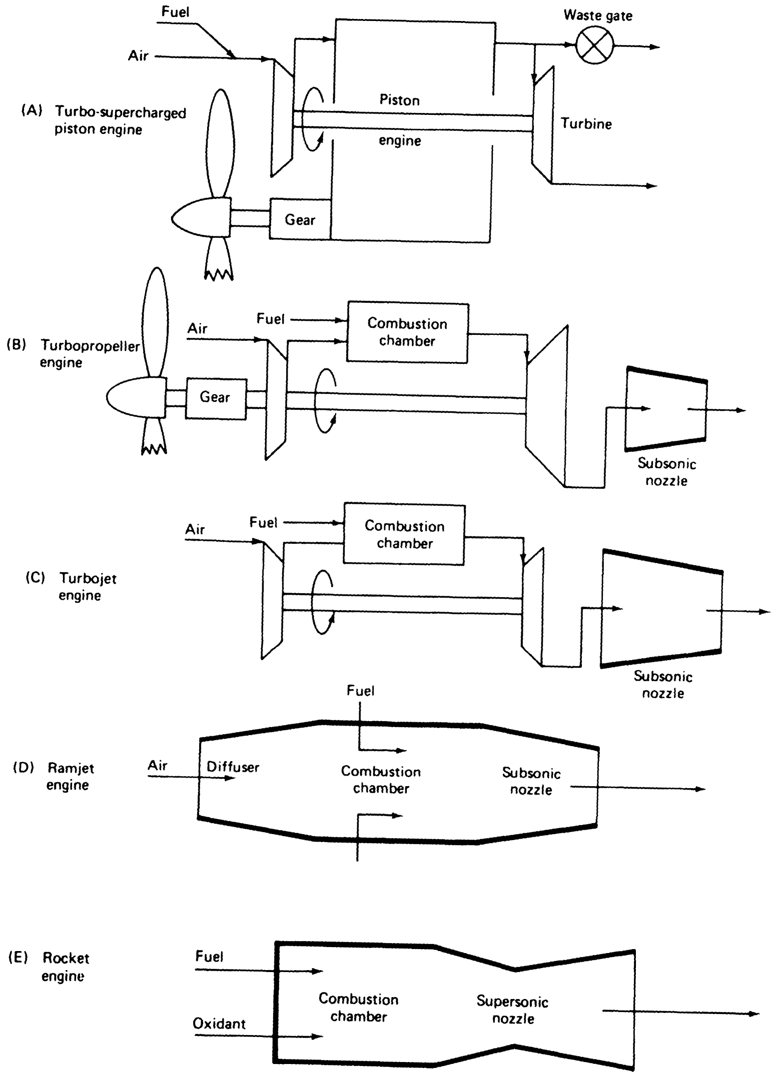

Figure 2.2 Schematic of aero engine type development

without the need for rotary turbine-driven compressors. In a relatively low-performance version of such a propulsive duct, an individual combustion takes place which momentarily closes the entry air valves and generates a pressure pulse leading to a compression wave along the duct. A fresh charge of air then opens the spring valves automatically, and 're-aspirated' air enters the rear of the duct as a result of the reflected rarefaction wave. The next combustion takes place, and the resulting compression wave ejects further combustion products rearwards, together with the re-aspirated air which helps to increase the momentum, and thus the thrust. This type of pulsejet is exemplified by the Schmidt-Argus engine fitted to the German V1 flying bomb which operated at 45 pulses per second, and achieved flight speeds of about 650 km/h.

At higher flight speeds, the effect of the increasing cross-sectional area of the entry diffuser is such that the increase of pressure resulting from the reduction in velocity is now sufficient for combustion purposes. When the flight speed is supersonic, the shock waves created at the duct entry further increase the air pressure by reducing the velocity. This is the principle of the ramjet engine, and the thrust necessary for high-speed propulsion is achieved by acceleration of the combustion products through an exit nozzle.

In all the above duct-types of continuous-flow engine, flame stability within the combustion chamber is established by some form of flow reversal so that the velocity of the fuel–air mixture can be reduced to match the relatively low level of its flame speed. Typically, an air velocity at entry to the combustion chamber of 0.2 Mach number is adopted. With very high flight speeds, of course, particularly in the hypersonic range ($>$ 5 Mach number), the degree of diffusion necessary would not be feasible, consequently diffusion down to, say, 2 Mach number only could be effected, and combustion would be sustained at supersonic level to give the supersonic combustion ramjet (scramjet) engine.

In order to be completely independent of entry air speed, and of atmospheric air for combustion, the rocket engine draws both its fuel and oxidant reactants from within the storage volume of the vehicle itself. Although limited by reactant storage space, the combustion process is freed of the inert nitrogen content of atmospheric air, and can carry diluent-free oxidants, which eases the storage problem and promotes particularly reactive combustion.

The regions of aero engine applications as they appear at present are shown in figure 2.3, and a review of representative data is given below.

2.2 Aero Piston Engine Data

Of the power units used for the propulsion of manned aircraft, the spark-ignition piston engine was the forerunner, and still represents a relatively high proportion. Having progressed from the original 4 cylinder, 850 rev/min, 9 kW unit in the Wright 'Flyer' of 1903, aero piston engines reached a peak of development with the 12, 24 and even 48 cylinder high-performance variants at the closing stages of World War 2, and have now returned to the more modest 4 and 6 cylinder in-line or opposed units of up to 300 kW output for such purposes as training, sporting

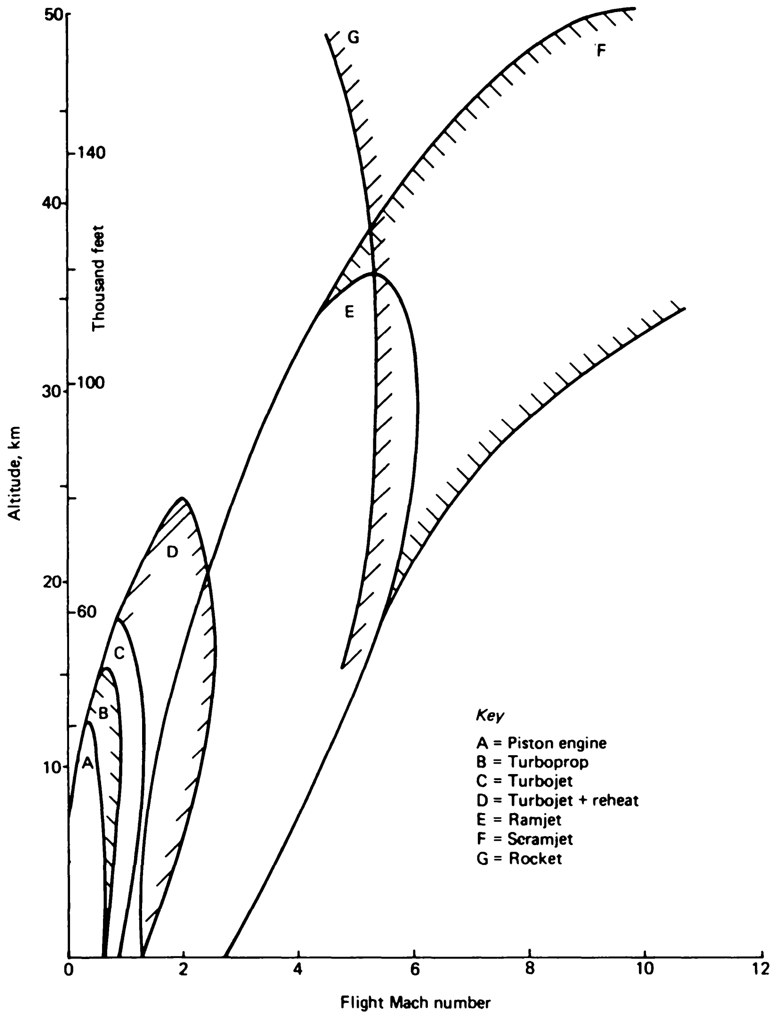

Figure 2.3 Operational regimes for main aero propulsion engines (derived from Allen and other sources)

events and light transport. Current design practice includes either air or water cooling, carburation or direct fuel injection, and normal aspiration or supercharging, usually turbine rather than gear driven. Compression ratios range from about 7 to 9, and engine speeds from 2750 to 5500 rev/min, with up to 6500 rev/min for some small two-stroke units.

A summary of some of the major features of aero piston engines is included in table 2.1.

Table 2.1 Representative performance data for aero engines

	Piston engine	Turboprop	Turboshaft	Turbojet	Turbofan
T.O. Power (kW)	300	4550	3580	–	–
T.O. Thrust (kN)	–	–	–	170	250
Cruise sfc (μg/J)	70	100	100	–	–
Cruise sfc (mg/N s)	–	–	–	25	16

2.3 Aero Turbine Engine Data

The higher-performance engines used for main transport and service aircraft are largely of the gas turbine type in view of their high levels of power per unit mass and per unit volume. In order to accept a high input of air for a given frontal area, the larger gas turbine engines incorporate axial-flow compressors with up to 17 stages, reaching pressure ratios of up to about 30. The smaller engines have returned to the less expensive and more robust centrifugal-flow compressors which suit the geometry of the combustor and turbine, and can now reach pressure ratios of up to about 10. In some of these cases, a low-pressure axial compressor is also fitted upstream.

The air flow from the compressor enters the combustor at about 150 m/s, and is diffused rapidly down to about 25 m/s. Initially, combustion chambers were of the individual tubular type only, but modern trends are towards the single annular chamber and, sometimes, the combined tubo-annular design, each with its own advantages and disadvantages. The fuel is usually introduced from some type of pressure-jet or airblast atomiser, or as vapour via a vaporiser tube, and the flame stabilised by means of air jets, coupled with an entry air swirler to promote recirculation and flow reversal. About 28 per cent of the chamber air, classed as primary, is used for combustion, the remainder entering progressively downstream, first as secondary air to reduce the temperature of the combustion products to about 1800 K to offset the effects of dissociation, and then as dilution air to bring the turbine entry temperature (TET) down further to the maximum level of about 1250 K permitted by the metallurgy of the turbine blades. Higher turbine entry temperatures of 1600 K and above are achieved by internal cooling of the nozzle guide vanes and turbine blades with air bled from

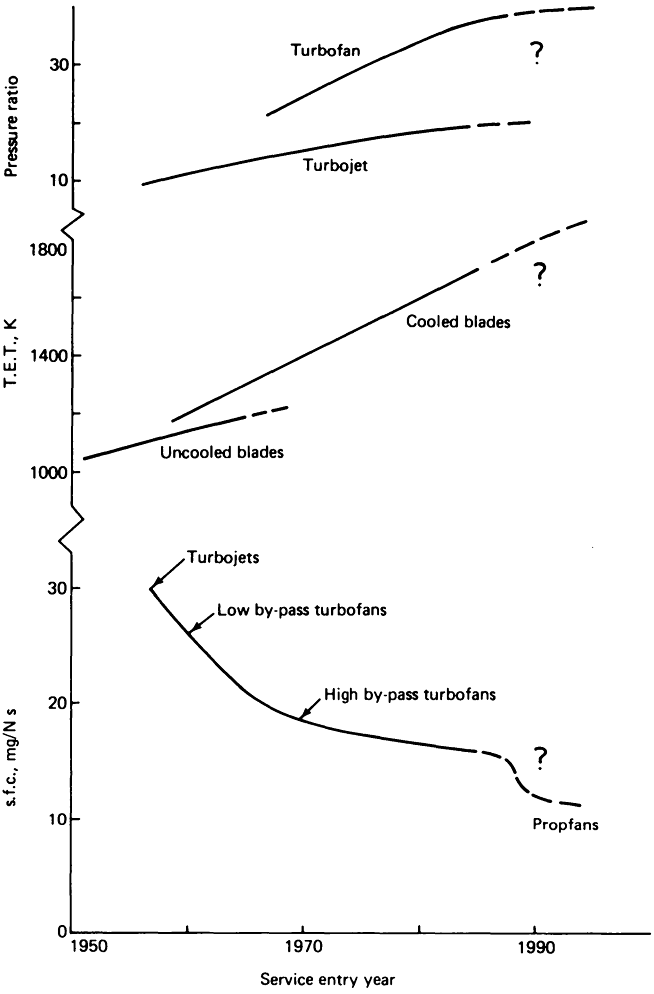

Figure 2.4 Progress in aero turbine engine development (derived from Bennett and other sources)

the compressor. Despite fuel residence times of a few milliseconds only, combustion efficiencies under design conditions are high, typically 99.5 per cent.

Turbine units are almost invariably of axial-flow design, and may extend to as many as six stages. In the turbojet engine, the turbine unit is designed to absorb just sufficient energy to drive the compressor unit (plus accessories), and is linked to it by single, double or triple co-axial shafting. The expanded gases then provide jet thrust by developing kinetic energy through a convergent propelling nozzle or, in the case of supersonic engines with high exit pressure, a convergent-divergent nozzle. Reheat downstream of the turbine is employed to give additional thrust for take-off, climb or transonic operation. Levels of take-off thrust, or equivalent shaft power, and minimum cruise specific fuel consumptions are shown in table 2.1. Thrust/weight ratios in excess of 6 are achieved with aero gas-turbine engines. Curves showing developmental progress in some of the major features of aero turbine engines are shown in figure 2.4.

Current turbine engine developments also include variable geometry so that more than one design point can be achieved by means of adjustable intakes, exhaust ducts, and bypass valves. The mechanical and thermal strengths of turbine blades are being improved by casting in a temperature gradient on a directionally solidified basis in order to reduce the number of weak grain boundaries between individual crystals. The casting of blades as single crystals is even more effective, and further improvement is expected when ceramic blades become practicable. Other developments likely to improve fuel performance in aero turbine engines are the increase of pressure ratios to the level of 40, geared-down turbofans, smaller faster-running compressors with fewer stages giving shorter and stiffer engines, samarium-cobalt generators to feed gearbox accessories mounted in non-drag-inducing locations, and matched expansion of blades and casing to minimise tip-clearance losses. When thrust level rather than fuel economy is the criterion, possibilities arise of a whole family of hybrid engines comprising turbines, ramjets and rockets in various configurations of turboramjet, turborocket, and air-augmented rocket combined with a turboramjet.

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3 Current Aviation Fuel Types

The nature of the fuel best suited to each type of propulsive engine is determined principally by the characteristics of combustion in that engine, but all aviation fuels must also meet the requirements of the aircraft fuel system, the distribution system, and the financial climate generally. The two major groups of aviation fuels that have developed in the above context are discussed below.

3.1 Aero Piston Engine Fuels

The abnormal form of combustion that primarily limits the performance of fuel in a spark-ignition piston engine is the spontaneous ignition of the end gases in the combustion chamber which gives rise to spark knock (see chapter 5). Resistance to spark knock therefore constitutes the major requirement of the fuel, and this can be met most effectively by the inherently low spontaneous ignitability of gasolines. As outlined in chapter 5, spark-knock resistance is expressed in terms of 'octane number' up to a level of 100, and of 'performance number' thereafter. Prior to the development of standardised methods of knock rating in the 1930s, fuel quality was assessed largely by the level of final boiling point, a lower value of which suggested higher resistance to spontaneous ignition, together with improved mixture distribution throughout the inlet manifold which, in itself, limits the onset of weak mixtures, hot running cylinders and consequent spark knock.

The development of aviation gasolines from the straight-run product of about 38 octane number used for the 1903 Wright 'Flyer' to the 115/145 performance number fuel of today is covered in chapter 9. In the U.K., aviation gasoline is given the Joint Services Designation of 'avgas', and the range of several grades available in earlier years was restricted to three types based on anti-knock grade ratings of 100/130 and 115/145. In each case, the first figure relates to the performance number under lean-mixture cruise conditions, and the second under rich-mixture boosted takeoff conditions. The lead content is limited to 0.85 g/l in the standard 100/130 grade avgas, to 0.56 g/l in a low-lead (LL) variant, and to 1.2 g/l in the 115/145 grade. Recently, 80/87 grade avgas has been re-introduced into the U.K. since aero piston engines are now restricted more to the lower end of the power range.

Complete specification details of the main grades of aviation gasoline are given in table 3.1, where anti-knock quality is seen to be the primary indicator of fuel quality. Nevertheless, volatility is still an important property for a fuel that is to be carburetted, and that must therefore find sufficient ambient heat to vaporise without the benefit of prior spraying. The limits specified for the distillation curves are discussed in chapter 5, but it can be appreciated that this property is less significant for engine operation when the fuel is finely divided by spraying as in injection systems of fuel metering. Its importance in relation to vapour generation in aircraft fuel systems, however, increases directly with the operating altitude, ambient temperature and aircraft speed.

Aviation gasolines are colourless blends of volatile hydrocarbon components ranging from about C_5 to C_{12}, but with average properties roughly equivalent to a fictitious molecule $C_{7.3}H_{15.3}$ of molar mass 103 g/mol, and hydrogen mass 14.98 per cent. Aviation gasolines comprise by volume some 65 per cent paraffins plus naphthenes, 25 per cent aromatics and 10 per cent olefins (see appendix 1), with a minimum level of 5 per cent aromatics set for the 115/145 grade in order to ensure sufficient swell for joint sealing and diaphragm operation. Avgas boils over the range 46-145°C, and has a density of about 0.72 kg/l.

3.2 Aviation Turbine Fuels

From the early days of aero turbine propulsion, no major combustion phenomena have been identified of significance comparable to that of spark knock in piston engines. This made the highly refined blending of gasolines, with its essential additives, unnecessary and enabled the heavier fractions to be accepted. In fact, the initial reaction was that the gas turbine, even in its aero configuration, was relatively insensitive to fuel quality. However, aircraft fuel system requirements would not accept the high viscosities and freezing points of fuel as heavy as gas oils, and subsequent development of the gas turbine engine to the limits of its performance capability has reflected similar combustion-related stresses on the fuel. The optimal aviation turbine fuel is now considered to be one that burns cleanly so that problems of metal temperature, combustion deposits, corrosion and particulate erosion are minimised. The kerosine fraction of petroleum emerged as the most suitable compromise fuel, and kerosine-fuelled turbojet aircraft entered service during the closing stages of the second World War.

Aviation kerosine, which is given the Joint Services Designation of 'avtur', is a colourless blend of relatively involatile hydrocarbon components with average properties roughly equivalent to $C_{12.5}H_{24.4}$ of molar mass 175 g/mol, and hydrogen mass 14.06 per cent. Aviation kerosine is similar in many respects to conventional 'lamp kerosine' used for wick-fed illumination, and more recently for domestic heating systems, but particular care is taken over general cleanliness and those properties controlling atomisation, combustion efficiency, smoke and freezing. Avtur comprises by volume some 79 per cent paraffins plus naphthenes, 20 per cent aromatics and 1 per cent olefins. Typically, avtur boils over the range 144-252°C, and has a density of about 0.8 kg/l. In the U.S.A.,

Table 3.1 Aviation gasoline specification DERD 2485 (Issue 9, June 1983)

Property	Limits			
Grade	80	100LL	100	115
Aromatics, % vol., min.	–	–	–	5
Colour, visual	Red	Blue	Green	Purple
Corrosion, copper classification	1			
Density at 15°C, kg/l	Report			
Distillation				
Initial boiling point, °C	Report			
Fuel evaporation				
10% minimum at °C	75			
40% maximum at °C	75			
50% minimum at °C	105			
90% minimum at °C	135			
End point, °C, max.	170			
Sum of 10% and 50% evaporated temps, °C min.	135			
Residue, % vol., max.	1.5			
Loss, % vol., max.	1.5			
Existent gum, mg/100 ml, max.	3.0			
Freezing point, °C, max.	– 60			
Knock rating				
Lean mixture, motor method				
Octane number, min.	80	99.5	99.5	–
Performance number, min.	–	–	–	115
Rich mixture				
Octane number, min.	87	–	–	–
Performance number, min.	–	130	130	145
Oxidation stability, 16 hour				
Potential gum, mg/100 ml, max.	6			
Precipitate, mg/100 ml, max.	2			
Reid vapour pressure at 37.8°C, kPa, min.	38.0			
max.	48.5			
Specific energy, net, MJ/kg, min.	43.5	43.5	43.5	44.0
or				
Aniline-gravity product, min.	7 500	7 500	7 500	9 800
Sulphur, total, % mass, max.	0.05			
Tetraethyl lead content, as g Pb/l, max.	0.14	0.56	0.85	1.28
Water reaction				
Interface rating, max.	2			
Separation rating, max.	2			
Volume change, ml, max.	2			
Electrical conductivity, pS/m, min.*	50			
max.*	600			

*When static dissipator added.

Table 3.2 *Typical aviation turbine fuel specifications*

Property	NATO F-40 Wide-cut gasoline AVTAG/FSII (note 1) DERD 2454 (JP-4) (MIL-T-5624)	NATO F-35 Kerosine AVTUR DERD 2494 (JET A-1) (ASTM D-1655)	NATO F-44 High-flash kerosine AVCAT/FSII (note 2) DERD 2452 (JP-5) (MIL-T-5624)
Composition			
Acidity, total, mg KOH/g, max.	0.015	0.015	0.015
Aromatics, % vol., max.	25.0	22.0	25.0
Olefins, % vol., max.	5.0	5.0	5.0
Sulphur, total, % mass, max.	0.30	0.30	0.30
Sulphur, mercaptan, % mass, max.	0.001	0.003	0.001
Volatility			
Initial boiling point, °C	Report	Report	Report
Fuel recovered			
10% vol. at °C, max.	Report	205	205
20% vol. at °C, max.	145	Report	Report
50% vol. at °C, max.	190	Report	Report
90% vol. at °C, max.	245	Report	Report
End point, °C, max.	270	300	300
Flash point, °C min.	–	38	60
Reid vapour pressure at 37.8°C, kPa, min.	14	–	–
max.	21	–	–
Density at 15°C, kg/l, min.	0.751	0.775	0.788
max.	0.802	0.830	0.845
Fluidity			
Freezing point, °C, max.	–58	–47	–46
Viscosity at –20°C, mm^2/s, max.	–	8.0	8.8
Combustion			
Specific energy, net, MJ/kg, min.	42.8	42.8	42.6
or			
Aniline-gravity product, min.	5 250	4 800	4 500
Smoke point, mm, min.	21	20	20
and naphthalenes, % vol., max.		3.0	

Corrosion			
Copper classification, max.	1	1	1
Silver classification, max.	--	1	1
Stability			
Thermal stability (JFTOT)			
Filter pressure differential, mm Hg, max.	25.0	25.0	25.0
Tube rating, visual (note 3)	Less than 3	Less than 3	Less than 3
TDR spun (note 3), max.	17	15	17
Contaminants			
Copper µg/kg, max.	150	150	150
Existent gum, mg/100 ml, max.	7	7	7
Water reaction			
Interface rating, max.	1b	1b	1b
Separation rating, max.	2	2	2
WSIM (note 4)			
min.	70 (note 5)	70 (note 6)	70 (note 7)
min.	Unlimited (note 8)	85 (note 9)	85 (note 10)
Conductivity			
Electrical conductivity, pS/m, min.	100 (note 11)	50	–
max.	600 (note 11)	450	–

Notes

1. This fuel shall contain between 0.1 and 0.15 volume per cent of Fuel System Icing Inhibitor, NATO Code No. S-748 (DERD 2451), Joint Services Designation (JSD) AL-31, and an approved corrosion inhibitor/lubricity improving additive as listed in Approved Products List (APL) 2461.
2. This fuel shall contain between 0.12 and 0.15 volume per cent of Fuel System Icing Inhibitor, NATO Code No. S-1745 (DERD 2451), Joint Services Designation (JSD) AL-41.
3. Conditional on no 'Peacock' or 'Abnormal' colour deposits.
4. The WSIM specifications are under review.
5. Without static dissipator additive.
6. With static dissipator additive but without corrosion inhibitor/lubricity improving additive.
7. With corrosion inhibitor/lubricity improving additive.
8. With static dissipator additive but 85 minimum prior to addition of both static dissipator and corrosion inhibitor/lubricity improving additives.
9. Prior to addition of both static dissipator and corrosion inhibitor/lubricity improving additives.
10. Without corrosion inhibitor/lubricity improving additive.
11. Applies only when static dissipator additive is incorporated.

the specification for Jet A-1 fuel is broadly equivalent to that for avtur, with its low freezing point of – 47°C suited to international routes, whereas Jet A fuel is specified down to – 40°C only and is used primarily for internal flights.

Once the viability of jet-propelled aircraft became apparent, the aviation fuel market began to swing from avgas to avtur, and problems of supply were envisaged. The strategic availability requirements of the military were therefore safeguarded by blending avtur with naphtha to promote a wide-cut gasoline, designated 'avtag', with average properties roughly equivalent to $C_{10}H_{20.3}$ of molar mass 141 g/mol, and hydrogen mass 14.56 per cent. Typically, avtag boils between 73 and 235°C, and has a density of about 0.77 kg/l.

Subsequent recognition of potentially dangerous concentrations of vapour vented from fuel tanks within the confines of aircraft carriers led to the adoption of a lower volatility kerosine of high flash point designated 'avcat', specifically for Naval use. Avcat has average properties roughly equivalent to $C_{13}H_{24.8}$ of molar mass 181 g/mol, and hydrogen mass 13.81 per cent.

The major specification details of the various aviation turbine fuels are given in table 3.2 and, together with those in table 3.1, are discussed in more depth in subsequent chapters. The specification numbering systems for U.K., NATO and U.S. aviation fuels are given in table 3.3, and the main applications shown broadly in table 3.4.

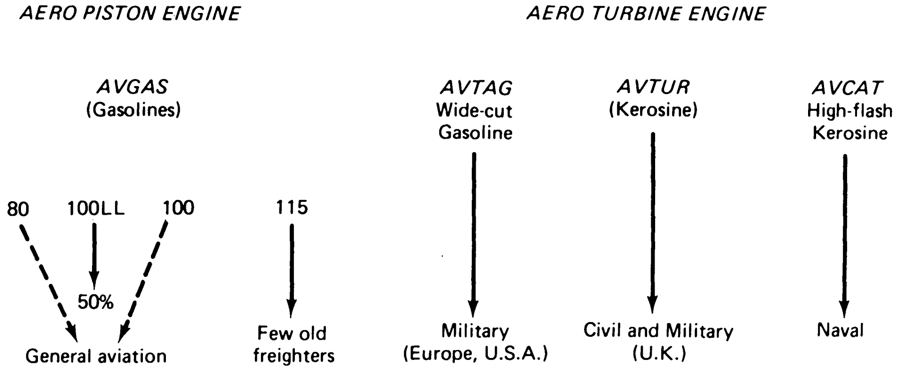
The fuels used by international airlines mostly conform to the standards devised by the major Western governments, but some differences do occur in the larger areas of the Eastern country groupings depending on the types of crude available, methods of refining, and supply policies. In comparison with Jet A-1, for example, the jet fuels of the U.S.S.R. tend to be slightly lighter and more volatile, with lower levels of viscosity and freezing point (– 60°C), and much lower flash point (28°C). Such differences also exist among the Comecon states, but appear to be lessening with the introduction of Western manufactured aircraft into their fleets. Furthermore, full tests on the Chinese export-quality

Table 3.3 Specification numbering systems for aviation fuels

Fuel		DERD Spec. No. (NATO Code No.) U.S. Mil. {ASTM Civil}	
		Without FSII	With FSII
Aviation gasolines	Avgas	2485 (inc. F-18)	
Aviation wide-cut gasoline	Avtag	2486	2454 (F-40) JP-4
Aviation kerosine	Avtur	2494 (F-35) {Jet A-1}*	2453 (F-34) JP-8
Aviation high-flash kerosine	Avcat	2498 (F-43)	2452 (F-44) JP-5

FSII = Fuel System Icing Inhibitor (DERD 2451).
*ASTM Jet A is similar to Jet A-1 except freezing point is –40°C instead of –47°C, and it is used primarily within the U.S.A.

Table 3.4 Aviation fuel types and application



jet fuel show international Jet A-1 standards to be met, with some properties well on the acceptable side of the specification limit.

The needs for thermal stability and high energy density of the aviation fuels used for high-speed flight have led to additional specifications of special fuels for gas turbine, ramjet, supersonic-combustion ramjet (scramjet), and rocket engines which are also covered in later chapters.

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4 Production

Aviation fuels can be produced from most crude oils, but the yields will vary according to the source. Crude oils consist of mixtures of many thousands of hydrocarbons, each of which has its own discrete chemical and physical properties. The physical property that is used initially in the refining of crude oil is boiling point. It is clearly not practicable to separate hydrocarbons individually, but they are divided by a process of distillation into product groups or 'fractions' boiling within pre-determined temperature ranges. These fractions are described as 'straight-run', and various processes are then used to refine the properties to meet their required quality. As seen in the previous chapter, the two major groups of product concerned in this study are the various grades of aviation gasoline, blended for use in aero piston engines, and of aviation kerosines for use in aero gas turbine engines. The initial distillation process, and the subsequent process routes for these two fuel groups, are discussed below.

4.1 Distillation

The crude oil is heated, under pressure to keep it in the liquid phase, firstly by heat exchange with the hot products, which are cooled in the process, and then by means of a pipestill furnace to a temperature of about 370°C. At any higher temperature the crude oil would become unstable and commence to crack, that is, the molecules would split apart forming smaller, and hence lower-boiling, molecules, with the formation of carbon on the inside of the furnace tube walls. Both these effects are undesirable as the resulting products would be difficult to predict, and the furnace would quickly foul up. The crude oil emerges from the furnace and is released into the fractionating tower at atmospheric pressure. At 370°C, most of the hydrocarbons in the crude oil are above their boiling points, and so immediately vaporise or 'flash'. The position in the tower at which this takes place is known as the flash zone. The fractionating tower consists of a series of trays which are perforated to allow the vapours to pass upwards. As the vapours rise they lose heat until they reach a position in the tower where the temperature matches their boiling point, at which level they condense onto a tray. The liquid on the tray then starts to run back down the tower where it meets rising vapours, the interaction of the liquid refluxing with the vapours making separation of the different boiling fractions more precise. At equilibrium conditions, each tray will collect liquid of a specific boiling fraction, which is then drawn off from the tower as a sidestream.

The heavy residues do not vaporise in the flash zone but fall to the bottom of the tower, taking some of the lighter boiling fractions with them. A coil fitted in the base of the tower introduces superheated steam which strips off the light hydrocarbons so that they can travel upwards and become sorted into their correct boiling fraction.

A typical single-stage distillation unit is illustrated in figure 4.1. This shows

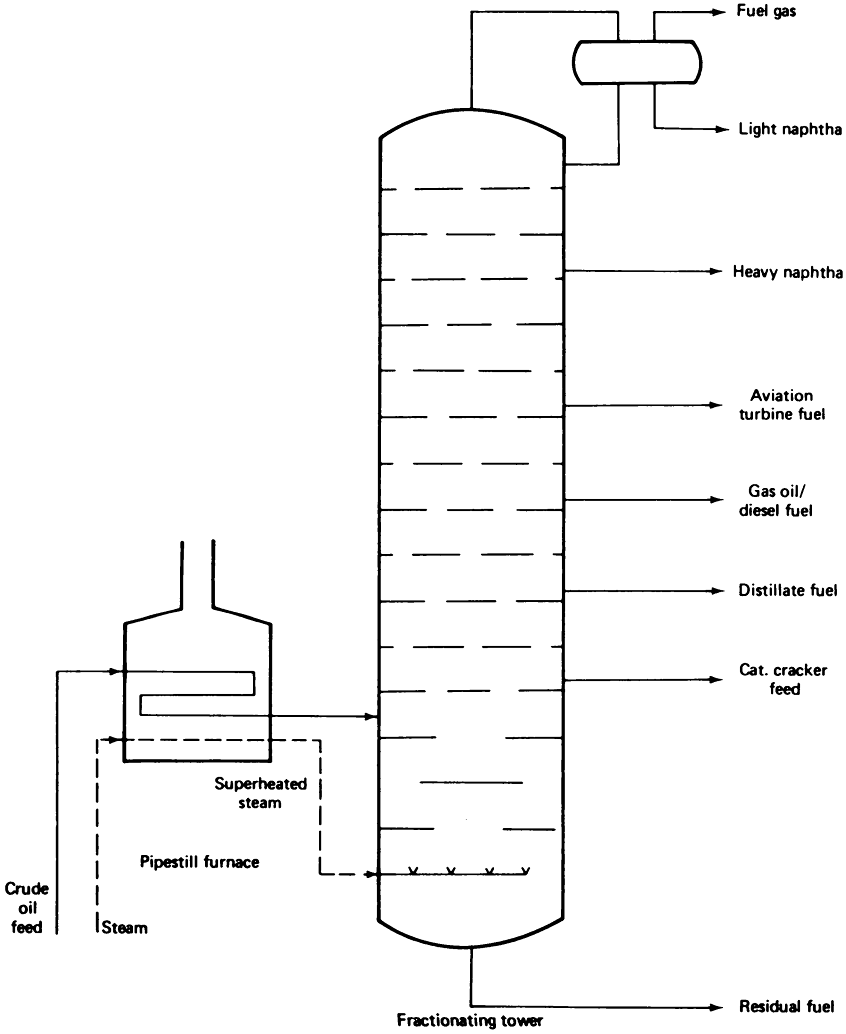


Figure 4.1 Typical single-stage crude oil distillation unit

the crude oil being separated into gas, two naphtha fractions, kerosine, diesel fuel, distillate fuel or heating oil, feed for the catalytic cracking unit and residual fuel oil.

4.2 Aviation Gasolines

From the beginning of powered flight, gasoline has been used for the propulsive spark-ignition piston engine, and the continuous incentives for more power from less weight, together with operational flexibility, have been spurred on considerably by two World Wars, in the second of which military aircraft played a very significant part. These incentives, in turn, promoted continuous research and development into the composition of aviation gasolines, and hence on the ways of producing them. This progress was achieved by the close relationship between the aircraft industry and engine manufacturers, as well as the airframe and systems manufacturers, civil and military operators, and the fuel suppliers.

In this field, the research effort on fuel quality and production processes virtually ceased at the end of the second World War in 1945 as, by then, the gas turbine engine had appeared on the scene, and all future effort, by similar close collaboration, was concentrated on jet aircraft.

The various grades of aviation gasoline discussed in chapter 3 all have similar chemical and physical properties, differing only in their combustion performance characteristics as defined by the knock rating tests at lean and rich mixtures, and by the maximum amount of tetraethyl lead (TEL) permitted in the specification to achieve this performance. Owing to very low usage of aviation gasoline today, the number of grades was reduced to three, but has recently increased to four.

Aviation gasoline, to be versatile and non-restrictive in its use, requires very closely controlled volatility limits indicated by the Reid vapour pressure and the distillation tests. This immediately restricts the components that can be used in its production. The fact that the performance requirements are high still further reduces the available components. Because of the low quantity requirements and the limitation on the type of components that may be used, very few refineries now produce aviation gasoline at all, probably only four or five in Europe and the Middle East.

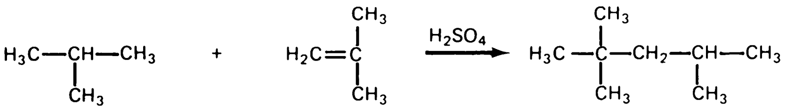
Aviation gasoline is produced by blending alkylate, *iso*pentane, catalytically cracked naphthas and an aromatic-rich extract in various proportions depending on the type of blendstock available at the refinery, and on the other products required from that refinery. If, for example, alkylation units were being used as a major means of producing high octane blendstock for motor gasoline, then some of this would be cut to make aviation alkylate. If, on the other hand, the refinery was making an aromatic chemical feedstock, then some of that would be used to achieve the high octane rating requirements necessary to meet the specification. There is a limit to the amount of aromatic components that may be added to an aviation gasoline since they reduce the specific energy of the blend. In practice, some 25-27 per cent by volume in the blend will meet the minimum specific energy requirement of the specification. As there is no aromatic requirement for the 100 grade in the U.K. specification, a light blend of approximately 95 per cent alkylate and 5 per cent *iso*pentane may be used. However, the U.S. 100 grade gasoline does have a minimum requirement of 5 per cent aromatics, as does the U.K. 115 grade. This was included to ensure good sealing of the bag-type tanks and fuel line seals by swelling the rubber. To achieve this in the light blend, 5 per cent alkylate would have to be backed out and replaced by some aromatic compounds. More probably, the aviation gasoline would consist of a blend of alkylate, *iso*pentane, aromatic extracts and some naphtha, normally catalytically cracked. *Iso*pentane is used because of its low volatility and good octane response to TEL. The blend is so made up that, with the specified amount of TEL added, it will meet the lean and rich mixture octane requirements of the specification.

4.2.1 Alkylation

In the petroleum industry, alkylation denotes a process to produce a high octane gasoline blending component by the combination of olefins with paraffins. Most commercial units react *iso*butane with olefins using sulphuric acid or hydrogen fluoride as catalyst. The sulphuric acid process was discovered independently in 1936 by Bataafsche Petroleum Maatschappij in the Netherlands, and the British Petroleum Research Laboratories in the U.K. This became a major production process for high octane *iso*paraffins.

The alkylation reaction is complex, producing a series of side reactions, but the main products are isomeric paraffins containing the sum of the carbons in the *iso*butane and the olefin. The primary reaction will be.

*Iso*butane + *iso*butylene $\xrightarrow{H_2SO_4}$ *iso*octane



$$H_3C-CH(CH_3)-CH_3 + H_2C{=}C(CH_3)-CH_3 \xrightarrow{H_2SO_4} H_3C-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$$

(2,2,4-trimethylpentane)

Initially, these alkylation units were used almost exclusively for aviation gasoline manufacture. Aviation gasoline demand required all that could be produced to supply the high anti-knock component which had a very good lead response. (This means that there is a significant increase in anti-knock quality for the amount of TEL allowed to be used in the blend.) With the fall-off in aviation gasoline demand, and the very large increase in demand for paraffinic or olefinic components for motor gasoline to supplement the production of aromatic components from catalytic reforming, alkylate is increasingly used in the U.S.A. in motor gasoline.

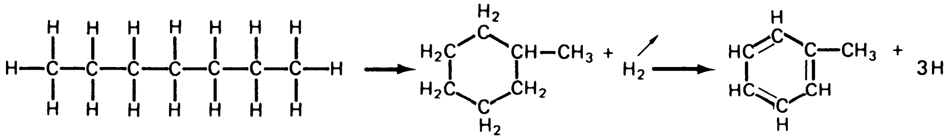
Alkylate is an excellent blending component for aviation gasoline, not only for its good lead response but also because it is essentially free from gum-forming materials, and its performance in supercharged engines is superior to that of catalytically polymerised gasoline. The quality of the alkylate produced depends on the volume per cent of *iso*butane in the reaction zone, and on the reaction temperature. Increasing temperature increases total alkylate yield but reduces aviation yield and quality. When making alkylate for motor gasoline, one can cut to an end point of 204°C, but this must be reduced to 170°C when cutting for aviation gasoline to meet the distillation specification.

A typical sulphuric acid alkylation unit is shown in figure 4.2.

4.2.2 Aromatics-Rich Blendstock

Where a refinery is run for chemical feedstock as well as for high octane motor gasoline, it is more than likely to have a catalytic reforming unit. In this unit, straight-run naphthas, essentially paraffins, are reacted over a catalyst so that they initially form cyclic compounds of the naphthene type which are then dehydrogenated to form aromatics. An example is

n-heptane $\longrightarrow$ methylcyclohexane + $H_2\nearrow$ $\longrightarrow$ toluene + $3H_2\nearrow$



In the total reforming reaction, only a portion of the feedstock completes the cyclisation and dehydrogenation reactions, and a typical feedstock with a boiling range of approximately 75-140°C would yield a reformate of similar boiling range but containing 6 per cent benzene, 20 per cent toluene and 16 per cent xylenes by mass, plus ethylbenzene. This product has high anti-knock quality and is a very valuable motor gasoline component. If, however, an aromatic chemical feedstock is required, the aromatic components may be extracted from this product by a preferential extraction using various solvents. The techniques are similar in both cases, but the solvents are different. The basis of the process is that the feed, which has been pre-heated, is mixed with the lean solvent in an extraction unit. The aromatics dissolve in the solvent, and the raffinate leaves the top of the extractor. The aromatics-rich solvent leaves the base of the extractor and goes to a column at a higher temperature and lower pressure. This boils off the non-aromatic hydrocarbons which pass overhead, and the bottom product passes to a stripper operating at about 190°C and reduced pressure. The aromatics then pass overhead, and the solvent remains in the stripper tower, passing out at the bottom and being recycled to the extraction column. This mixture of aromatics is suitable for aviation gasoline blending

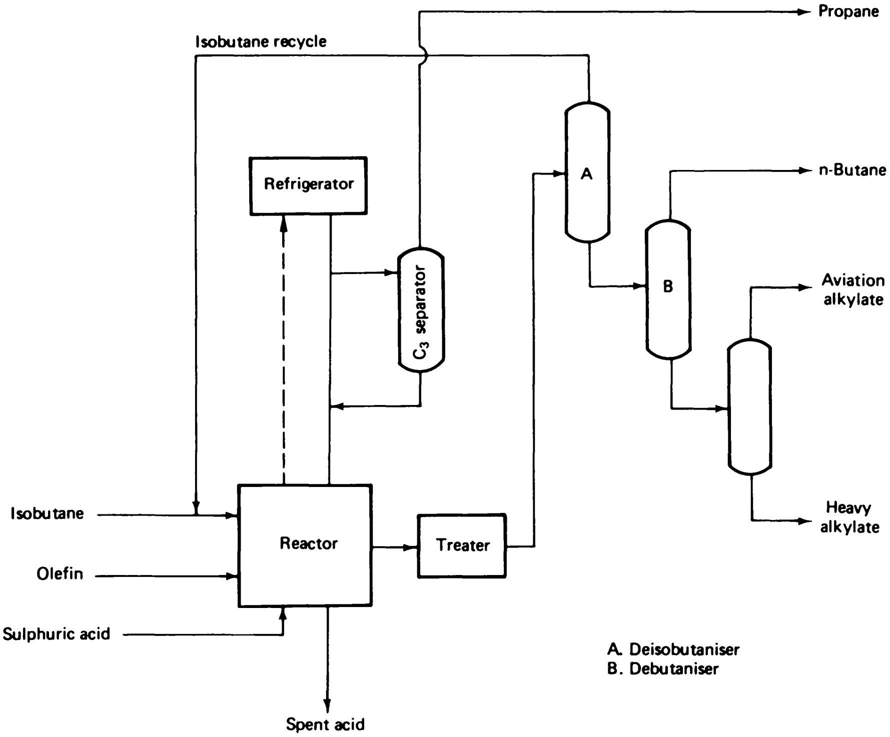


Figure 4.2 Schematic of sulphuric acid alkylation unit (derived from Penniston-Bird)

as all the products have high anti-knock values and are within the correct boiling range. If they are required as aromatic solvents or intermediates in a petrochemical process then they will proceed to a conventional fractional distillation column and be separated out into pure compounds.

The aromatics extracted in this process, and their boiling points, are as shown

Aromatic	*Boiling point (°C)*
Benzene	80.1
Toluene	110.6
Ethylbenzene	136.1
para-Xylene	138.3
meta-Xylene	139.1
ortho-Xylene	144.1

4.3 Aviation Kerosines

The kerosine fraction of the crude oil is the aviation turbine fuel known as avtur or Jet A/A-1. To obtain this fraction, the temperature conditions in the tower would have to be adjusted to give the boiling range required on the tray at the required sidestream draw-off point. Although the specifications are generous with respect to distillation, no minimum initial boiling point being stated and the final boiling point being 300°C, there are several restrictions on the boiling range of the product. The front end, or initial boiling point (IBP), is set by the minimum flash point of 38°C. This eliminates all the low boiling fractions, and gives a typical IBP of 150°C. Similarly, the maximum freezing points of −40°C (Jet A) and −47°C (avtur/Jet A-1) effectively set the final boiling point at around 250°C. These figures are only approximate, and will vary according to the crude oil used. The demand for aviation turbine fuel and other products from the refinery will also determine the percentage yield of aviation turbine fuel. If, for example, the refinery wished to maximise its gasoline production, it may take a wide heavy naphtha cut and so reduce the aviation turbine fuel yield by cutting to an IBP of, say, 160°C. Similarly, it may wish to maximise diesel fuel by cutting it as light as possible, again controlled by a minimum flash point, and so reduce the FBP of the aviation turbine fuel. In these examples, the flash point of the aviation turbine fuel would rise in the former, and its freezing point would be lower in the latter, but as both would be well within the specification for this fuel, it would have no detrimental effect on fuel quality.

From this it can be seen that there is a maximum yield of aviation turbine fuel that can be obtained from a specific crude oil to keep within specification, but the actual yield at any one time will depend on the demands of both the aviation turbine fuel and all the other products derived from the crude oil.

4.3.1 Hydrocracking

High-pressure hydrogenation has been used for over 50 years as a method of refining petroleum, mainly for gasoline. The original plants were by I.G. Farbenindustrie in Germany in 1927, and both Standard Oil of New Jersey (Exxon) in the U.S.A., and ICI in the U.K. operated similar units, all at about 21 MPa.

In the early 1940s, the introduction of catalytic cracking at atmospheric pressure, together with the vastly increased production required, made the hydrogenation process uneconomic, and it was hardly used thereafter.

The mid 1950s brought about another change in the U.S.A. in order to satisfy a very high demand for high-quality gasoline and very little fuel oil. In Europe the product balance from a barrel of crude oil was much more uniform as there was a high demand for cheap fuel oil for power generation, so this imbalance did not exist. Also, in the U.S.A., to meet the demand for high-quality gasoline, there had been extensive installation of catalytic reforming units. These release significant volumes of hydrogen as a by-product. In this situation, the U.S.A. recommenced hydrogenation, and the hydrocracking unit made its appearance. This has many advantages over the old hydrogenation units. Firstly it can destroy heavy products by using the unwanted fuel oil as a feed, and secondly it is extremely versatile in its operation as it can be adjusted to obtain different product yields. Using a gas oil feed it can be set to produce gasoline, initially of prime importance to the U.S.A., but equally, with the heavier feed incorporating high-boiling aromatic cracked stock derived from catalytic cracking and coking operations, it produces gasoline and/or aviation turbine fuel and/or diesel fuel. An example of these operations is shown in table 4.1.

Table 4.1 Typical hydrocracking operation

Feed	Density, kg/l	0.920
	Sulphur, wt %	2.9
	Nitrogen, ppm	820
	Boiling range, °C	360-530

By shifting the operating conditions, the major products may be altered to fit demand.
The following examples show the product distribution in volume per cent for three operating conditions.

Prime operation products	Gasoline	Aviation turbine fuel	Diesel fuel
Butanes	11	7	4
Gasoline	89	38	27
Aviation turbine fuel	–	55	–
Diesel fuel	–	–	69

The mechanism of hydrocracking is similar to that of catalytic cracking but with hydrogenation superimposed. In catalytic cracking, the major reaction is the breaking of a carbon-carbon bond of paraffins into a lighter paraffin and an olefin. This bond rupture occurs at definite locations and is not random. Paraffins tend to crack in or near the middle of the carbon chain, with large molecules cracking at several places at the same time. Olefins are the most reactive hydrocarbons in catalytic cracking and, once formed, they tend to crack rapidly. In hydrocracking, once the carbon chain has cracked, the cracked portions are rapidly hydrogenated by the hydrogen, owing to the fact that the system is operated under high hydrogen partial pressures. The rapid hydrogenation prevents the olefins being adsorbed onto the catalyst and then being dehydrogenated to lay down coke, as occurs in catalytic cracking.

Hydrocracking reactions require a dual function catalyst to crack and to hydrogenate. The cracking function is supplied by the base, typically hydrogen fluoride treated clay, alumina or silica alumina on which is supported the hydrogenation function supplied by metals such as nickel, tungsten, platinum and palladium. These catalysts are very sensitive to nitrogen compounds, which readily break down to ammonia in the reaction and neutralise the acid sites. If a heavy feed, of the type illustrated, is used with high nitrogen (and some can go up to as high as 2500 ppm in nitrogen), then a hydrofining step for denitrogenation and desulphuration is necessary.

A number of hydrocracking processes are now available. Since the 1973 oil crisis, coupled with the severe tightening of environmental controls, particularly with respect to air pollution, interest has increased in Europe for this type of equipment. Fuel oil demand has shown a rapid decline, but although total demand for crude oil products has reduced, gasoline is holding to a small volume increase, and aviation turbine fuel is increasing. This means that more conversion units are needed to meet a changing product demand from less crude oil. One such unit of great interest in aviation turbine fuel production, therefore, is the hydrocracker. Its overall interest centres on its versatility. As shown in table 4.1, it can be a major producer of gasoline, aviation turbine fuel or diesel fuel, and so can go a long way to help with a refinery balance where only small quantities of fuel oil are required. Modern catalytic cracking units with improved catalysts can also achieve high conversion of heavy products to gasoline and heating oil components, but there would need to be further processing to obtain the thermal stability required for an aviation turbine fuel. By cracking and hydrogenating, that is by hydrocracking, this objective is achieved, and at the same time the aromatic content of the product is reduced to below that typically obtained by straight distillation of a Middle East or North Sea crude oil. The product also has a good smoke point, for good combustion, and a good freezing point to eliminate low-temperature operational problems. A typical hydrocracking unit is shown in figure 4.3.

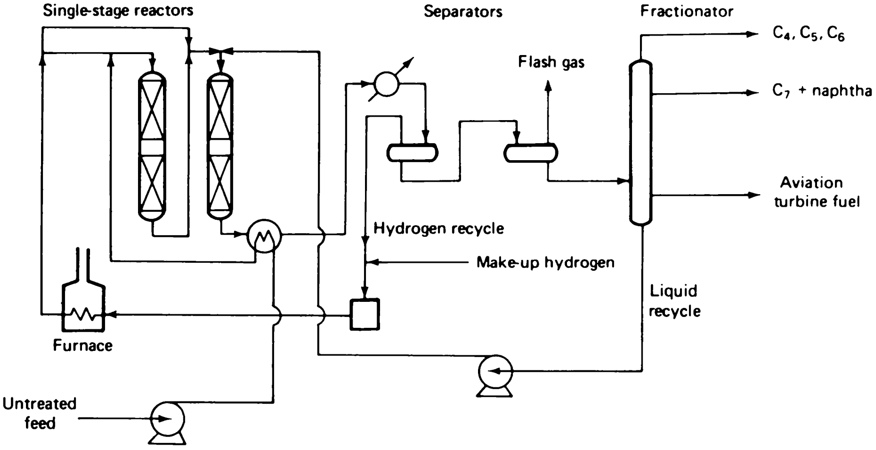


Figure 4.3 Hydrocracker – single stage UOP unicracking unit (derived from Ward)

A product with the correct boiling range is produced, as above, with the flash point and freezing point also within specification, but most crude oils used in Europe and the U.S.A. are described as 'sour' since they contain sulphur compounds of various forms which are corrosive to the components used in an aircraft fuel system and engine. Before the product is ready for use it has to go through a finishing process to ensure that it is 'sweet', or non-corrosive with no objectionable odour.

4.4 Finishing Processes

Since middle distillates are light products, the 'sour' components are not too difficult to remove or convert into acceptable components, and so one of several finishing processes is used. These are known as sweetening processes as they convert 'sour' components into 'sweet' ones by oxidation. The generic types of sour components are mercaptans, which have objectionable odours and are corrosive. They occur to some extent in sour crudes, with hydrogen sulphide which also has an objectionable odour and is corrosive, but are formed mainly by thermal and catalytic decomposition of sulphur compounds during distillation, cracking and reforming processes. For the kerosine type aviation turbine fuels, the primary process is distillation.

4.4.1 Copper Sweetening

A sweetening process widely used for kerosine type fuels is known as copper sweetening, in which the sour products are sweetened by direct oxidation. This can be achieved by means of a liquid, slurry or fixed bed process. For kerosine type fuels, the following fixed bed process is generally used. The sour charge is sweetened by caustic washing to remove traces of hydrogen sulphide which, if left in the feed, would deactivate the copper. The charge then passes through a sand filter to remove any residual caustic soda and/or water haze, and subsequently through rock salt driers to remove all traces of free water. This is critical as an imbalance of water in the reactor will adversely affect the process, which is a net water producer. The charge is then warmed in a pre-heater to ensure that all water formed during the reaction is kept in solution. Air is injected into the line, and the air and fuel feeds flow upwards through the reactor bed of fullers' earth which has been impregnated with cupric chloride. The product, which is now sweet, is water-washed to remove all traces of acidity, and passed through a sand filter to coagulate the fine water droplets, allowing them to settle, and finally pumped to storage.

The main reactions may be represented as follows

$$1.\quad \underset{\substack{\text{Cupric}\\ \text{chloride}}}{2\,CuCl_2} + \underset{\substack{\text{Organic}\\ \text{mercaptide}}}{2\,RSH} \longrightarrow \underset{\substack{\text{Organic}\\ \text{disulphide}}}{RSSR} + \underset{\substack{\text{Cuprous}\\ \text{chloride}}}{Cu_2Cl_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid}}}{2\,HCl}$$

$$2.\quad \underset{\substack{\text{Cuprous}\\ \text{chloride}}}{Cu_2Cl_2} + \underset{\text{Oxygen}}{\tfrac{1}{2}\,O_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid}}}{2HCl} \longrightarrow \underset{\substack{\text{Cupric}\\ \text{chloride}}}{2\,CuCl_2} + \underset{\text{Water}}{H_2O}$$

The first equation shows the sweetening operation, and the second equation the regeneration stage. In fact, there is a series of complex reactions occurring almost simultaneously, but the overall reactions may be represented simply by the above two equations.

A simplified flow diagram of a copper sweetening unit is shown in figure 4.4.

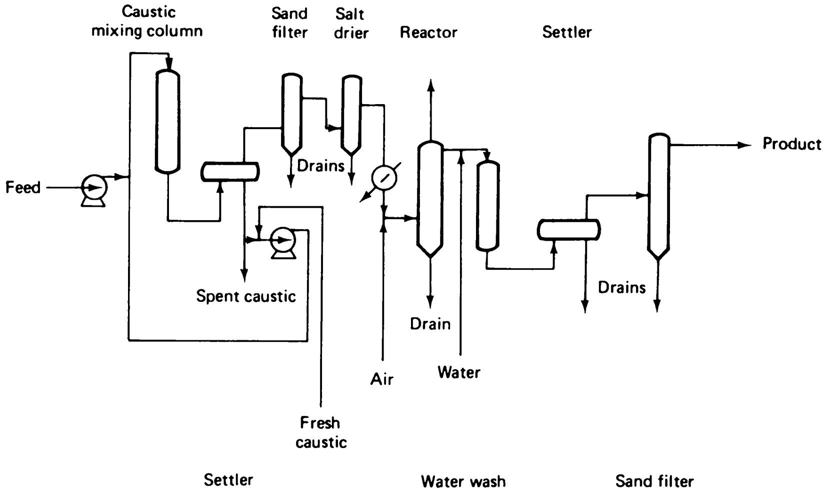


Figure 4.4 Schematic of a copper sweetening unit (derived from Berridge)

4.4.2 Merox Sweetening

Another method of sweetening often used is the Merox process, developed by Universal Oil Products. The reaction takes place in an aqueous caustic soda solution in the presence of a metal chelate catalyst. The sour feed is mixed with air and passed through the solution. The caustic soda extracts the organic mercaptan in the form of an aqueous mercaptide, which is then oxidised to organic disulphide, so regenerating the caustic soda. As the organic disulphide is not soluble in the aqueous solution, but is soluble in the oil, and as the oil has a significantly different density, the two phases separate in the settling tank, with the oil passing out from the top, and the caustic soda solution plus catalyst being drawn off from the bottom and recycled for further use.

The reactions may be represented as follows

$$\mathrm{RSH} + \mathrm{NaOH} \longrightarrow \mathrm{NaRS} + \mathrm{H_2O}$$

$$2\,\mathrm{NaRS} + \tfrac{1}{2}\,\mathrm{O_2} + \mathrm{H_2O} \longrightarrow \mathrm{RSSR} + 2\,\mathrm{NaOH}$$

A simplified flow diagram is shown in figure 4.5.

Probably the most used sweetening process for many years was the 'Sulphuric acid treating process'. Of late, its use has almost ceased, mainly because of the environmental problem of disposing of the acid sludge formed during the reactions. Two other processes which were used to sweeten aviation turbine fuels in the 1950s were the old Doctor treatment process using a solution of sodium plumbite and adding a controlled amount of flowers of sulphur, and the 'Hypochlorite process' in which the fuel was mixed with an aqueous solution of sodium hypochlorite for oxidation. Unfortunately, it was very difficult to stop

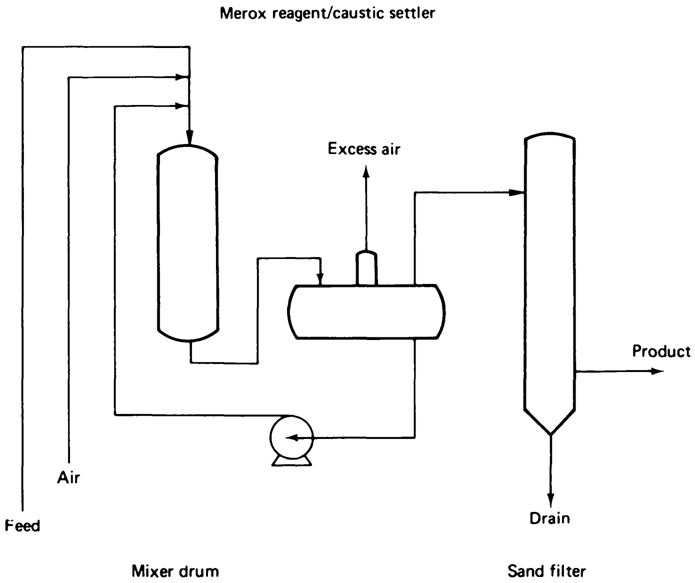


Figure 4.5 Schematic of a Merox sweetening unit (derived from Berridge)

chlorides being carried over, and as specifications became more critical, the process ceased to be used. Although no longer used as a treatment process, the 'Doctor test' is still employed as a control for sweetening, and a Doctor sweet product is still accepted in specifications; for example, 'Doctor sweet or has a mercaptan content of less than 0.001 weight per cent.' Doctor sweetness is very critical, and a fuel will fail the Doctor test if it has a mercaptan content of 0.0004 weight per cent, and hence is well within the specification limits. It is used for quality control because it is a simple and quick test to perform.

4.4.3 Caustic Treatment

Some crude oils, although not sweet, contain small quantities only of hydrogen sulphide and light mercaptans, mainly methyl mercaptan with a little ethyl mercaptan. In such cases, the kerosine distillate fraction, which has been cut to meet the aviation turbine fuel flash point and freezing point requirements, will require only a mild finishing treatment. This is achieved by the use of caustic soda. An aqueous solution of caustic soda is added to the distillate and intimately mixed to ensure good contact. This removes the hydrogen sulphide and the mercaptans as the mercaptide, which is water soluble. The mixture goes to a settling drum where the oil and the aqueous phase separate out, and the oil is taken off at the top of the drum. The oil is given a water wash to remove traces of caustic soda which may have been carried over, settled again to remove water, and then passed through a sand filter to remove traces of water by coagulation before being passed to tankage.

4.4.4 Hydrotreating

Another process, now extensively used in Europe to produce aviation turbine fuel, is known as hydrotreating. There are various names given to specific processes such as hydrodesulphurisation and hydrofining. The process may be used to treat a wide range of refinery products from straight-run naphtha through kerosine to light and heavy gas oil, and light catalytically cracked gas oil. It is a net user of hydrogen and so is normally found in a refinery complex that includes some form of gasoline reforming process that is a net producer of hydrogen. To produce hydrogen, by steam reforming for example, is an expensive process and, although hydrotreating is a very satisfactory way to produce middle distillate products, it is not economic to use this method for aviation turbine fuel production if plentiful supplies of good-quality hydrogen are not available.

The basis of the process is that the raw feed is mixed with hydrogen, preheated in a heat exchanger with reactor products, and finally heated in a furnace to achieve reaction temperature. The mixture is then passed in the gas phase through a series of fixed bed reactors of catalyst. The reactor product is cooled, through heat exchange with the reactor feed and with water and/or air cooler, so that the product condenses back to the liquid phase. The cooled reactor product is separated from the gaseous phase in a separator, the liquid phase going to the stripper where, by adjusting the heat at the base of the tower with steam and controlling the pressure overhead, all the hydrogen sulphide produced in the reaction is removed overhead together with traces of light product, known as wild naphtha, that may have been formed. This stripper tower may also be used to remove any light ends to ensure that the flash point is above the minimum required by the specification. A simplified flow diagram of a unit is shown in figure 4.6.

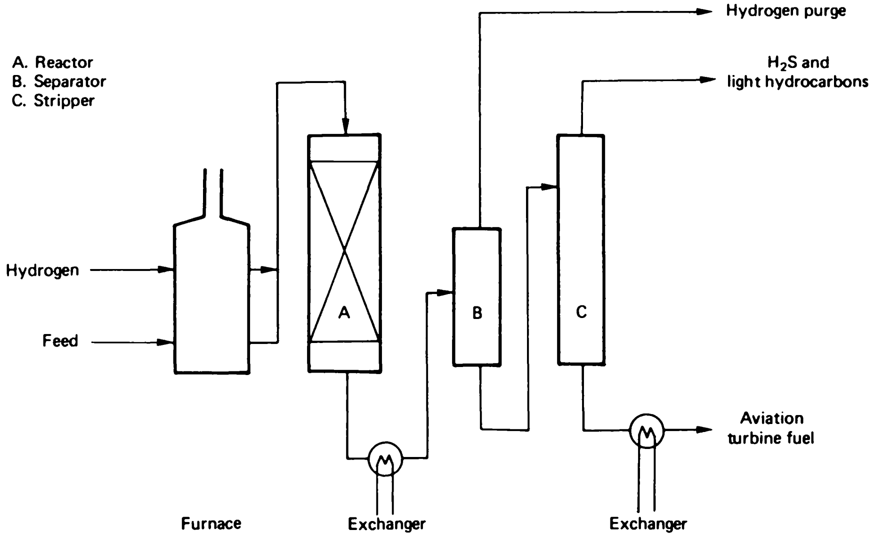
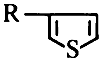


Figure 4.6 Schematic of a hydrofining unit (derived from Berridge)

The catalyst used in this process consists of cobalt/molybdenum salts on an alumina base, typically 1 to 5 per cent cobalt oxide and 5 to 20 per cent molybdenum trioxide, but these soon become partially sulphided in use. They are usually used in a fine pelleted form which is physically hard, not brittle, and has a large surface area. The fixed bed should remain active for several years on an aviation turbine fuel operation owing to its excellent physical properties which prevent the catalyst from disintegrating. It very slowly deactivates as traces of carbon are laid down on the catalyst covering the active sites. This can easily be regenerated, *in situ*, by passing a steam/air mixture over it to achieve a controlled burn-off of the carbon.

The action of a hydrotreater is primarily to desulphurise. It removes sulphur in the form of hydrogen sulphide (H_2S), and replaces the sulphur atom in the molecule with hydrogen. In the aviation turbine fuel case, the main sulphur required to be removed is mercaptan sulphur, but in practice some at least of the sulphides, disulphides and thiophens are also removed. The typical reactions are as follows

$$
\begin{aligned}
RSH + H_2 &\rightarrow RH + H_2S \\
RSR' + 2\,H_2 &\rightarrow RH + R'H + H_2S \\
RSSR' + 3\,H_2 &\rightarrow RH + R'H + 2H_2S
\end{aligned}
$$



$$+ 4\,H_2 \rightarrow RCH.CH_3CH_2CH_3 + H_2S$$

Mercaptan sulphur is one of the easier sulphur compounds to remove and so the treatment may be light, that is, low in hydrogen consumption; in fact, the hydrogen is recirculated with a small amount of fresh make-up hydrogen, the H_2S being removed. If the refinery has a sulphur recovery unit, the H_2S is likely to be absorbed in a solution of diethanolamine in a Girbotol process, passed to the sulphur recovery unit where it is boiled off from the diethanolamine, which is recirculated, and used in the feed gas to this unit. If, however, the refinery does not have such a sulphur recovery unit, once the H_2S has been completely separated from the purified liquid product it may be diverted into the refinery fuel gas stream for disposal by combustion.

In the newer refineries, to save energy, especially heat, it is usual to install sidestream hydrofiners; in this case the reactor is located beside the fractionating tower on the distillation unit, and the product from the sidestream goes straight into the hydrotreater, the finished aviation turbine fuel product going into tankage after an oxidation inhibitor has been added.

4.5 Storage

Once a product has been completed on a refinery process unit it is transferred to a storage tank, which is effectively the last section of the process unit. In this context it is known as the 'run-down' tank, as the product is run down the line from the process unit to this tank. When the tank is full, the product is transferred to the next receiving or run-down tank, and the first one now becomes a storage tank. As such, it is isolated from the system and the product sampled and tested. When all the inspection tests are satisfactorily completed, the product in the storage tank is ready to be shipped off on the first stage in the distribution system.

4.5.1 Aviation Gasolines

Aviation gasolines are produced, as stated earlier, by blending the various components by means of proportionating blending pumps from the intermediate product tanks into the aviation gasoline product tanks. For safety, these tanks will be of the 'floating roof' type, in which the roof actually floats on the surface of the liquid product, so eliminating any vapour space. This not only reduces vapour loss, but also the fire and explosion hazard in storage.

4.5.2 Aviation Turbine Fuels

Once an aviation turbine fuel has been produced by fractionation to the correct cut, or distillation range, on the pipestill to ensure that the flash point and freezing point are within specification, it is treated in a finishing process, probably by copper sweetening, Merox treatment or hydrofining. It is then pumped off the production unit and out to product tankage. For a wide-cut (avtag/Jet B/JP-4) type of fuel, this tankage may be either floating roof or cone roof, whereas for kerosine type fuels a cone roof tank is normally used. If the product, or a component of it, is hydrofined for future blending then an antioxidant should be added to it, at the rate laid down in the specification, as it leaves the product area in the run-down line on its way to tankage. This is done to prevent the formation of peroxides or hydroperoxides in the fuel. The presence of these in the fuel can have an adverse effect on certain synthetic rubbers used for diaphragms in the fuel control system. If the product has been made by hydrocracking, there is a fractionator at the end of the unit and the finished product goes from the appropriate sidestream to tankage.

4.5.3 Tankage

When a tank receiving production is full, it is sealed off from the plant and the distribution system by placing 'spades' into all the lines both into and out of the tank. These spades are metal inserts over and above the normal valves to ensure that contamination of the tank cannot occur. The spades may be solid metal discs manually fitted into the line between flanges in the pipe, normally between two gate valves, or certain proprietary 'blinds' which may be mechanically operated but give a positive seal. In the U.K., the type of seal used must be approved by the Director, Quality Assurance/Technical Services of the Ministry of Defence, who exercise an overall quality surveillance on all aviation turbine fuel production, storage and distribution systems. The product is manufactured to a specification of the DERD (Director, Engines Research and Development), which is issued and controlled by the Procurement Executive of the Ministry of Defence. When a tank is spaded off, all the valves into and out of it are sealed by an inspector. This sealing includes the sample hatches or sample valves, so that samples may be taken only by approved personnel who then reseal the tank, using their own personal seal which is readily identifiable.

When in tankage, the product is allowed to settle, and the fine water droplets slowly coagulate and sink to the bottom, from where they are removed daily by means of a water draw-off point. This is a small valve on the side of the tank, preferably only 18 mm ($\frac{3}{4}$ inch) diameter, connected to a pipe of similar diameter leading to the bottom of a sump below the floor of the tank. The water droplets drain into the sump, so allowing for easy draw-off. After settling for some 24 hours, the tank is sampled for a full test against the inspections required in the appropriate specification. For this, top, middle and bottom samples are taken, and also a composite of the whole tank. It is a first essential that the product is clear and bright and free from suspended matter, and so the top, middle and bottom samples are tested for these criteria. It is noteworthy that a clear and bright or 'water-white' sample can, in fact, contain traces of free water, since this is not always visible to the naked eye. There has to be some 80 ppm of free water present before it becomes visible. As will be seen later, there are special tests used at airports to ensure that free water over the tolerance limit is not loaded onto an aircraft.

Having established 'clear and bright', the next essential is for the product to be homogeneous. Where the product has been manufactured from one cut from a fractionator, it is most unlikely to be anything but homogenous. However, where the product has been blended in the tank from two or more components, or where the tank contains a large heel (the product left from the previous batch), then this product may not be mixed homogeneously. This test is done by checking the density of the top, middle and bottom samples. They must all agree within the tolerance of the test method. If they do, then the samples may be bulked and tested as one. If they do not, and mixing in the tank is possible, then the product must be stirred until homogeneity is achieved. On systems where components are mixed in tankage, it is usual to have some form of mixing device fitted to the tank. One form is a paddle mixer in the side of the tank driven by an electric motor fitted outside the tank wall. The paddle resembles a ship's propeller of coarse pitch. Another technique is the use of a jet mixer; here product is taken from the tank and pumped back through a jet nozzle set tangentially to impart a swirling motion and so mix the contents of the tank. If this procedure is not possible and the product is not homogeneous, then the top, middle and bottom samples must be fully tested separately to ensure that each portion fully meets the specification. When this has been done, the average of these results may be used on the test certificate for the batch in that tank. In the U.K., this certificate has a unique test report number and a unique batch number for the product of that tank. When the product moves on through the distribution system, it is accompanied by a batch certificate with its number, and containing details of the composition of the batch and the test report certificate.

Copies of these certificates are also sent to the Director, Quality Assurance/Technical Services of the Ministry of Defence. All subsequent movements are covered by certificates, including rebatching and retesting along the distribution system, so that in the unlikely event of a problem the origin of the fuel may be traced.

4.6 Bibliography

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5 Specification Test Methods

The combined expertise derived from fuel production, handling and use permits a pattern of property limitations to be specified which together help balance the opposing demands for satisfactory performance, production availability and cost control. In the event of a problem in service, the tightening of existing limits and/or the need for limits on additional properties are investigated. Conversely, fuel availability and costs are generally improved if easement of existing limits is found to be practicable.

Details of the apparatus and procedures for the measurement of fuel properties by laboratory bench testing are standardised, and published annually, by such authorities as the Institute of Petroleum in the U.K., and the American Society for Testing and Materials in the U.S.A. In a growing number of cases, test methods are adopted jointly by the two organisations. Standardisation helps to achieve results with acceptable repeatability (differences with same operator and same apparatus) and reproducibility (differences with different operator and similar apparatus). The relevant test methods to be used for the measurement of fuel properties are also indicated in the fuel specifications.

The United Kingdom specifications are adopted here as representative of current practice and, in their most recent versions for the aviation turbine fuels, related properties have been grouped under the following headings: composition, volatility, fluidity, combustion, corrosion, stability, contaminants, water separation and electrical conductivity. Limits for the aero piston-engine fuels are not so grouped, and differ according to their different requirements. For convenience here, however, limits for these fuels have been dealt with under the same subheadings as for the aviation turbine fuels.

Brief descriptions are given below of the test methods, together with a broad indication of the significance of the results. In what follows, the ASTM number is given first, and the IP number second, the symbols used here being (D. . . ./IP. . .) when the ASTM and IP test methods have been adopted jointly, and (D. . . .) (IP. . .) when the methods differ in some respect. In practice, each designation is followed by a two-figure number indicating the year either of original adoption or of latest revision, but these numbers have been omitted here for brevity. Note that use of the general term 'aviation gasoline' here implies all four grades of avgas, and the term 'aviation turbine fuel' implies avtag, avtur and avcat (in the U.S.A., JP-4, JP-8/Jet A, and JP-5 respectively) unless stated otherwise. If neither term is used, the test method applies to both groups of fuel. This point is illustrated further by the tests shown relevant in the specification tables in chapter 3.

5.1 Composition

Aviation fuel specifications start with a general requirement that the fuel concerned shall consist wholly of hydrocarbon compounds, unless stated otherwise, and that only the specified additives be permitted. In appearance, the product should be clear, bright and free from solid matter and undissolved water at normal ambient temperature.

5.1.1 Total Acidity (D3242/IP354)

The sample of aviation turbine fuel is dissolved in a mixture of toluene and *iso*propyl alcohol, and the solution titrated with alcoholic potassium hydroxide to the orange-to-green end point of an added indicator comprising *p*-naphtholbenzein dissolved in a toluene-*iso*propyl alcohol-water solution. The total acidity is reported to the nearest 0.001 mg KOH/g sample, and is indicative of the corrosive potential of the fuel in storage, together with the presence of trace organic acids which can adversely affect water separation properties.

5.1.2 Aromatics and Olefins (D1319/IP156)

A small quantity of sample is adsorbed in a column packed with activated silica gel, a small layer of which contains a mixture of fluorescent dyes. The sample is desorbed by the addition of alcohol, and forced down the column under gas pressure. The differing adsorptivities of the aromatics, olefins and saturates cause separation into zones, together with red, blue and yellow dyes which become visible at the zone boundaries under ultraviolet light. The volume percentages of aromatics and of olefins are reported to the nearest 0.1 per cent from measurements of the relevant distances between the zone boundaries. The concentration of aromatics is a direct indicator of the swelling tendency for both rubber and plastic seals in fuel systems, and of flame temperature and radiation in gas-turbine combustion chambers, together with tendencies towards the production of smoke and the deposition of carbon. The concentration of olefins indicates a degree of instability with aviation turbine fuels in storage.

5.1.3 Total Sulphur (D1266/IP107)

The sample is burnt in air, and hydrogen peroxide solution is used to convert the sulphur oxides to sulphuric acid which is precipitated as barium sulphate and weighed. Alternatively, the sample may be burnt in an atmosphere of 70 per cent carbon dioxide and 30 per cent oxygen to obviate formation of nitrogen oxides, the absorbed sulphur oxides being determined by precipitation, as before, or by titration with sodium hydroxide. The result is reported to the nearest 0.01 per cent sulphur.

In avgas, the total sulphur content severely inhibits the anti-knock effectiveness of alkyl lead additives. In aviation turbine fuels, sulphur tends to increase the formation of carbon in combustion chambers, together with the corrosivity of the cooled combustion products.

5.1.4 Mercaptan Sulphur (D3227/IP342)

Any hydrogen sulphide is first extracted from the sample of aviation turbine fuel. The sample is then dissolved in an alcoholic sodium acetate solvent and titrated potentiometrically with silver nitrate solution. The mercaptan sulphur content is expressed on a basis of percentage mass.

Mercaptan sulphur attacks certain elastomers and metals used in fuel system construction, and has a strongly offensive odour.

5.1.5 Doctor Test (D484) (IP30)

As an alternative to the above test for mercaptan sulphur content, a sample of aviation turbine fuel is shaken with sodium plumbite solution, and then shaken again after the addition of a small quantity of powdered sulphur. Discoloration of either of the liquid phases or of the sulphur floating at the interface indicates the presence of mercaptans and/or hydrogen sulphide.

5.2 Volatility

The volatility of a fuel is indicated by its ability to vaporise, and is determined by its distillation characteristics and vapour pressure. With petroleum-based fuels, volatility also bears indirect relationships with density and flash point.

5.2.1 Distillation (D86/IP123)

The fuel sample is evaporated at a prescribed rate by heating in a flask fitted with a thermometer, condensed in an ice-cooled tube, and collected in a graduated cylinder. Condensate volume percentages are reported to the nearest 0.5 per cent, and temperatures to the nearest 0.5°C, the corresponding readings being plotted as a distillation curve showing the boiling levels of the various components. The initial boiling point (IBP) is taken as the temperature observed at the fall of the first droplet of condensate, and the final boiling point (FBP) as the highest temperature reached during the test. With petroleum fuels, the maximum distillation temperature is limited to 370°C in order to avoid cracking of the heavier hydrocarbon molecules. In automatic versions of the distillation apparatus, the mercury-in-glass thermometer is replaced by a thermocouple or platinum-resistance thermometer, and the rising meniscus of the condensate is followed by a photocell, the data being either printed out or traced on an X-Y plotter.

Since the heavier fuels are less volatile, distillation temperature levels rise with fuel density. Distillation data give a broad indication of the type of fuel blend, and of its components. They also relate to engine starting, warm-up, carburettor icing, vapour locking, acceleration, mixture distribution, engine wear and crankcase oil dilution with piston-engine fuels, and to such properties as flash point and freezing point with aviation turbine fuels, as discussed in chapter 9.

5.2.2 Flash Point (D3828/IP303) and (IP170)

The sample of aviation kerosine is heated in a cup at a prescribed rate with continuous stirring, and a small test flame introduced at regular intervals into the vapour space above the free surface of the sample. The temperature at which the vapour-air mixture is just able to sustain momentary combustion on the application of the test flame is reported as the flash point to the nearest 0.5°C. The first group of tests (Setaflash and Abel) is used for avtur, and the second test (Pensky-Martens) for avcat (high-flash kerosine). In an automatic version of the Pensky-Martens tester, a control unit determines both the heating rate and the insertion of an electrically heated incandescent test bead. The temperature of the sample is recorded continuously, and locked when the pressure wave resulting from the flash operates a balanced-vane device.

Each fuel burns over a range of fuel-air mixture strength and, for all the petroleum-derived fuels, the limits of these ranges are common at about 1 per cent (weak) and 6 per cent (rich) volume of fuel vapour in the mixture with air. The weak *temperature* limits, that is the flash points, at which this common weak *mixture* limit of 1 per cent is reached are not themselves common, of course, because of the differences in volatility, hence the flash point level rises with fuel density. The volatilities of avgas and avtag are such, in fact, that their flash points lie well below ambient, and so are not specified. Flash point represents a measure of fire safety in handling, and is used to classify flammable and combustible materials. It is also very sensitive to the presence of volatile contaminants.

5.2.3 Vapour Pressure (D323 or 2551) (IP69 or 171)

In the Reid test (D323 and IP69), the fuel sample is located in a cylindrical container connected to an air chamber fitted with a pressure gauge. The apparatus is heated in a bath at a constant temperature of 37.8°C (100°F), the resulting absolute pressure indicated by the gauge being reported to the nearest 1 kPa (0.01 bar) as the Reid vapour pressure. In the micro method, a small evacuated glass bulb is used for the sample, and the resulting vapour pressure measured on a mercury manometer is converted to a predicted Reid vapour pressure to the nearest millibar.

The level of vapour pressure falls sharply with increasing density and, since it lies below 1 kPa for aviation kerosine, and even lower for the heavier fuels, it is specified for avgas and avtag only. Vapour pressure gives an indication of venting loss and vapour lock with fuel systems at altitude, and has some direct relationship with cold starting of aero piston engines, and of gas turbines using avtag/JP-4 in such cold locations as Northern Canada and Norway.

5.2.4 Density (D1298/IP160)

A glass hydrometer is floated in the sample at a constant test temperature, and the relative density is read from the level at which the sample surface cuts the scale within the hydrometer stem. The result is converted to a standard temperature of 15°C (or 60°F), and reported to the nearest 0.0001.

Relative density is defined as

$$\text{rel d at } t_1/t_2 = \frac{\text{mass of given volume of sample at } t_1}{\text{mass of equal volume of pure water at } t_2}$$

North American practice for petroleum products is to use the gravity system of the American Petroleum Institute defined by the Tagliabue formula, as follows

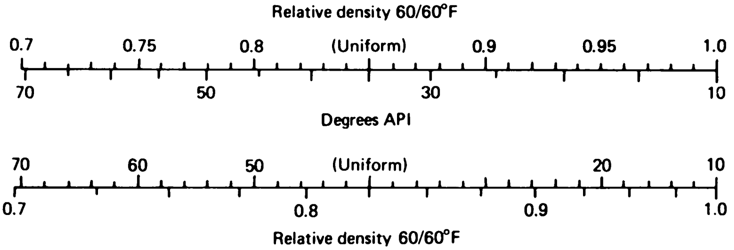
$$\text{degrees API} = \frac{141.5}{\text{rel d } 60/60^\circ\text{F}} - 131.5$$

This relationship is illustrated in figure 5.1. For aviation fuels in the U.K., the result is converted to 15°C and expressed directly in terms of

$$\text{density } (\rho) \text{ at } 15^\circ\text{C} = \text{mass of unit volume of sample at } 15^\circ\text{C}$$

in units of kg/l.

The energy involved in any aircraft mission dictates the fuel quantity required, which is commonly expressed on a mass basis. A knowledge of density is therefore necessary since aviation fuel is loaded by volume. Fuel density gives a broad indication of the type of a petroleum fuel, and has a direct effect on droplet size in spray formation. A specified density range is necessary to calibrate the fuel metering system for correct engine control. The variations of volatility characteristics with fuel density are illustrated in figure 5.2.



$$\text{Degrees API} = \frac{141.5}{\text{rel d } 60/60^\circ\text{F}} - 131.5$$

Note: rel d 15/4°C = 0.99904 (rel d 60/60°F)

Figure 5.1 Relationship between relative density and degrees API

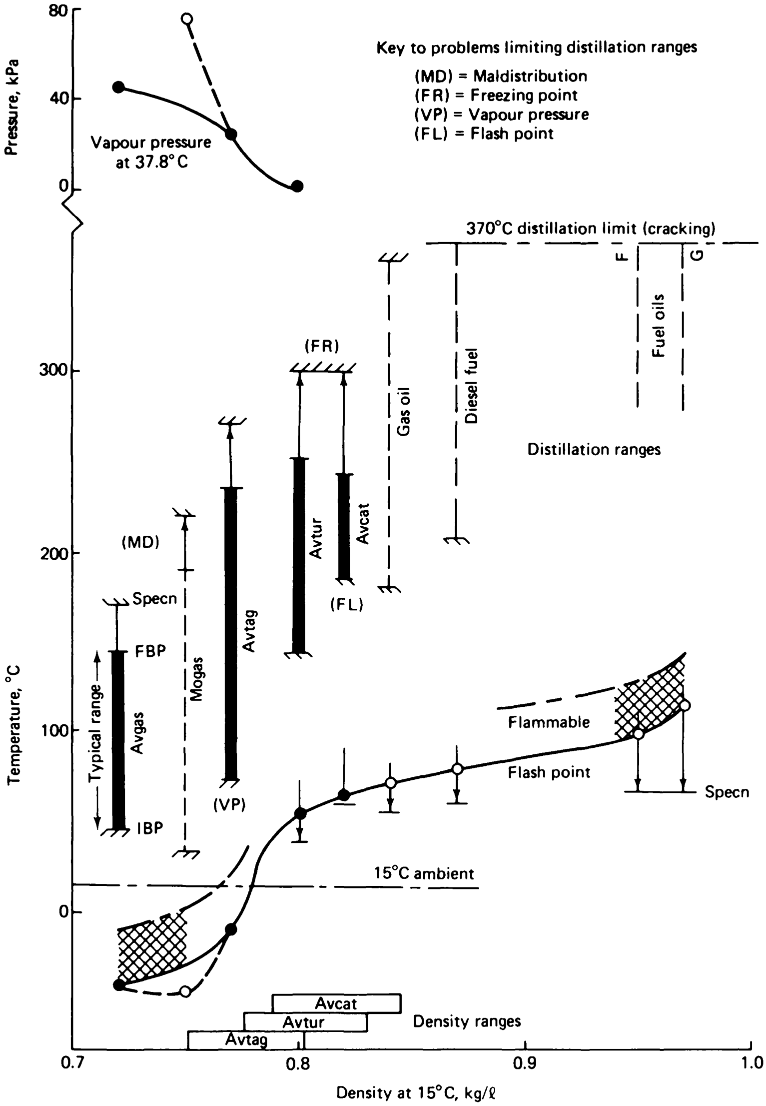


Figure 5.2 Representative volatilities and specification limits of aviation and other petroleum fuels

5.3 Fluidity

The requirement for aviation fuels to remain as liquids under all conditions of operation implies satisfactory flow properties at low temperature (see figure 5.3).

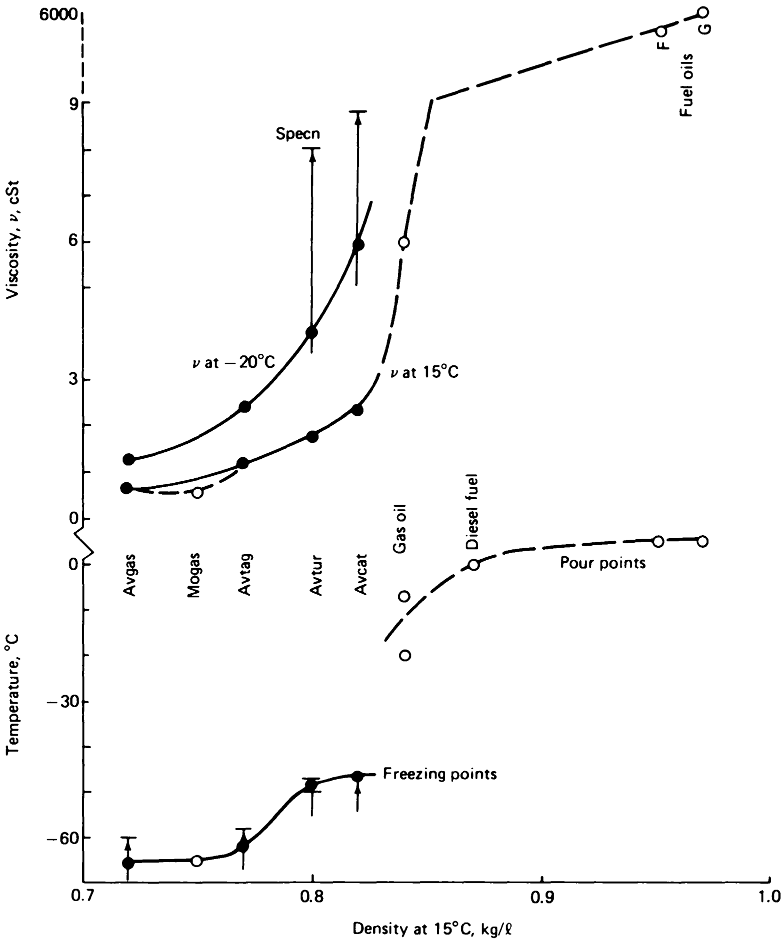


Figure 5.3 Representative low-temperature characteristics and specification limits of aviation and other petroleum fuels

5.3.1 Freezing Point (D2386/IP16)

The fuel sample contained in a double-walled glass tube is cooled by means of an external refrigerant, with continuous stirring. On the appearance of hydrocarbon crystals, the tube is removed from the refrigerant and allowed to warm slowly in the ambient air, with continued stirring. The temperature at which the hydrocarbon crystals disappear completely is reported to the nearest 0.5°C as the freezing point. This test result lies close to the cloud point, being the temperature at which the hydrocarbon crystals first appear on cooling without stirring, but differs significantly from the pour point where the crystals are so numerous that they interlock and give apparent solidity. Both cloud and pour points apply to fuels used outside the aviation sphere.

Freezing point increases with density since the bonding forces between the larger molecules are stronger and require more energy input to permit their free movement as liquid. Freezing point gives an indication of possible blockage of fuel filters, pipelines and nozzles by wax separating out at the low temperatures encountered in Arctic regions and subsonic cruise at high altitude.

5.3.2 Viscosity (D445/IP71)

The coefficient of dynamic viscosity (η) of a fluid is defined as the ratio of the applied shear stress and the rate of shear, and indicates the resistance of the fluid to flow. It therefore represents the tangential force required on either of two parallel plates within the fluid for the planes to move at unit relative velocity when separated by unit distance, and is given in units of poise, P, where 1 P = 1 g/cm s. The kinematic viscosity (ν) is defined as the ratio of the coefficient of dynamic viscosity and the density, and thus equals η/ρ, in units of stokes, where 1 stokes = 1 cm^2/s. The kinematic viscosity of an aviation kerosine is determined by timing the displacement of a given volume of sample through a capillary comprising one leg of a U-tube viscometer maintained at a controlled temperature. The pressure head promoting the flow is proportional to the fuel density, and the resistance to the viscosity. The kinematic viscosity is then determined as the product of the flow time in seconds and the calibration constant of the viscometer, and reported in centistokes (cSt) or mm^2/s to the nearest one part per thousand.

Since the intermolecular attraction between the hydrocarbon molecules changes with distance on an inverse square basis, the contraction accompanying a fall in temperature results in an increase in the dynamic viscosity coefficient. It also raises the density, but to a lesser extent, consequently kinematic viscosity also rises with temperature fall until it approaches infinity a few degrees below the freezing point.

Kinematic viscosity also increases with fuel density since the heavier fuels contain more of the larger molecules with stronger bonding forces. The maximum viscosity limit set at a low test temperature ensures adequate flow through the fuel system, and maintenance of pressure at the spray nozzles. In a general way, viscosity is related to the lubricating ability of a fuel within the delivery pump, but this is also influenced by the chemical nature of the fuel components and contaminants (see section 7.6 (Lubricity) in chapter 7).

5.4 Combustion

The ultimate objective of a fuel is that it should burn in a satisfactory manner over the full range of engine conditions. Suitability for this major requirement is assessed, in the case of gasolines, by measurement of the anti-knock quality and of the TEL content. Determination of the heat released by combustion applies to all fuels, whereas assessment tests of combustion cleanliness apply to the aviation turbine fuels alone.

5.4.1 Knock Rating (D2700/IP236) and (D909/IP119)

The anti-knock quality of an aviation gasoline is determined in both lean mixture, equivalent to cruising conditions, and rich-mixture supercharge, as at take-off. The test unit is a standard single-cylinder ASTM-CFR engine in which the compression ratio can be varied over a wide range during engine operation by moving the complete cylinder-and-head body axially to change the clearance volume.

For the lean-mixture test (D2700/IP236), the engine is operated first with the sample, and the compression ratio raised until the onset of a standardised intensity of spark knock (see chapter 8), detected by means of a pressure-sensitive magnetostriction pick-up and hot-wire ammeter type instrument. Corresponding knock-limited compression ratios are then determined in a similar manner for two reference blends selected to bracket the sample closely, and the rating of the sample then expressed by interpolation between the reference blends. The main reference fuel is the paraffin *iso*octane, i-C_8H_{18}, (2,2,4-trimethylpentane) and, for samples inferior to it, the paraffin normal heptane, n-C_7H_{16}, is used as a lower reference fuel. The rating of the sample is then expressed as an *octane number* equal to the interpolated volumetric percentage of *iso*octane in the matching reference blend with normal heptane.

For samples superior to *iso*octane, reference blends of leaded *iso*octane are used, and the rating of the sample derived from the interpolated concentration of TEL in the matching reference blend, the concentration being converted empirically to an equivalent octane number extrapolated up to 120. The conditions of the test, shown in table 5.1, are now selected as those relating to the determination of Motor Octane Number (MON) of a motor gasoline, the results being converted empirically to the former scale for lean-mixture rating of aviation fuels. At and below the level of 100, these ratings are described as octane numbers, and above 100 as performance numbers, both being reported to the nearest 0.1.

For the rich-mixture test, a variable supercharge is employed with a constant compression ratio of 7 over a range of fuel/air ratio. The degree of supercharge is increased until the onset of a standardised intensity of light knock, detected aurally. The variation of the knock-limited indicated mean effective pressure (imep) with fuel/air ratio is plotted for the sample and for two bracketing reference blends (each comprising i-C_8H_{18} + n-C_7H_{16}, or i-C_8H_{18} + TEL, as above). At the fuel/air ratio for the imep peak of the lower reference fuel, the rating of the sample is determined by interpolation between the two reference imep values.

Table 5.1 Test conditions for CFR anti-knock rating
(Derived from *Annual book of ASTM Standards*, Part 47, Test methods for rating motor, diesel, aviation fuels (1980))

Method	Research	Motor	Supercharge
Rev/min	600 (Mild)	900 (Severe)	1800
Inlet, °C	15.6-51.7 related to barometric pressure	149	107
Coolant, °C	100	100	191
Ignition, °btdc	13	14-26 related to r_v	45
Primary reference fuels	*iso*octane, $i\text{-}C_8H_{18}$ (2,2,4-trimethylpentane) n-heptane, $n\text{-}C_7H_{16}$ $i\text{-}C_8H_{18}$ + TEL		
Rating procedure*	A	A	B
Rating scale	Research octane no. (0-120)	Motor octane no. (0-120) Aviation octane no. (0-100) Aviation performance no. (100-130)	Supercharge octane no. (0-100) Supercharge performance no. (100-160)
Significance	Low speed (urban) driving	High speed (motorway) driving. Aviation cruising at lean mixture	Aviation full power at rich mixture

*A. (i) At r_v giving standard knock intensity of sample, bracket reading of knockmeter for sample with readings for two reference blends, OR

(ii) Convert r_v giving standard knock intensity for sample directly to octane or performance number from data checked frequently with reference fuels.

B. At constant r_v of 7/1, bracket power curve limited by light knock intensity for sample with curves for two reference blends. Ratings above 100 converted directly from lead content of *iso*octane.

r_v = compression ratio.

As before, this rating is described as octane number at and below 100, and as performance number above, although conversion from octane to performance number is possible below 100.

It is customary to express both anti-knock ratings to indicate the grade of an aviation gasoline, hence 100/130 grade indicates 100 octane (or performance) number at lean mixture, and 130 performance number at rich. The level of anti-knock quality is an indication of the fuel economy possible from high compression ratio at cruising conditions, and of engine power output from high supercharge at take-off.

5.4.2 Tetraethyl Lead (D2599/IP228) or (D2547/IP248) or IP270

In the former method, the sample of avgas is placed in an X-ray beam, and the intensity of the lead L-α_1 radiation compared with the intensity of the L-α_1 radiation of either the added bismuth or the incoherently scattered tungsten. In each case, the ratio of the radiations is converted by means of calibration factors to total lead content, reported to the nearest 0.003 g Pb/l at 15.5°C.

In the alternative methods, the lead alkyl additive is converted to lead chloride and extracted with hydrochloric acid. After evaporation to dryness, organic material is removed from the extract by nitric acid, and the lead precipitated as lead chromate. After dissolving in lead chromate solution, potassium iodide is added, and the liberated iodine titrated with sodium thiosulphate solution using a starch indicator. The result is reported to the nearest 0.01 g Pb/l at 15°C.

In the U.K. reference method, the tetra-alkyl lead compounds are extracted from the sample by reaction with iodine monochloride. After evaporation to low bulk, organic material is removed by nitric acid, as before, which also renders the lead compounds inorganic. The residue is dissolved in distilled water, buffered and titrated with EDTA (disodium salt of diaminoethanetetra-acetic acid) using xylenol orange as indicator.

Lead is a very potent anti-knock additive, which helps to reduce the energy required for the production of high knock-resistant gasolines. Excessive accumulations of lead in the combustion chamber are avoided by the concurrent use of dibromoethane as a scavenger to convert the lead to volatile compounds able to accompany the exhaust gases from the chamber. Permitted lead concentrations in gasolines are now being progressively reduced in view of the possible harmful biological effects of their emissions in the environment.

5.4.3 Heat of Combustion (D240) (IP12)

The fuel sample is weighed and burnt in oxygen at a pressure of 30 bar in a constant volume bomb calorimeter. Measurement of the resulting rise in temperature of the surrounding water, together with knowledge of the effective heat capacity of the calorimeter system, indicates the quantity of heat absorbed by the system. This quantity of heat is divided by the mass of the sample to give the heat of combustion to the nearest 20 J/g (0.02 MJ/kg). Since the final temperature of the test is a mere 3°C approximately above the initial, near ambient, temperature, the water generated by combustion will be largely in the condensed phase, having released its latent heat of vaporisation to the calorimeter system. The experimental result is thus described as a *gross* value, Q_g, and is corrected to 25°C. Since product gases are invariably hot at exit from the combustion chamber, a *net* value of heat of combustion is more meaningful, and is derived as

$$Q_n = Q_g - 212.19 H \text{ J/g}$$

in cases where H, the hydrogen content of the sample in mass percent, is known, and

$$Q_n = 10\,023 + 0.7195\,Q_g \text{ J/g}$$

where the hydrogen content of the sample is not known.

The thermodynamic conditions of the test, being a non-flow process at constant volume, ensure that all the chemical energy is released in the form of heat, which can be measured simply by a rise in temperature, and none as work, which would be more difficult to measure.

In aviation practice, the heat of combustion is described as the 'specific energy', being the energy released per unit mass of fuel, with units MJ/kg, as recommended by the Institute of Petroleum. In some applications, it is important to convert this information onto a fuel volume basis, which is then termed 'energy density', in recommended units of MJ/l. Selection of these units permits the direct conversion

$$\text{energy density (MJ/l)} = \text{specific energy (MJ/kg)} \times \text{density (kg/l)}$$

Since low-density hydrogen has some four times the specific energy of high-density carbon, values of specific energy vary directly with hydrogen content, and therefore reduce with increasing fuel density, as shown in figure 5.4. This reduction, however, is small in relation to the corresponding increase in density, consequently the energy density rises with fuel density, as also shown in the figure. Intrinsically, heavier-than-air craft tend to be mass-limited, consequently, on a specific energy basis, subsonic aircraft favour low-density fuels. With supersonic aircraft, on the other hand, the thin aerofoil wing sections restrict the space for fuel storage, and this volume limitation calls for heavier fuels of high energy density. However, these storage requirements may well be over-ruled by engine and other operational requirements, as discussed later.

5.4.4 Aniline-Gravity Product (D611/IP2) and (D1298/IP160) plus (D1405/IP193)

In cases where an estimate of heat of combustion is considered satisfactory, the precise calorimetry of the conventional method may be avoided by the joint measurement of the aniline point and the API gravity, the mathematical product of these results giving a value that correlates with heat of combustion, as follows

$$Q_n = k_1 + k_2\,(A \times G) \text{ MJ/kg}$$

where k_1 = constant for fuel type (41.9557 for avgas, and from 41.6680 to 41.8145 for aviation turbine fuels)

k_2 = constant for fuel type ($0.205\,43 \times 10^{-3}$ for avgas, and from $0.245\,63 \times 10^{-3}$ to $0.254\,07 \times 10^{-3}$ for aviation turbine fuels)

A = aniline point, °F

G = gravity, degrees API.

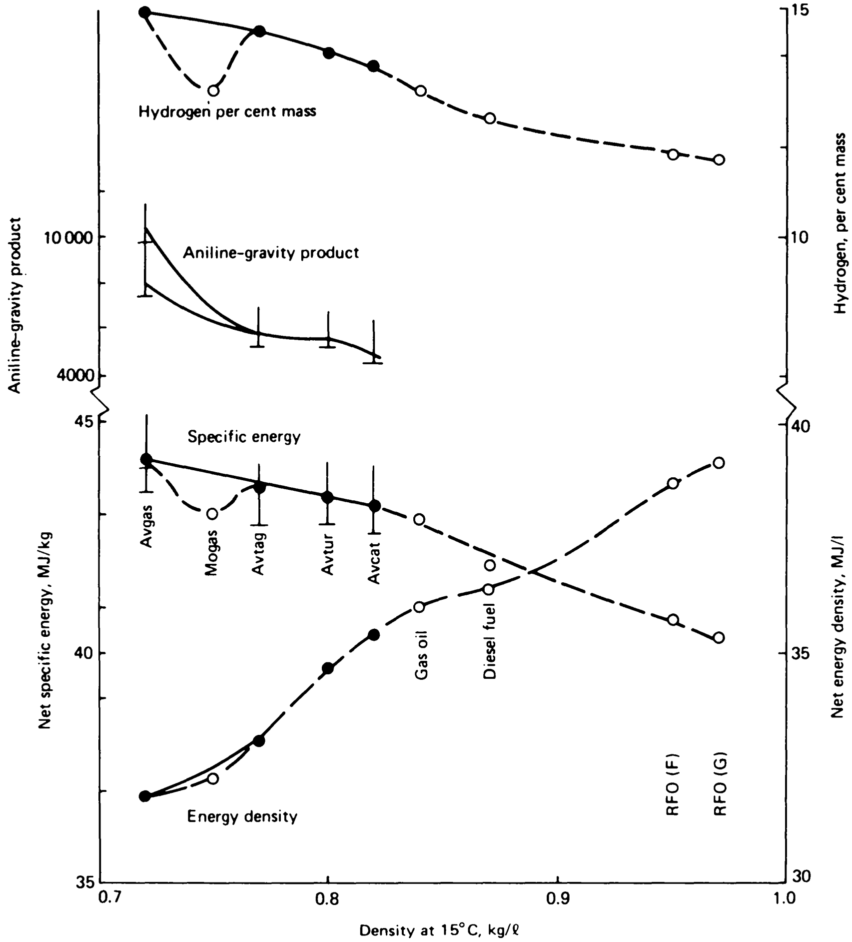


Figure 5.4 Representative energy characteristics and specification limits of aviation and other petroleum fuels

When sulphur is present in the fuel, a multiplication factor of

$$(1 \quad 0.01\,S)$$

is used, together with the addition of 0.1016 S, where S = mass per cent of sulphur in the sample.

The aniline point of a fuel is determined by mixing the sample with an equal volume of aniline, heating until the two fluids become miscible, and then finding the temperature, during controlled cooling, at which the fluids separate. This temperature is reported as the aniline point, to the nearest 0.05°C. Being an aromatic structure, aniline is more easily miscible with other aromatics, consequently the aniline point varies inversely with the concentration of aromatic components, and directly with the concentration of paraffinic and other non-aromatic components. The API gravity was covered in section 5.2.4.

5.4.5 Hydrogen Content (D3701/IP338)

The fuel sample is subjected to a magnetic field together with a matched frequency of radiation in a continuous-wave low-resolution nuclear magnetic resonance spectrometer. Measurement is made of the net energy absorbed by the hydrogen nuclei in transferring from lower to higher levels of spin energy, and this is compared with a corresponding measurement for pure n-dodecane as a reference standard of known hydrogen content. The mass concentration of hydrogen is reported to the nearest 0.01 per cent. In the U.K., this measurement is not yet a mandatory requirement in aviation fuel specifications, but is likely to be adopted following the gathering and analysis of relevant data. Currently, if such a determination gives a result of 13.8 per cent mass or above, the requirements for measuring olefin content, specific energy, aniline-gravity product, smoke point and naphthalene content are waived. In the U.S. specifications for military fuels, minimum mass hydrogen contents of 13.6 (JP-4) and 13.5 (JP-5 and JP-8) are set as alternatives to minimum smoke points of 20 mm and 19 mm respectively. Also permitted is measurement by weighing of the water produced by combustion of the sample from a cotton wick in purified air (D1018), and assessment by calculation using the average distillation temperature (D3343). Hydrogen content limits are not specified for the civil fuels (Jet A, A-1 and B).

Hydrogen content reduces as fuel density increases in the direction from elemental hydrogen to elemental carbon (see figure 5.4). It relates directly to specific energy, but indirectly to combustion temperature. Increased hydrogen content tends to signify a higher combustion quality of aviation turbine fuel, and the above test may prove superior to previous controls exerted jointly by smoke point, smoke volatility index, aromatic content and luminometer number.

5.4.6 Smoke Point (IP57)

The fuel sample is burnt in a circular-wick illuminating lamp, and the wick is adjusted vertically to find the maximum flame height to give a smoke-free flame. A graduated millimetre scale built into the lamp is then used to measure this flame height, which is reported to the nearest millimetre as the smoke point. The lamp is designed to permit a certain rate of air flow into the combustion zone and, when the fuel concentration becomes excessive, fuel molecular cracking occurs with a resultant carbon release in the form of smoke.

With aviation turbine fuels, smoke point gives an indication of the tendencies to carbon deposition and smoke generation in the combustion chamber. In earlier specifications for avtag, a fuel volatility factor was included with smoke point to give the smoke volatility index, SVI, where

$$\text{SVI} = \text{smoke point} + 0.42\ (\text{per cent distilled below } 204^{\circ}\text{C})$$

This practice was adopted since carbon formation tends to increase with boiling point, and a minimum SVI of 54 was set, but the smoke point alone has been re-adopted for this fuel. Since smoke formation generally increases flame radiation, which can reduce flame tube life, a luminometer test has been devised to determine the relationship between radiation and temperature rise. The basic smoke lamp is modified by the addition of thermocouples below and above the flame, and also a radiation-measuring photocell circuit. At a standardised extent of radiation, the flame temperature rise (ΔT) is determined for the fuel sample, and calibrated against the upper and lower reference fuels *iso*octane (2,2,4-trimethylpentane) and tetralin (tetrahydronaphthalene, $C_{10}H_{12}$, a dicyclic aromatic with a relatively high carbon mass content of 91 per cent), which are assigned values of 100 and 0 respectively. The resulting luminometer number, LN, of the fuel sample is then expressed as

$$\text{LN} = 100\left(\frac{\Delta T\text{ fuel sample}\quad \Delta T\text{ tetralin}}{\Delta T\textit{ iso}\text{octane} - \Delta T\text{ tetralin}}\right)$$

The significance of high values on the LN scale has been questioned on the grounds that radiation is being assessed only in the visible region where energy levels are low, and that fuels are rated on a basis of constant luminosity rather than constant heat release. In the U.S. specifications for civil fuels (Jet A, A-1 and B), a minimum luminometer number of 45 is set as an alternative to a minimum smoke point of 25 mm, or of 20 mm together with a maximum naphthalene content of 3 per cent volume.

5.4.7 Naphthalenes (D1840)

The sample of aviation kerosine is diluted to a specified level with either *iso*-octane or cyclohexane, and the absorbance of a specified radiation measured in an ultraviolet spectrophotometer. The resulting concentration of naphthalenes is derived in terms of mass, and converted to volume.

The concentrations of such polycyclic aromatics as naphthalenes provide an indication of combustion cleanliness, and also relate directly to freezing point.

5.5 Corrosion

Aircraft and engine fuel systems experience long-term contact with their fuel contents, sometimes at high temperature, hence it is necessary to check for any corrosive tendencies of the fuel, resulting from the various types of sulphur compound that may remain as contaminants after refining.

5.5.1 Copper Corrosion Classification (D130/IP154)

The fuel sample containing a polished copper strip is heated at 100°C for 2 hours in a test bomb, after which the copper strip is washed and compared with coloured reproductions of corrosion standard strips. Copper corrosion is classified from 1 (slight tarnish) to 4 (corrosion) against the standard strip most closely matching in colour. Copper corrosion is a problem that may arise with the valves, bearings and other copper components incorporated in aircraft and engine fuel systems.

5.5.2 Silver Corrosion Classification (IP227)

The sample of aviation kerosine containing a polished silver strip is maintained at 50°C for 4 hours, after which the silver strip is washed, and the appearance classified from 0 (no tarnish) to 4 (blackening). Silver corrosion is a problem that may arise with the silver-faced slipper pads and port face inserts used in some of the older plunger type engine fuel pumps.

5.6 Stability

With rise in temperature above ambient, the most unstable and/or energetic molecules in bulk fuel may react partially with atmospheric or fuel-dissolved oxygen to generate gum and other solids which can cause blockage of fuel systems.

5.6.1 Oxidation Stability (D873/IP138)

The sample of aviation gasoline is heated at 100°C for 16 hours in oxygen under pressure in a bomb container. The sample is then filtered to remove any precipitate. The sample container is washed with gum solvent, and any increase in weight of the container during oxidation is reported as insoluble gum. The container washings are also filtered, and the total filtrate evaporated under controlled conditions by means of a flow of air or steam (by IP131 in section 5.7.2). The increase in weight of the filtrate container is reported as soluble gum. The potential gum is reported as the sum of the insoluble and soluble gums, the precipitate being reported separately. The total potential residue comprises the precipitate, insoluble gum and soluble gum. All these results are reported in mg/100 ml sample.

Oxidation stability provides a safeguard of freedom from gum formation during long-term storage.

5.6.2 Thermal Oxidation Stability (D3241/IP323)

Using a Jet Fuel Thermal Oxidation Tester (JFTOT), the sample of aviation turbine fuel is pumped at a specified rate along the outer surface of a resistance-heated aluminium tube, and then through a heated stainless-steel cloth precision filter fitted with a manometer. The thermal stability of the fuel is reported indirectly in terms of the extent and colour of the deposits on the heater tube, rated against colour standards, and of the pressure drop across the filter at the end of the test. Alternatively, the stability is reported directly in terms of the time required to reach a specified pressure difference across the filter.

Thermal stability indicates the tendency to deposition of degradation products in fuel systems and burners when fuels are subjected to high temperatures for prolonged periods, particularly in high-speed flight.

5.7 Contaminants

Any non-combustible component of a fuel, whether derived from the parent crude or picked up during subsequent preparation and handling, may be classed as a contaminant, and may have negative, rather than zero, effects on performance.

5.7.1 Copper Content (IP225)

Sodium hypochlorite solution is added to the sample of aviation turbine fuel, and the copper extracted by washing with hydrochloric acid. Prescribed chemicals are then added in order to eliminate interference, and the copper is complexed with sodium diethyldithiocarbamate. After extraction with chloroform, the colour intensity is measured in a spectrophotometer, and the copper content in μg/kg estimated from a calibration curve. This test applies only at the production stage of fuels containing copper sweetened components (see section 4.4.1).

5.7.2 Existent Gum (D381/IP131)

The sample is evaporated under controlled conditions by means of a flow of air or steam, and the weight of the resulting residue reported as existent gum to the nearest mg/100 ml sample.

The level of existent gum predicts fuel stability since unstable fuel will oxidise to form polymeric gums in induction manifolds and carburettors, and on valves, in piston engines. It is also used to check for aviation fuel contamination within product distribution systems.

5.7.3 Water Reaction (D1094/IP289)

The fuel sample is shaken at room temperature with a phosphate buffer solution in a graduated glass cylinder for 2 minutes. The interface between the solution and the sample is rated from 1 (clear and clean) to 4 (tight lace or heavy scum). The separation of the two liquids is then rated from 1 (complete) to 3 (incomplete) in the form of emulsions, precipitates or bubbles in either fluid. With aviation gasoline, the change in volume of the aqueous layer is also reported to the nearest 0.5 ml.

The test serves as a check against the inclusion in the fuel of alcohol, or any other water-soluble components, as combustion improvers. In aviation turbine fuels, it also checks for trace contamination by surfactants which will disperse any free water, and resist its coagulation to large droplets which are easier to remove in storage tanks and filter/separators.

5.8 Water Separation Characteristics (D2550) or (D3948)

A sample of aviation turbine fuel is emulsified with water, and passed through a glass-fibre coalescer. Any turbidity of the outflow generated by water remaining in suspension is measured by the reduction in light transmission to a photocell. The second test comprises a miniaturised, portable, version.

The test serves as a check on the emulsion-forming tendency of a fuel which would clog filters or orifices by surfactant pick-up. It applies mainly to the production state, and gives an indication of contamination by surfactants. It is noteworthy that both the static dissipator and corrosion inhibitor additives used in turbine fuels are surfactants.

5.9 Electrical Conductivity (D2624/IP274)

Two electrodes are immersed in the sample of aviation turbine fuel, and a voltage applied, resulting in a small current (microamps) which gives a direct reading of conductivity in picosiemens/metre (pS/m), which are now termed conductivity units (CU).

The presence of free ions within a fuel, generated by molecular contact between fuel and some other material (wall or contaminant), represents a streaming current during fuel transfer operations, and the build-up of high static charges within the filter/separator or receiver tank. At a sufficiently high potential gradient between fuel surface and container wall, the mixture of air and vapour would break down electrically, resulting in a discharge of incendiary strength. However, these same ions promote electrical conductivity which enables the generated charge to dissipate to the walls through the liquid. The conductivity of aviation turbine fuels is very low owing to the high levels of cleanliness and purity maintained, consequently high-speed transfer will cause the build-up of potentially dangerous static charges. Most fuels now require the addition of a static dissipator to bring the conductivity within prescribed limits. Increasing the conductivity by increasing the ions produces a higher charge rate but also a higher relaxation rate, so that the possibility of incendiary discharge is eliminated.

5.10 Quality Control Testing

When a refinery product tank is filled with aviation fuel, the valves are closed and the tank is spaded off from the rest of the product system. After allowing time for settlement, and draining off the free water, samples are taken from the top, middle and bottom of the tank, together with a composite of all three, and tested for density. If homogeneity is shown by equal values of density, the composite sample is subjected to a full test covering all the properties given in the product specification.

In the U.K., all these tests are recorded on a test report certificate, which is given a unique number so that the history of the product can be traced in the event of a problem. A copy of all aviation fuel test report certificates is sent to the Director, Quality Assurance/Technical Services (DQA/TS), and sealed samples of every batch are held for 3 months. The DQA/TS calls up at random a certain number of these retained samples, as an extra check of one or more specification parameters. In this way, a very strict control is maintained on the quality of all aviation fuel produced. Also, when batched at the refinery, the tank contents are given a batch number. A batch certificate is also issued to give details of the make-up of the batch, the volume just made and the process used, plus the volume and method of manufacture of the heel, that is, the quantity left in the tank from the previous batch. The test report number is also given. These documents go forward with the fuel and, if rebatching is required, the new certificate refers to the original so that the full history of the fuel is known.

When aviation fuel stocks are transferred by tanker, barge, pipeline, road or rail, every precaution is taken to obviate any contamination from dirt, water or other petroleum products. Where possible, aviation fuel products are handled in segregated or dedicated systems, particularly when close to the airfield. Ocean tankers and long-distance pipelines, however, are not normally so dedicated, hence, after such movements, tests must be conducted to confirm that specification properties have not been affected by contamination with other products. These tests are routine, and are carried out at ocean terminals and multi-product pipeline terminals after the receipt of every aviation fuel cargo.

Stocks received in tankage are sealed, allowed to settle, sampled, tested and issued with a new batch certificate and test report. Any future movement in a non-dedicated system will require this procedure to be repeated. Batch records are kept, relating each batch to the previous one, right back to the original batch at the refinery.

At terminals and depots, and sometimes also at airfields, tanks are cleaned on a routine basis, and usually when the tank contents are changed to a higher grade. After the first refilling of these tanks, inspection tests will be required to ensure that all traces of cleaning materials, or the previous fuel grade, have been removed, and that the properties of the aviation fuel now in the tank have not been affected.

If aviation fuel is stored for long periods, deterioration can take place. Avgas can suffer evaporation loss in hot climates which may lower the Reid vapour pressure, and possibly increase the TEL content. Long-time storage can also cause loss of TEL by precipitation. In time, all aviation fuel can increase in gum content or become corrosive, particularly if trace water is present, as a consequence of sulphate-reducing bacteria. For these reasons, all static stocks are retested at set intervals, typically every 6 months (periodic tests) to check that they still meet the specification.

In all these cases, it is not necessary to carry out a full inspection test, as this may be traced back through the batch numbers. Instead 'short tests' are conducted to check those properties most likely to show any change under these conditions. This not only reduces the cost, but enables the work to be carried out by smaller, local, laboratories which would not normally have the facilities for full-scale specification testing. Sometimes these tests are known as

Table 5.2 Short tests

Test	Avgas	Avtag	Avtur
Appearance	✓	✓	✓
Distillation	✓	✓	✓
Flash point	–	–	✓
Vapour pressure	✓	✓	–
Density	✓	✓	✓
Freezing point	–	✓	✓
Knock rating (lean mixture)	✓	–	–
TEL content	✓	✓*	✓*
Copper corrosion	✓	✓	✓
Existent gum	✓	✓	✓
Water reaction	–	✓	✓
Water separation characteristics	–	✓	✓

*To check for contamination after pumping through multi-product pipelines.

'Recertification Tests', as they are the tests required to recertify the product to ensure that it meets the original 'full test' specification.

A list of short tests for aviation fuels is given in table 5.2.

5.11 Bibliography

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6 Operational Handling

In the previous two chapters, production methods were dealt with and the resulting product was isolated, tested and certified as meeting the required specification. The product, however, is still within the refinery, and the next stage is to move the product towards the aircraft where it will be used. In doing so, it is most important that it does not become contaminated with dirt, water or any other product. To ensure that this does not happen or, should it do so, that the contamination is detected and the product not used in aircraft, a strict handling procedure is observed.

6.1 Distribution

Starting at the refinery, the aviation fuel has been 'boxed up', that is, physically isolated from the rest of the system by means of spades in a tank, tested and certified as on specification. It has now to be moved to the terminal. Nowadays this is done either by transporting it in an ocean-going or coastal tanker or, as on the large rivers in Europe, by barge or by pipeline (figure 6.1). For large volume movement, the use of pipelines over both short and long distances is becoming preferable.

6.1.1 Ship

In considering first the movement by water, a large tanker is unlikely to have a dedicated cargo, that is, one cargo for all its tanks. Tankers up to, say, 25 000 tons, however, not infrequently carry a dedicated cargo of aviation turbine fuel. Before any product can be loaded, whether as a sole or mixed cargo, the receiving tanks must be washed and cleaned out to free them of the previous cargo and of any dirt and free water. When the cleaning is completed, qualified inspectors enter each tank designated to receive the cargo and inspect it for fitness to receive a cargo of aviation fuel. Normally the lines from the product tank to the jetty are dedicated to the specific aviation fuel product. If they are not so dedicated, then the lines to be used must be flushed out with the product and samples taken out at the jetty end for short testing to see that they match up with the quality of the product in the shore tank. When the lines are clear and the inspectors have certified that the ship's tanks are ready to receive the cargo,

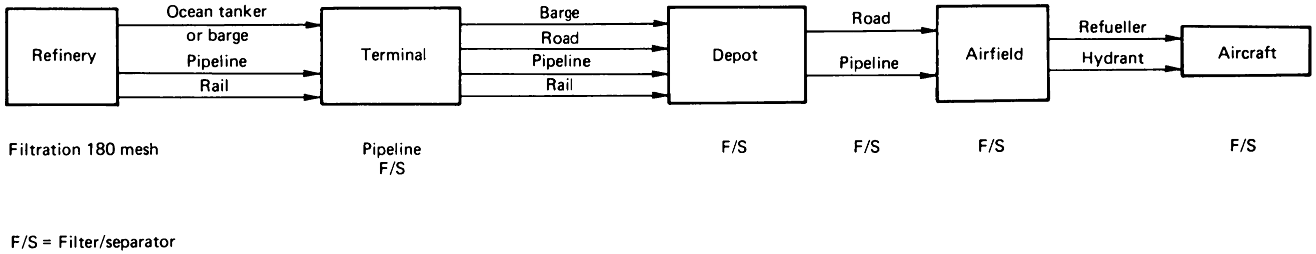


Figure 6.1 Schematic of distribution system

loading can commence and the product goes into all the ship's tanks due to receive this cargo. After each tank has been filled to a depth of about 60 cm, loading is stopped, a sample is taken from each tank and tests are done for density, distillation, freezing point, existent gum and, in the case of an avtur type fuel, flash point. For an avtur type fuel, the density and freezing point should be carried out on each tank, and if these match the shore tank, composite samples for the rest of the testing are used in order to save time. If there is any doubt, however, each tank's sample would be tested individually. If a mini-sonic separometer or micro-separometer is available, it is also advisable to check for WSIM at this stage, the object being to ensure that all the water had been drained off the ship's lines, and that these lines and the jetty loading arms did not contain any traces of previous cargo loaded onto the ship.

The tests chosen will rapidly identify contamination. If, for instance, there was some contamination with diesel fuel, the density, flash point and freezing point would all increase, as would the existent gum, because it is actually a 'residue on evaporation' test and the heavy end would not evaporate under the conditions of the test. The tests are carried out at this stage of the loading because the contaminants are most likely to enter at the commencement of loading, further addition of aviation fuel only serving to dilute the contamination.

If the cargo fails these initial loading tests, then it is usual to pump the cargo ashore, recheck the ship's tanks for cleanliness and start again. If the initial loading tests are passed, as is normal, loading is recommenced and continued until the full cargo is aboard. Once again, all the ship's tanks are sampled, this time from top, middle and bottom. All samples are tested for density to ensure that they match that of the shore tank, and that each tank is homogeneous. A composite is then made up of the whole ship's cargo, and short tested.

Before the ship sails, the Master will be given a batch certificate to identify the cargo, together with a test report certificate referring to the full test on the shore tank, and a final loading certificate, being the results of the short tests carried out on the 'ship's final' samples. Also, in the U.K., he will be given a release note, signed by the authorised inspector to the effect that the cargo was as stated on the various certificates. He will also be given sealed samples taken from the ship's tanks at the completion of the loading. These sealed samples will be handed over at the port of discharge.

On arrival at the terminal or discharge port, representatives of the receivers will take samples of the cargo from each tank and short test them to ensure that the specification is met. If they are satisfied that it is, they will authorise the discharge into their shore tankage. In the event of a dispute regarding quality, then the sealed samples taken at the time of loading may be broached and tested. If these differ from the ship's samples then any contamination now revealed must have happened during the sea voyage. For example, if the ship was carrying a mixed cargo and there was a valve fault, the cargos could intermix. As before, this sort of contamination would show up in the short tests. If the contamination of avtur, say, was with gasoline, then the flash point would drop, whereas with diesel fuel the freezing point would rise.

If the ship has been carrying a mixed cargo, the aviation fuel would be pumped into the terminal (shore) tank, and allowed to settle before being sampled from top, middle and bottom for full testing. If it had been a dedicated cargo, a short test would be acceptable. From this a new batch number would be issued, with a new test report certificate. The batch certificate would give the volume put into the tank together with its previous batch number plus the volume of the heel, that is, the quantity left in the tank before the arrival of the new product, and the new batch number. In this way the history of all the product can be checked in the event of any problem arising.

Shipment by barge would be treated in the same way as with ocean tankers, as already described. Rail car shipments are regarded as dedicated, but each rail car has to be tested on arrival, not just a representative sample of the whole train.

6.1.2 Pipeline

Many transfers are now made by pipeline, and from refinery to terminal most of these are in multi-product pipelines. In the case of aviation fuels, the major product is aviation turbine fuel. By controlling the pumping rate there is very little mixing of one product with another in spite of differences in density and viscosity. Hence the time in the pipe can be measured, and the interface location is known exactly. As well as the calculated time of arrival, most receiving stations have detectors that use density monitors. These will not only record the density of the product passing them but will react instantly to a change in density. So by both time calculation and density monitor, the arrival of the interface between two products is known at the terminal, and the tankage valves can be changed over with no loss of product. This can be done because the percentage contamination permissible in any product before it will fail specification has been determined, and from this the time to make the cut between the two products is known. The fuel is run into dedicated tankage and, when it has all arrived, the tank is sealed, as was the refinery tank, allowed to settle, drained of free water and the product then sampled for testing. Normally a full test would be required, resulting in a new batch certificate and test report. In specific cases where the operation has been proved over a period of 2 or 3 years, it may be possible for the product to be accepted from a short test and thermal stability measurement.

Movement from terminal to depot could again be by ship/barge, pipeline or rail/road car. The procedure is exactly the same as has been described above, with the issue of a new batch certificate and test report. Any other similar movements are treated in the same way.

6.1.3 Dedicated System

Consider next a movement from the depot to an airfield by dedicated pipeline into dedicated tankage. It is now worth while starting the final clean-up process by filtration, since filtration in depth has been shown to be not only the safest but also the most economic way of bringing the product to the correct standard.

The testing in depot tankage has shown the product to be 'on specification', and from now on the effort is concentrated on cleanliness. The product is first pumped through a micro-filter, using 1 or 5 micrometre porosity, to take out fine particulate matter, and then through a filter/separator.

After this filtration the product goes through the dedicated pipeline to the airfield where it will pass through another filter/separator and into tankage. It is allowed to settle in tankage, and the water drainage checks are carried out daily. Although very little free water should have been brought into the tanks, they are air-breathing and the dissolved water in the fuel will soon establish an equilibrium with the moisture from the humidity of the air. As the air humidity and the fuel temperature change, so the fuel may absorb water or release it from solution. In the latter case, it will coalesce into particulate droplets and settle to the bottom, sometimes by condensing on the tank walls. The floors of most aviation fuel tanks on airfield installations now slope some 3° down from the horizontal in order to 'cone down' to a central sump. Water impinging on this floor is then able to run into the sump, from the base of which an 18 mm draw-off line leads outside the tank wall to a valve and drain.

Since the fuel has arrived in this tank via a dedicated pipeline, further quality control tests are not necessary, but it is normal practice to check the conductivity. Static dissipator additives have a tendency to plate out onto the metal surfaces of pipelines and tanks. Once the system has been conditioned to these additives, and assuming that the pipeline length from the depot to the airfield is less than 25 km, the loss in the system will be small, and will have been allowed for at the time of injection. Nevertheless, it is worth while checking as the specification demands a conductivity level 'at the point and time and temperature of delivery to the purchaser', and the main reason for using the additive is to prevent any static discharge during loading.

The next movement of the fuel is to the aircraft, and this can be achieved via

(a) hydrant pipeline system, or
(b) refueller vehicle.

If method (a) is used, the fuel will be pumped from the airfield storage tank through a filter/separator and into the hydrant. Assuming that there is no flow in the hydrant, the pump will shut down as soon as design pressure is reached. On the airfield apron the aircraft will have been parked, conveniently close to hydrant valves set in small covered pits at suitable locations. A hydrant cart arrives on the scene, the valve pit cover is removed and the hydrant cart is electrically bonded to both the pit and the aircraft. The cart is then connected to the hydrant valve via a heavy-duty hose. Some airlines also insist on earthing the aircraft and refuelling equipment. Refuelling hoses are then connected from the hydrant cart to the aircraft fuelling manifold. On large jet aircraft the manifold is usually on the aircraft wing, and the nozzles are situated under the wing. When the aircraft's engineer is satisfied that the aircraft fuel system is ready, loading can commence. The fuel comes from the hydrant to the hydrant cart, where it passes through its final filter/separator, fuel meter and fuel pump onto the aircraft. As soon as the pressure drops in the hydrant system, the pumps at the airfield storage depot will restart to ensure that the hydrant is always full of fuel.

On a large airport installation such as London, Heathrow, or Paris, Charles de Gaulle, several aircraft will be refuelling from the hydrant simultaneously. In this case automatic controls ensure that there is always sufficient volume in the hydrant, bringing in extra pumps at the tank farm, as required, and shutting them down when they are no longer needed.

At the commencement of loading aviation turbine fuel to an aircraft, a free water check by a chemical detector should be carried out on the fuel actually being loaded. The fuel specification states that the maximum tolerable free water shall not exceed 30 ppm. This level is not visible to the naked eye, hence chemical detection methods are used. On the airport apron, use is made of go/no go testers of the type that are simple to operate and give a colour change if the permitted water level is exceeded. Typical of this type of detector are the Exxon Hydrokit and the Shell Detector. If water is found, a repeat test will be carried out immediately and, if this confirms the first reading of excess water, the loading will be stopped and not recommenced until the reasons for the presence of the water have been determined, and remedial action taken. At the end of loading, all valves must be closed and hoses disconnected before the bonding wires are removed.

If loading is by refueller, as in case (b), then this vehicle is filled from airport storage via a filter/separator. The refueller goes to the aircraft and the same procedures are used for the refueller as with the hydrant cart, except that the fuel is already being carried in the vehicle and so no connections are made to a hydrant.

6.2 Equipment Checks

On an airfield, the following routine checks are carried out on refuelling equipment. Daily, at the start of the morning shift, a visual water and sediment check is carried out by drawing off a 1 litre sample from all micro-filter and filter/separator drain valves. During pumping, a check must be made of the differential pressure across filtration equipment to ensure that the maximum limit is not exceeded. Monthly, a hose end check of the quality of the fuel on each refueller and hydrant cart is carried out using a millipore test kit. This may be either colorimetric or gravimetric, but quarterly the check must be gravimetric. This test passes a known volume of fuel, from a hose end, through a 0.8 micrometre membrane. Any rust or dirt particles will stain the membrane, and the intensity of this stain can be matched against numbered colour standards for the colorimetric test. For the gravimetric test, pre-weighed and tared membranes are used. The fuel is not acceptable if the ‘dirt’ level exceeds 1 mg/litre of fuel. On the major airfields in Europe, typical readings are less than 0.1 mg/litre.

If an accurate check on the free water in a fuelling system is required, particularly at the outlet from a filter/separator, then one such device that may be used is the Exxon Aqua-Glo. A filter pad, sensitised with a fluorescent type of chemical is put into a holder and a known volume of fuel from the line passed through it. The pad is then transferred to a reflectance type instrument which shines ultraviolet light onto the test pad and onto a standard. By adjusting the amount of light onto the sample, a nil point on a galvanometer is obtained, giving a direct reading of free water in ppm. The range of the instrument is from 0 to 60 ppm, but its most sensitive scale reads from 0 to 12 ppm free water. This is a portable hand-held device for use on an airfield or similar installation.

6.3 Filter/Separator

A filter/separator consists of filtration and stripping stages which carry out three functions when subjected to a flowing stream of fuel containing a water emulsion and/or dispersed particles. These are as follows,

(a) Filtration or solids removal.
(b) Coalescence of finely emulsified water droplets into larger droplets.
(c) Separation of the water droplets from the flowing stream of fuel by means of a hydrophobic barrier.

The first two functions are normally combined in a fibreglass element made by wrapping different layers of resin-treated fibreglass around a cylindrical cone on a metal screen or pleated paper, and covering the wrappings with a cotton sock. The third function is usually performed in a separate element consisting of a metal screen, cylindrically shaped and of specific pore size, which has been treated to make it hydrophobic.

The heart of the filter/separator operation is coalescence of dispersed water. The filtration of solids alone is a straightforward process, being a process of providing an in-depth barrier of fine passages to stop dirt particles if the same fibrous bed was not used also to coalesce water. Separation of the coalesced droplets alone is equally straightforward, being a process of providing a hydrophobic barrier of controlled pore size. The success of the system depends on good coalescence to produce water droplets larger than the pore diameter of the separator.

With a filter/separator, the differential pressure may be continuously measured but its ability to coalesce is not readily known. Upstream and downstream water tests with an Aqua-Glo provide a check, but a very efficient method of actually checking the activity of individual coalescer elements in a system is represented by a 'Single Element Tester' rig, popularly known as a 'Visi-Rig'. One such type is shown in figure 6.2A. The element is removed from the filter/separator and placed in an acrylic cylinder, the whole system then being filled with fuel. Fuel may be pumped through the element at the design flow rate and, with pressure gauges fitted at the inlet and outlet, the differential pressure recorded. Water at a controlled rate may be injected into the fuel flow and properly mixed before entering the element. Coalescence and bubble size may be observed as shown in figure 6.2B and, from downstream samples, the free water content determined.

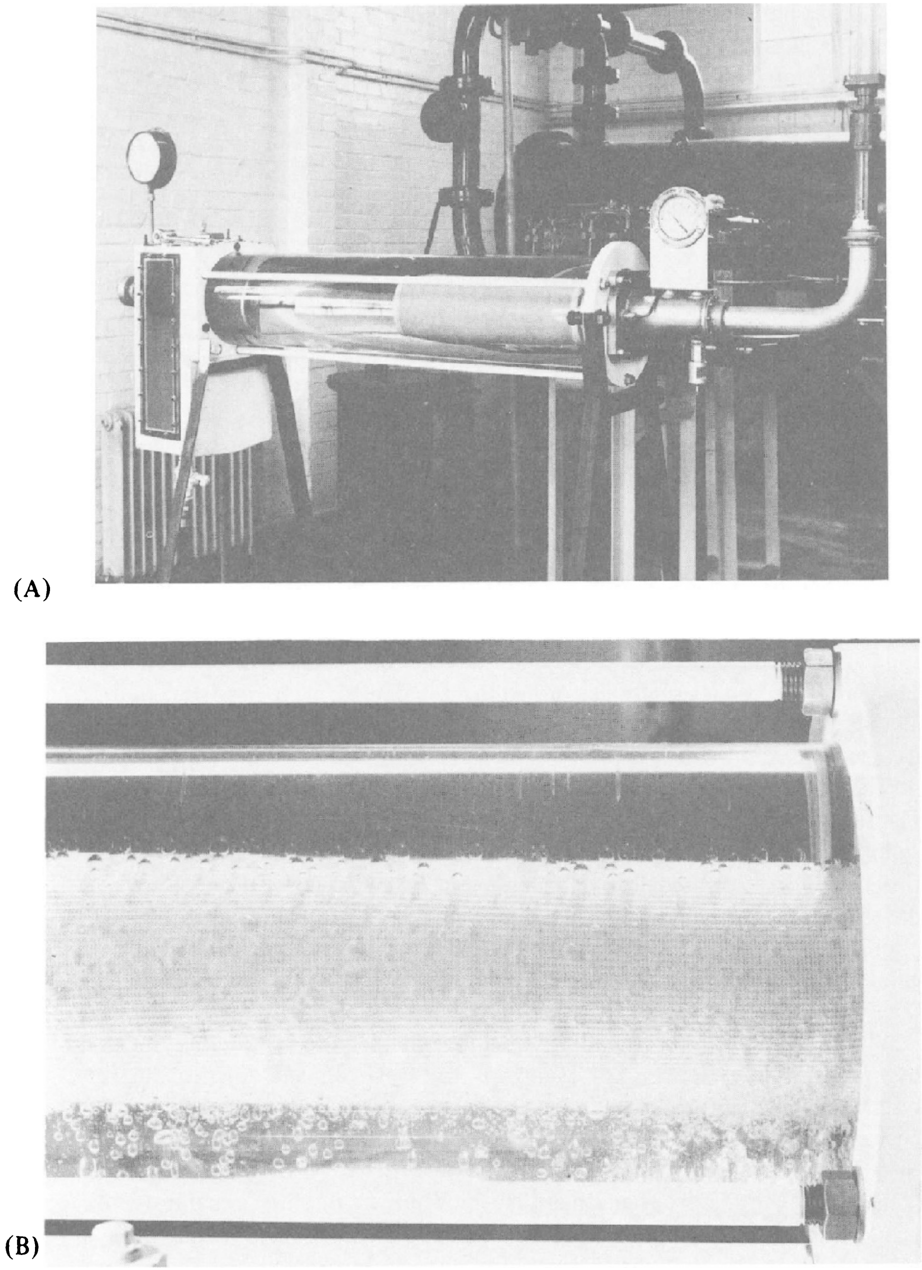


Figure 6.2 Single-element tester: (A) rig assembly; (B) coalescence and bubble size (both courtesy Alan Cobham Engineering Ltd)

In this way, it is possible to see not only if the element coalesces, but also how well it does so. Similarly, standard dirt samples may also be injected with or without water.

This is a good method for checking element efficiency, but ideally it should be carried out immediately after removing the element from the system, and at design flow rate. The former is often not possible and, if away from the main fuel supply fuel volumes, both flow rate and used fuel disposal can be problems. Also opinions are held by some that once an element is removed from a system it should not be replaced in it. The equipment shows whether or not the element is time-expired, and gives indications of the state of that particular system.

A small-scale test technique, based on an instrument known as a sidestream sensor, has been developed by Exxon Research and Engineering Company to assess the coalescence performance of a filter/separator. It is fitted in parallel with a filter/separator using standard sampling probes inserted into the centre portion of the line immediately upstream of the filter/separator, and returns the sample to the stream in the same manner below. Flow enters the sensor through the inlet probe, and the flow rate is controlled by means of a Rotameter. By setting this to maximum when the filter/separator is at a maximum, proportional flow will be maintained to the monitor for variations in the main stream flow. The monitor receives a portion of the fuel whenever flow is taking place, and so will reflect the history of the main filter/separator performance. Periodically the sensor holder, which contains a cross-section of the filter coalescer, is removed from the box and tested for remaining filter activity. A micro-separometer or mini-separometer is used for this testing (figure 6.3). A reference fuel containing a set amount of free water, emulsified in the standard way in either a micro- or mini-separometer, is passed through the sensor at 200 per cent of the rated flow capacity, and the effluent stream is then measured for relative turbidity. The more cloudy the effluent, the lower the remaining activity of the sensor. Because of the parameter symmetry between the sensor and the main elements, the activity of the main elements in the filter/separator can be extrapolated from the activity of the sensor. The sensor is then replaced in the system.

The sensor is designed to act as a guide to the quality of the effluent and so indicate the onset of deactivation of the element. This signals the need to change the elements in the main system to maintain downstream fuel quality. Once fully developed this equipment, together with the differential pressure gauge currently in use, should indicate the performance efficiency of the filter/separator. The elements would need to be changed only when either the sensor indicated deactivation, or the pressure drop had reached its maximum permitted level instead of the time or pressure drop as at present. At certain locations this could lead to extended element life, so reducing the cost of the operation. The sidestream sensor is currently under industry evaluation organised by the CRC in the U.S.A., and by the IP in Europe.

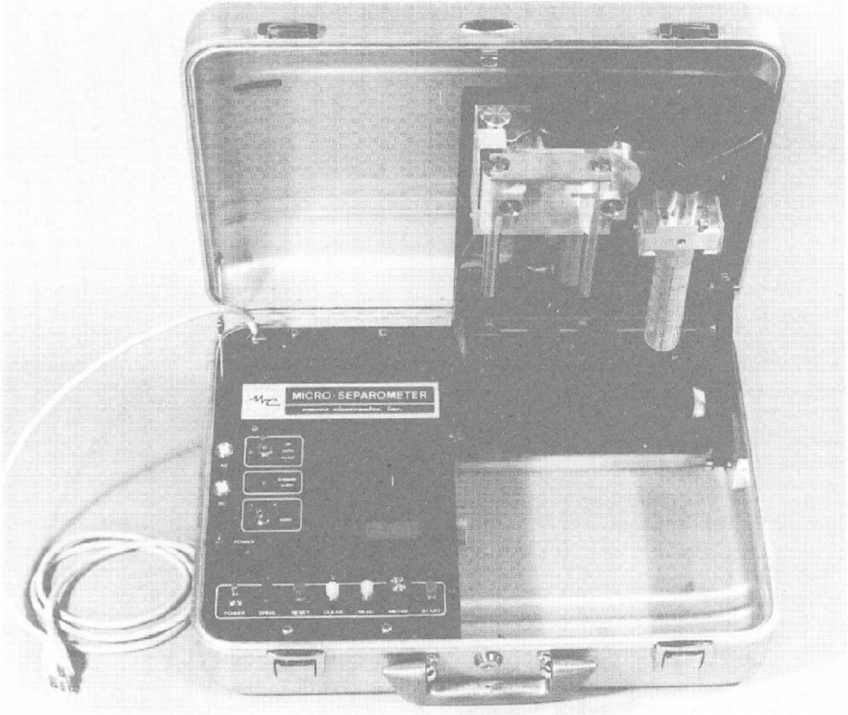


Figure 6.3 Micro-separometer (courtesy Emcee Electronics Inc.)

6.4 Microbial Activity

In the early 1960s, before the present very strict handling and cleanliness regulations were applied, there was a series of attacks of sulphide corrosion in aircraft fuel systems caused by the fuel. This was traced to slow moving storage tanks where the water bottoms had not been removed. This water lost its oxygen, and the system became infested with anaerobic bacteria known as sulphate reducing bacteria, or SRB. They lived in the water phase but took sulphur from the fuel. Unfortunately, the process emits hydrogen sulphide, H_2S, which goes into the fuel, so causing the sulphide corrosion. This problem was overcome by improving quality control and ensuring that water was kept out of tankage by daily water draining, and that any slime or scum at the interface was removed from the system.

It then became the turn of aerobic fungi to cause a problem, the most common of these being *Cladosporium Resinae Lindau de Vries*. These originated in the Middle and Far Eastern countries where typical storage tank temperatures are 35-40°C, which are ideal for fungal breeding. In fact, only 15-20 years ago it was stated that they did not exist in locations above 30° latitude North. With aircraft travelling larger distances around the world, these fungi not only travelled north, but quickly acclimatised themselves to the colder regions. Their rate of growth was slowed down, but they most certainly exist. In aircraft systems, they will cause very severe corrosion of the aluminium, and have been known to corrode holes through the wings, causing fuel to leak through. Attempts have been made to produce suitable fungicides that could be used in the fuel, but so far this has not been successful. Although effective as fungicides in the fuel, they always manage to fail some of the critical specification parameters.

Again, constant attention is essential to draining all the water off the tank bottom. Nowadays, many systems are sterilised with an alcohol after a tank clean. This does not cure the problem but partially inhibits the system and keeps the infestation under control. If it grows out of control, apart from the severe aluminium corrosion in aircraft wings, the fungus can block filters and filter/separators.

Many airlines use a periodic shock treatment in the aircraft fuel tanks in the form of a very active biocide, Biobor JF. This is added to the fuel when the aircraft is out of service for maintenance, at a concentration of 270 ppm, and ideally left for 3 days. This will kill all the bacteria and fungi, and sterilise the system. If this treatment is repeated on a 3-4 month cycle, the problem is kept under control.

Military aircraft use an anti-icing additive or fuel system icing inhibitor FSII, at a concentration of 0.10–0.15 volume per cent, in the fuel to prevent water freezing in the system and blocking fuel filters which, on these aircraft, are not heated. The additive used is ethylene glycol mono-methyl ether, EGME, or diethylene glycol mono-methyl ether, (di-EGME), in avcat and JP-5 because these are high flash fuels (60°C minimum), and the EGME will depress the flash point at this level and so make the product even more difficult to produce. The EGME or di-EGME acts by having a partition coefficient of some 300/1 water to oil and hence it gets into the water at a concentration of some 20 per cent by volume, so depressing the freezing point. At this concentration, it also acts as a biostat and inhibits the growth of bacteria and fungi. So although the FSII is added to prevent icing problems, as a bonus it keeps the system corrosion-free by inhibiting growth of bacteria and fungi.

6.5 Static Electricity

Owing to the high state of cleanliness and the chemical purity of aviation turbine fuels, a typical fuel has a conductivity of some 1-3 picosiemens/metre, pS/m, (now known as a conductivity unit, CU). For comparison, demineralised water has a conductivity of 10×10^6 CU, hence aviation turbine fuel has a very low conductivity. This property of a fuel affects the rate at which charged ions are removed from the fuel, a process known as charge relaxation. The time taken for the charge to fall from a given value to half that value (the half-value time, $t_{1/2}$) is an important factor and indicates whether static charges generated in the fuel are hazardous or not. In practical units

$$t_{\frac{1}{2}} = \frac{12}{\text{conductivity, CU}} \text{ seconds}$$

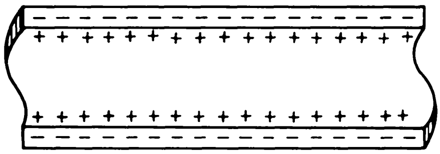
Typical values of $t_{1/2}$ are 12 seconds for aviation turbine fuel of 1 CU, and 48 microseconds for demineralised water of 10×10^6 CU. Charges can only accumulate to an appreciable extent if the relaxation time is high, that is, if $t_{1/2}$ is large.

The question arises as to the mechanism of charge formation. Consider a pipeline system where, with no flow, a charge transfer takes place across the fuel/pipeline interface, with the establishment of a double layer of charge. This is illustrated in figure 6.4A for the case where positive ions accumulate within the fuel, and negative ions (electrons) on the pipe wall. Under flow conditions, as shown in figure 6.4B, the positive charge in the flow is carried downstream, and the negative charge on the pipe wall is now free to flow harmlessly to earth. In a pipeline system, therefore, a continuous process of contact and separation of fuel occurs with the pipe wall, and there is a gradual build-up of charge in the fuel. Figure 6.4C shows how charge separation occurs on a filter. The micronic filters have very large surface areas exposed to the fuel and, since static generation is a surface phenomenon, high charge separation rates result. Flow through filters and filter/separators causes charge densities much higher than those obtained from flow through a pipe. At a sufficiently high level of potential gradient in the vapour-air mixture occupying the ullage space above the liquid surface, a spark discharge of incendiary strength will occur, initiating an explosion if the vapour-air mixture lies within the flammable range.

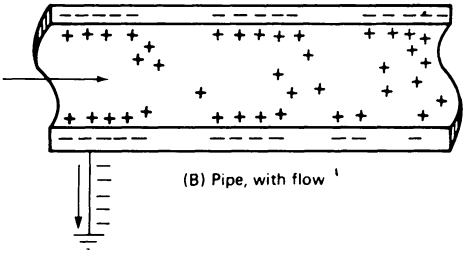
Because of the low conductivity of the fuel, charged particles take a considerable time to dissipate or relax. Increasing velocity will increase the charge in the fuel, and flow through a filter will by itself generate a considerable charge. Equivalent charges will be generated in the pipelines and filter elements but, as the equipment is usually made of metal that is electrically conducting, it will be earthed and so the charges tend to leak away to earth rather than accumulate on the equipment. In a fuel transfer system, it is most important that all parts of the system are adequately bonded electrically, that is, that all the parts are at the same potential, preferably with the system earthed.

The generation of static electrical charges in the handling of aviation turbine fuels has long been recognised as a potential hazard. A number of rules covering pumping rates, line velocities, bottom loading (no splash filling), and settling times have been generally adopted by the major oil companies as standard practice for the safe handling of these products. The success of these practices may be measured by the fact that there have been no reported incidents of fire or explosion that have been positively attributed to the generation of static electricity during the underwing refuelling of commercial jet aircraft.

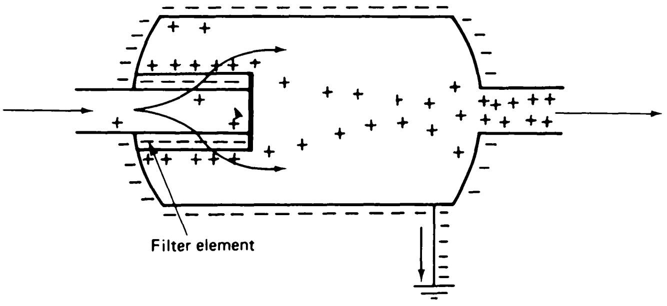
As an additional safety precaution, an anti-static additive, or more correctly a static dissipator additive, may be incorporated in aviation turbine fuels. The additive permitted for use in the DERD 2494 specification is known as ASA-3, and its concentration in the fuel is limited to 1 mg/l maximum. The conductivity limits at the point, time and temperature of delivery to the purchaser are



(A) Pipe, no flow



(B) Pipe, with flow



(C) Filter, with flow

Figure 6.4 Charge separation in flowing fuel

50–450 CU. The amount of additive required depends on the crude oil source from which the fuel was produced, since varying the detailed composition of the fuel affects the additive response. Another static dissipator additive, Stadis 450, has recently been approved for use in DERD 2494, but in this case its concentration in the fuel is limited to 3 mg/l maximum. With a static dissipator additive in the fuel, a typical conductivity value will be 100–150 CU. If the value is 100 CU, then $t_{1/2}$ will be 0.12 seconds. Although the greater conductivity will produce higher charge generation, the relaxation time will be very short, which greatly reduces the chance of a static discharge.

The conductivity of a fuel in a tank may be measured directly by portable meters manufactured by Maihak, or by Emcee Electronics Inc. The Maihak

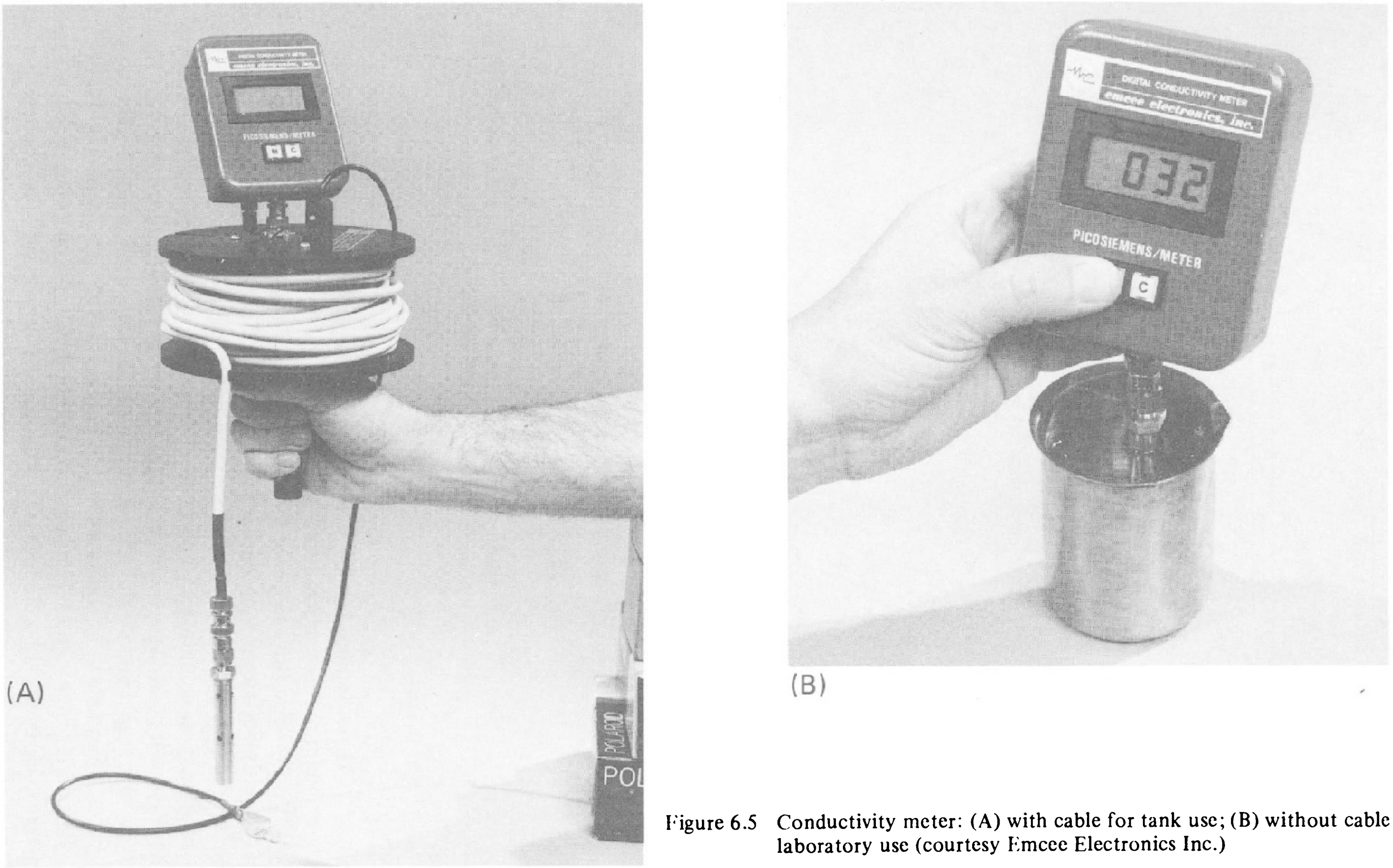


Figure 6.5 Conductivity meter: (A) with cable for tank use; (B) without cable for laboratory use (courtesy Emcee Electronics Inc.)

instrument has a conductivity cell on the end of a cable wound onto a drum. The cell is lowered on the end of the cable into the tank through the sampling hatch, and the direct reading meter is attached to the drum. With the Emcee instrument, which may be carried in the pocket, the conductivity cell may be attached directly to it, and the instrument put into the fuel in a sample container, or the cell attached to the end of a probe and inserted into the tank. In both cases, a direct reading may be taken from the instrument.

The latest Emcee conductivity meter is a digital read-out model, as shown in figure 6.5A. The figure shows the meter attached to a cable with the cell on the other end. By inserting the probe into the liquid in the tank, via a sample hatch, the conductivity may be read off directly on the digital meter at any desired level in the tank, or at a series of levels such as top, middle and bottom, to check for homogeneity with respect to conductivity. Note the earth/bonding wire which must always be attached to the tank before inserting the cell. Again, with this model the cable may be detached, and the cell fitted directly to the meter to give a laboratory model for determining the conductivity of a small sample in a beaker, as shown in figure 6.5B.

7 Fuel Characteristics within Aircraft Fuel Systems

The development of aircraft and aero engines has not been without its problems. Some of these have been overcome by design and engineering modifications, but others needed modification of the fuel, normally by tightening the specification and making it more restrictive.

The fundamental problem with aviation gasoline concerns its ability to resist spark knock. In the early days this not only had to be recognised, but also to be understood before means of measurement could be devised. This took many years to achieve. The ability to produce fuel to the quality required was, at that time, also difficult. Yet another problem was volatility to ensure that the fuel, as supplied, provided sufficient vapour to the engine at all times. With the aero piston engine, the development of the fuel specification so closely followed the engine development programme that it will be dealt with in chapter 9.

By the time the aero gas turbine engine appeared there was already a considerable knowledge of fuel specification requirements learnt from handling aviation gasoline. Also, the gas turbine seemed initially to be non fuel-critical, but this was not sustained. By 1951, however, only four years after the first main U.K. specifications had been published, there were meaningful specifications for both wide-cut and kerosine type fuels. As the engine developed, and this took place very rapidly, problems arose which were often overcome by adding another specification parameter.

7.1 Freezing Point

Kerosine type fuels used by most civil operators originally had a freezing point specification of −40°C maximum. With the introduction in the 1950s of the long-range transports flying at over 30 000 feet for several hours, concern was expressed that the then current specification might not be adequate. Fuel temperature surveys carried out by an IATA study group in 1956 showed that, with jet propelled aircraft flying in excess of 500 mi/h, minimum fuel temperatures were only −29°C but that, at lower speeds, this could fall to −40°C. However, it was claimed that for the slower turbopropeller-driven aircraft like the Britannia, the fuel temperatures would fall to −50°C on long haul operations. As a result of this, the U.S.A. and U.K. decided that, for civil operations, there should be a

–50°C freezing point kerosine type fuel. In the U.S.A., the ASTM Committee Tech. J on Aviation Fuels commenced writing commercial specifications in 1956, and published them in 1958 as ASTM D1655. Two kerosine grades were specified, Jet A (–40°C freezing point) for domestic use, and Jet A-1 (–50°C freezing point) for long-haul flights, plus a wide-cut fuel, Jet B, corresponding to the military JP-4 fuel. In the U.K., DERD 2494 was first published in 1957. This was equivalent to DERD 2482 but required a –50°C freezing point, which became the international standard low-temperature criterion for civil aircraft, and remained so until a change occurred in 1979, which will be discussed in chapter 10.

In countries large enough to have significant regional differences in climate, two types of fuel may need to be specified for the same type of aircraft and mission. In Canada, for example, the lower temperatures experienced in the north-west and in the western Arctic require the use of wide-cut fuel, whereas Jet A-1 is suitable for use in eastern Canada. In the northern regions where the ability to restart after landing in a remote location is essential for survival, wide-cut fuel is also preferred by most helicopter operators, whereas Jet A is likely to be found suitable in southern Canada during the summer.

7.2 Thermal Stability

It had always been recognised that aviation turbine fuel could be unstable in storage and, to control this, the specifications had included gum tests and unsaturates limitations, originally bromine number and then olefin content. It soon became obvious that these tests were not protecting hot fuel systems against nozzle deposits. Clogged nozzles distorted fuel spray patterns, leading to overheating, burnt out combustors and distorted turbines.

Major research by many companies looked into techniques to measure high-temperature oxidation reactions in aviation turbine fuel. The only candidate that protected engines in the field was a laboratory-scale heat-exchanger and filter called the Fuel Coker. This simulator was proposed by Pratt and Whitney, and co-operatively evaluated by the Co-ordinating Research Council (CRC). Although it was hoped that the only control parameter would be the pressure drop across the filter, so that a finite quantitative limit could be set easily, this was not to be. Early investigators observed that the pre-heater tube deposits related to heat-exchanger fouling in the aircraft fuel system. A scale of pre-heater tube deposit ratings was therefore set up and, when the resulting Thermal Stability test was incorporated into military specifications in 1957 (Mil-F-5624D), the procedure called for both pre-heater deposit ratings and filter pressure drop. The Fuel Coker test for thermal stability was soon incorporated into all major specifications.

Thermal stability of fuels remains the foremost fuel quality problem for the immediate future. Great advances have been made since the 1950s in understanding this phenomenon. An investigation into new and improved techniques to measure fuel stability was carried out in the early 1970s, and the Jet Fuel

Thermal Oxidation Tester (JFTOT) was produced as a result (see figure 7.1). This in many ways is a miniature fuel coker having fuel flowing over a heated tube and out via a filter. Once again, tube deposit ratings and pressure drop are the measurements called for. However, with better control, a much greater temperature range of operation is available, and accurate threshold temperature limits may be obtained. The threshold temperature, or breakpoint, is the temperature at which the fuel fails the test. Modifications have been made to the JFTOT to increase the severity of the heat treatment of the fuel, and various techniques are used to more accurately assess the deposit. These make the JFTOT a very useful research tool to assist in defining fuels for the future.

The JFTOT is mandatory in both U.K. and U.S. military specifications, whereas ASTM D 1655 specifies JFTOT but still allows the old Fuel Coker as an alternative method.

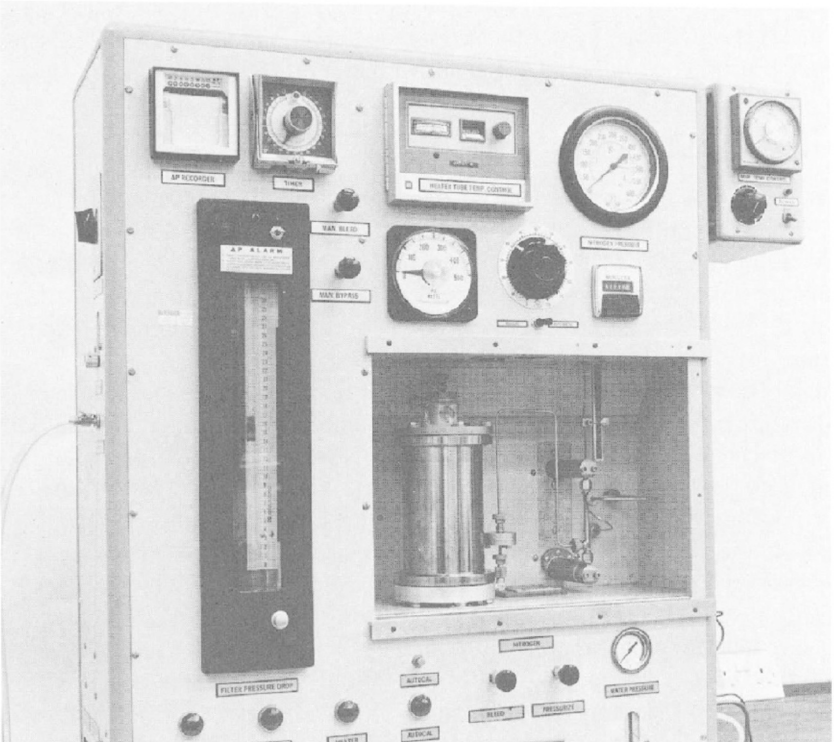


Figure 7.1 Standard JFTOT apparatus (courtesy Esso Petroleum Co. Ltd.)

7.3 Additives

From the early days of aviation turbine fuels, additives have been considered for inclusion to improve performance.

7.3.1 Anti-oxidants

The first additives to be used were anti-oxidants, and the first selection was taken from those successfully used in aviation gasoline. With the advent of hydrotreated fuels it was very soon discovered that this treatment tended to remove the natural oxidation inhibitors that were normally present in fuels. This in turn allowed the formation of peroxides and hydroperoxides in the fuel, and these could seriously affect diaphragms in fuel control systems. As a result of this, the addition of an anti-oxidant into all hydrotreated fuels became mandatory. Even after this, control diaphragm problems arose in the Far East where the fuel had been in storage at about 35°C for some 2 years and still contained some unused anti-oxidant. But, at that low level, it was discovered that it was not enough to inhibit peroxide/hydroperoxide formation. A U.K. industry group was set up to overcome the problem. Since no accurate control test could be applied in the field, it was decided to increase the anti-oxidant addition to the fuel. This has cured the problem.

Originally the anti-oxidants were of two basic types, the butyl phenol derivatives and the phenylenediamine type, both of which are effective. Complaints arose that the phenylenediamine type was reducing the life of synthetic rubber seals in the fuel systems, and adversely affecting the operation of filter separators, as well as presenting a potential health hazard during handling the additive. For these reasons, the phenylenediamine type of additives were withdrawn from aviation turbine fuel specifications.

7.3.2 Metal Deactivators

Metal deactivators (MDA) were used in those fuels that were sweetened by the copper sweetening process. From this process, trace quantities of copper may be carried over in the fuel from the reactor to tankage. The presence of copper in the fuel catalyses oxidation reactions, and the fuel will readily fail the thermal stability test. As little as 60 μg/kg of copper will be sufficient to fail the specification. Hence if a metal deactivator is added to the fuel, it will form a chelate with the copper and effectively passivate it. In the chelate form, copper will not promote oxidation. Clearly, the total amount of copper carried over must always be very small, and so the maximum amount of MDA allowed to be added to the fuel is limited to 5.7 mg/l. This figure originated from the old refinery measuring scale of 2 pounds per thousand barrels (PTB), and is an exact conversion.

Originally, the two compounds permitted for use as metal deactivators were

N,N′-disalicylidene,-1,2,-ethylenediamine
N,N′-disalicylidene,-1,2,-propanediamine

Unfortunately, the former came out of solution at the low temperatures encountered in high altitude flight, and deposited on the fuel system filters as a pink deposit. This became known as 'pink plague' and its cause was discovered only after an extensive investigation. The problem was overcome when this compound was withdrawn from service. The latter compound is still used when required, and is problem-free.

7.3.3 Compatibility

In recent years, as more additive types have been proposed for approval in aviation turbine fuels, each type comprising several compounds, an extensive system of additive evaluation has been set up, not only to prove the additive itself, but also to check on its compatibility with all other additives that could be present, and all fuel system components. This is a long and tedious task but, since it has been in operation, this sort of problem has not recurred.

7.4 Stiction

A problem occurred in 1962 and 1963 involving a piston type fuel pump on turboprop aircraft. When the engine was running all was normal, but on pre-flight propeller checks when turning by hand to inspect each blade, it was occasionally reported as 'tight to turn'. This could sometimes be freed by a sharp pull on the propeller, when there would be a cracking sound in the engine and the system would again be free. At other times this action would shear the quill shaft to the fuel pump, and put the engine out of action. An industry committee was set up to investigate the problem. The fuel was suspected of being a cause and, from the areas in which it occurred, the culprits seemed to be those fuels that were either hypochlorite or copper sweetened. The only common factor in fuel from these processes is that they contain chlorine, and this was considered to be the most likely cause. An Oil Industry committee of analysts developed a special set of test methods to measure the amounts of active chlorine in the fuel. These methods, described as 'SEB' (Shell, Esso, BP), determined the cold and hot hydrolysable chlorides and the hydrolysable acidity of the fuel. By setting control limits on these methods it was hoped to eliminate the problem, which had been called stiction. Despite all the fuel being within the defined control limits set, stictions were still occurring. A programme was started to determine the cause of stiction and hence formulate a cure.

A rig was constructed with the object of identifying fuel components or contaminants that would cause stiction in the pump. It consisted of a fuel pump cam-plate set horizontally with two silver-plated slipper pads rotating on it, and set vertically above it. Fuel cooled to −1°C to simulate flight conditions was circulated over the cam-plate and rotating slipper pads, and contaminants were added separately to the fuel as an aqueous solution and kept in suspension by stirring. At the end of a run the vessel, still full of fuel, was rapidly heated to 82°C to simulate heat soak on shut-down. Static torque measurements were taken at the beginning and end of each run, and after the heat soak and shut-down period.

Contaminants in the fuel were sodium chloride, hydrochloric acid, ferric chloride, ferrous chloride, ferrous sulphate and benzyl sulphonyl chloride. Only the ferrous chloride caused a stiction, and the conditions of the system were similar to those of pumps that had failed in service. If a metal deactivator is added to the fuel containing ferrous chloride at 3 ppm, no stiction occurs. As ferrous chloride can occur only in acid solution with a chloride present, tighter control on the sweetening processes was introduced by either caustic washing or extra water washing at the end, and the problem was overcome. An addition of 3 ppm MDA was made in some areas as an added precaution.

A further simultaneous investigation found that most fuel filters on the aircraft involved were of the felt type, and water retention was suspected. On another rig, tests were carried out using both paper and felt filters to see which had the greater water retention, and which could desorb it under operating conditions. As can be seen from table 7.1, the felt filter gives off a significant amount of water from a hot fuel, simulating the switching on of aircraft fuel heaters prior to landing, whereas the paper one does not. As a further precaution, as well as for improved fuel control, the use of felt filters was discontinued. As the SEB tests were not correlating with any field results, and as the action on fuel quality and fuel filters had been taken, the SEB tests were discontinued.

Table 7.1 Water desorbed from felt and paper type fuel filters, mean ppm

Fuel condition ex fuel heaters	Felt	Paper
Cold	2	1
Hot	18	3

7.5 Sulphide Corrosion

Initially the piston type fuel pump had silver flashing on the slipper pads, and there were three series of incidents of sulphide corrosion on these pads. In the first two series there was severe sulphide attack on the pads, but in the third there were in-flight shut-downs caused by the failure of the fuel pump. The first of these was in 1958, and was due principally to the presence of sulphate reducing bacteria in the water bottom of storage tanks, and to an inadequate control procedure. These incidents were prevented from recurring by removing the water from the bottom of aviation turbine fuel storage tanks, by making daily checks to see that no water had accumulated, and also by increasing the severity of the copper strip corrosion test.

In 1963 a second series of unexplained incidents occurred in Australia. As a result of this, Shell developed a silver strip corrosion test known as the 'CL-1' test to act as a monitor and hopefully indicate a control.

In 1965 Indian Airlines suffered very severe silver corrosion problems including three in-flight shut-downs. The fuel used had been produced in the Middle East, and fully met the then DERD 2494 specification. Testing by the CL-1 test gave it the worst rating of 4. A survey of Indian fuel storage showed that of 75 samples tested by the CL-1 test, 37 had zero ratings (satisfactory), and 38 had either 3 or 4 ratings (severe sulphiding). The Indian Government immediately imposed a CL-1 rating control of zero on all imports, and the U.K. Government was asked to include this test in the DERD 2494 specification. After some further research and correlation with the CL-1 test and the effect of the fuel on the sulphiding of the silver slippers, DERD 2494 imposed the CL-1 test, now known as the Silver Strip Corrosion Test, with a maximum rating of 1. This has certainly contained the problem. Since that time, however, because of this problem and another, pump modifications have been introduced to replace the silver slipper pads with carbon, and in many pumps the silver flashing on the port insert face has been replaced. Also, as new engines are equipped with gear pumps with no silver in them, the need to continue to have this control in the specification is questionable.

7.6 Lubricity

The major developments in fuel quality during the 1960s concentrated on fuel stability and cleanliness, which was an excellent move. New processes were brought in, especially hydrotreating, and these did indeed produce fuels of high thermal stability and, after filtration, a high degree of cleanliness. In so doing, however, these processes had removed traces of impurities which later transpired to be natural oxidation inhibitors and natural lubricants. The natural oxidation inhibitors could be, and were, replaced by anti-oxidant additives, but the fuel derives its lubrication from natural lubricants within itself, and at that time it was not realised that they were being removed.

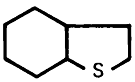
In 1968 problems arose in engine fuel systems, particularly in fuel pumps, which were thought to have been associated with deficiencies in the lubricity properties of the fuel. (The aviation industry appears to produce new words for new problems, for example 'stiction', and now 'lubricity'.) Lubricity is defined as follows: if two liquids have the same absolute viscosity but one gives lower wear, lower friction, or a lower tendency to scuff, then this will be considered to have better lubricity.

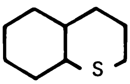
In fact the problem, not then recognised as such, first showed itself as sticking and hang-up of fuel control systems using JP-4 fuel produced to the Mil-T-5624G specification, but from 1968 it appeared in Europe as a problem of wear and seizure of fuel pumps with both kerosine (avtur/Jet A-1) and wide-cut (avtag/Jet B) type fuels.

A fundamental research programme to investigate the lubricity properties of high-temperature aviation turbine fuels was carried out in the U.S.A. by the then Esso Research and Engineering Company which showed that lubricity in fuel was dependent on the presence of trace polar compounds, most probably high molecular weight aromatics. Differences in the lubricity of fuels were generally related to the degree and type of refining to which they had been subjected. Any process, therefore, such as solvent extraction, absorptive percolation, clay treatment or catalytic hydrogenation, that will remove polar compounds will affect lubricity. It was also shown that the most likely wear mechanism is corrosive wear owing primarily to dissolved oxygen in the fuel, and accelerated by the presence of water. It would seem, therefore, that a polar compound that can form a film on rubbing surfaces would be a logical lubricity agent.

A complementary research programme was carried out in the U.K. at the Esso Research Centre specifically to investigate European fuels with regard to lubricity, and to find a means of overcoming a potential lubricity problem in fuels that were shown to be poor in this respect. Because of the high proportion of hydrotreated fuel used in Europe, the study restricted itself to a comparison of the performance of hydrotreated fuels with that of a typically chemically treated fuel. Although the early field problems in Europe had all arisen from using hydrotreated fuel, in 1970 several incidents of pump failure occurred where the fuels concerned were not hydrotreated, so this problem could not be solely related to this treatment.

A test rig was built using the metallurgy of a piston type pump which could rate fuels in an order of merit with respect to lubricity. Although designed to measure several parameters, it soon became evident that the most significant variable was wear. Using the rig, samples of European aviation turbine fuel were rated and put into an order, and this showed that hydrotreated fuels exhibited higher wear rates than the non-hydrotreated fuels. To establish whether wear rate was in fact a function of hydrotreating, an aviation turbine fuel distillate was taken and severely hydrotreated in a pilot scale reactor. This produced an experimental fuel with a much higher wear rate than any production fuel tested, indicating that hydrotreating could affect the lubricity of a fuel. A detailed analysis of the experimental fuel and a production copper sweetened fuel showed, by thin layer chromatography, that the production copper sweetened fuel contained a component that was entirely absent from the experimental fuel. This component was called 'Spot A', and analysis by mass spectrometer and infrared techniques identified it as essentially thiahydrindane and thiadecalin:





Samples of Spot A were added to the experimental fuel, and this significantly improved its lubricity. Spot A was also synthesised and added to the experimental fuel, with the same result. So it appears that, as well as the known polycyclic aromatic compounds, other highly polar compounds consisting of fully saturated heterocyclic compounds also act as active lubricity agents.

These heterocyclic compounds are not readily available and would be very expensive to produce commercially either by selective extraction from hydrocarbon streams or by synthesis. The questions arose as to whether an additive could be used, and whether there was one available that had been screened and cleared for use in aviation turbine fuel. Anti-oxidants were already used, but even massive doses had no effect on lubricity as measured by the rig. Similarly, no effect was seen with the metal-deactivator, anti-static or anti-icing additives. The corrosion inhibitor did, however, give a significant reduction in wear rate. It was also found that trace peroxide/hydroperoxide formation in a fuel improves lubricity. This, of course, cannot be allowed as it will adversely affect diaphragms in the control systems, and has to be prevented by using anti-oxidants. From the fuel viewpoint, therefore, lubricity may be improved if it contains polycyclic aromatics, specific heterocyclic compounds and/or corrosion inhibitor.

On the mechanical side, the problem may be overcome in the piston type pump by modifying it to the all-carbon standard. In this modification, the slipper pads are made of carbon, the piston bores have carbon sleeves and the port face also contains carbon. This gives the best protection because, as an aircraft flies around the world, the fuel quality with respect to lubricity cannot be accurately known.

A few years later, the lubricity effect of high wear rate was seen on gear pumps. These pumps would show excessive gear tooth wear plus bearing and spline wear. This could lead to severe vibration, misalignment and, at times, pump failure. Fuels with natural or added lubricity agent did not show this problem, and modification of the gear pump by changing its metallurgy would also cure it.

Any change or modification costs money. New engines are equipped with pumps to the improved standard, and so the problem affects a decreasing number of aircraft each year. Military fleets have tended to go for the additive solution as a precaution that avoids retrofitting aircraft, and also because they have direct control of their own fuel supplies. Since several airlines have now modified their pumps to the improved standard, this is under control and no longer represents a major problem.

7.7 Salt Water Corrosion

The ingestion of salt water into a gas turbine engine has always been considered a serious problem, because the sodium will cause very severe corrosion of the hot turbine blades. Many specifications for ground-based gas turbines used for pipeline pumping or power generation, often in isolated locations, stipulated that the sodium content of the fuel must not exceed 0.1 ppm. This is to ensure that trace water in the fuel is not contaminated from the salt often used as a drying agent in refineries. This has not generally been a problem for aviation turbine fuels with their strict quality control and ground handling procedures. A few years ago, however, a Boeing 747 coming in to land at London, Heathrow, had to shut down two engines because of salt water ingestion, although it had flown successfully from the Middle East without problem. An industry inquiry was held, and work carried out to assess how this could have occurred. Many fuel samples were tested at random from major uplift points, and this confirmed that the maximum solubility of salt in a kerosine type fuel is of the order of 0.06 ppm. Any massive salt ingestion, if from the fuel, must be from water contamination. As the water on board this particular aircraft was excessive, and contained significant quantities of salt, it was concluded that it was loaded on the aircraft by human error and not noticed. This incident has, however, tightened refuelling procedures, and extra attention is now paid to the routine water drain check at the completion of every refuelling.

7.8 Vapour and Air Release

The solubility of air in petroleum products is very low on a mass basis but, at normal temperatures and pressures, air can dissolve in light hydrocarbons, such as gasoline, up to some 25 per cent by volume; for kerosines of the aviation turbine fuel type the figure is about 12 per cent, and even some 7 per cent for heavy lubricating oils. These figures do not vary significantly for a wide variation in the composition and properties of the aviation fuels. The solubility is, however, closely related to the surface tension of the product, and normally both air solubility and surface tension decrease with a rise in temperature.

Air solubility obeys Henry's Law which states that the amount dissolved is proportional to its partial pressure in the vapour phase, that is, the difference between atmospheric pressure and fuel vapour pressure. In the case of aviation kerosine which has a very low vapour pressure, air solubility is approximately proportional to atmospheric pressure. This means that dissolved air will be evolved from the fuel as the aircraft climbs, but the amount released will be dependent on the degree of agitation of the fuel. Under quiescent conditions, for example, the fuel can be supersaturated, but under severe agitation there will be a violent release of air, causing foaming and frothing. In an extreme case, this could block the venting system and introduce vapour into the fuel line if these systems are inadequately designed.

Another point to be considered is that, because the solubility coefficient for oxygen is much greater than that for nitrogen, the gaseous mixture evolved from the fuel becomes richer in oxygen as the atmospheric pressure falls. Assuming that the vapour space above the fuel in the tank consists entirely of a mixture of fuel vapour and the gases released from the fuel, the altitude temperature conditions which give explosive mixtures will be altered from those of vapour-air mixtures at normal temperatures and pressures.

Air released from the fuel is saturated with fuel vapour, and this involves loss of fuel. When the total pressure in the tank falls to the vapour pressure of the fuel at the prevailing temperature, the fuel boils and is lost as vapour.

In the case of gasolines, because of their high levels of vapour pressure, the main problems are fuel losses, since air release problems are insignificant. The reverse is the case for subsonic operations with aviation turbine fuels. As an example, an aviation turbine fuel at sea level (101 kPa) would contain some 11.5 to 12 per cent by volume of dissolved air. At 10 000 m altitude the equilibrium concentration of air in the fuel would be down to 3.0 per cent, and the atmospheric pressure 26.7 kPa. In considering a fuel load of 90 000 l in equilibrium at sea level with 11.5 per cent by volume of air, then in equilibrium at 10 000 m, 8.5 per cent by volume of air would be expelled from the fuel, taking fuel vapour with it. This is some 7700 l of air, with saturated fuel vapour entrained. This sort of problem has to be taken into account in the design of the aircraft's fuel tanks and venting systems.

With supersonic aircraft such as Concorde, the fuel in the wing tanks absorbs a significant amount of heat from the skin friction of the air over the wing surface, and at the end of the flight the fuel temperature could reach 80-85°C. (A subsonic aircraft cruising at Mach 0.6 will experience a temperature rise of about 25°C from skin friction but, as the air temperature at cruise altitude is around - 65°C, this is an aid and not a potential problem.) At the cruising altitude of 19 500 m, the atmospheric pressure is only 7 kPa, and it was feared that under those conditions the fuel would boil. For this reason, the original design had wing tanks pressurised to 15 kPa. Fuel surveys carried out in 1967 showed that the vapour pressure of most fuels then available would not exceed 6 kPa at 80°C. As extreme agitation was unlikely, the decision was taken to use tanks vented to the atmosphere with a well-designed vent system. This has proved most effective, and no problems have been encountered.

7.9 Fire Safety

In order to improve the fire hazard and safety aspects of aviation turbine fuels, efforts have been made to produce a safety fuel, that is one that will not easily or readily ignite except in the engine combustor.

7.9.1 Gelled Fuels

One such type of safety fuel was the gelled fuel made by mixing JP-4 with emulsifying agents. The most successful example of this type contained 98 per cent JP-4 and produced a stable gel or jelly-like substance that would not ignite in a gunfire test. The test was to fire an incendiary round through the barrel of the sample without causing ignition. The other criterion was that the shear force energy in the aircraft engine fuel pump should be sufficient to break down the emulsion and so produce the original JP-4 fuel into the combustor. The big problem, however, was how to transfer the fuel from the tank to the pump prior to the fuel being degraded back to its normal state. Pumping was not possible, and a gravity feed not practicable, although a hopper type design for a helicopter was considered.

This type of fuel based on JP-4 was, of course, designed for military purposes, especially for helicopters. Since these aircraft fly low and relatively slowly, they are vulnerable to destruction by incendiary gunfire. On large helicopters, the landing wheels are replaced by pontoons which are used as the fuel tanks, and are thus even more vulnerable to ground fire. The gelled fuel was designed specifically for this situation.

Although the fuel proved to be gunfire proof, and could be broken down to the original fuel in the pump, it was not possible to transfer it to the engine system in flight, and so it was never used in service.

7.9.2 Anti-Misting Fuel

More recently there has been a lot of interest shown in the use of an anti-misting additive which can be added to a kerosine type fuel. The possibility that this would reduce the risk of, and perhaps prevent, a post-crash fire is of great interest to civil airline operators. This additive is a polymer of very high molar mass which, when mixed with kerosine, has the effect of preventing mist formation at high rates of shear.

In a crash or heavy landing, the main fuel tanks within the wing are likely to rupture, with the fuel being thrown forward owing to its momentum. A normal kerosine fuel would experience a high rate of shear and be carried forward as a series of very tiny droplets in the form of a mist. Fuel is much more easily ignited as a mist than as bulk liquid, and the mist will ignite if it passes any source of ignition such as the hot engine. Also, the flame propagation rate in the mist is much greater than in the bulk, and so the mist will rapidly form a large fire ball which will flash back to the main fuel and ignite it, forming a large conflagration.

With a kerosine fuel containing an anti-misting additive at 0.4 per cent concentration, however, the fuel is thrown forward in large droplets, as the shear forces are insufficient to generate a mist. These droplets may catch fire at their edges but do not have sufficient energy to burn completely, and hence there is no flame propagation back to the bulk fuel located in the wing tanks.

Safety demonstrations on ground test tracks, comparing normal kerosine fuel with a fuel containing an anti-misting additive, show the effectiveness of this additive. As with other safety fuels, however, there are problems. In this case, one problem is that the additive must be introduced at the time of refuelling, and it then requires 20 minutes before it becomes effective. This creates a very serious problem with ground handling and monitoring equipment, as well as the delay time involved. If the aircraft with a full load of fuel takes off too soon and crashes, it is essential that the fuel has full anti-misting properties. Furthermore, the major problem is the need to 'degrade' the fuel back to its normal state for combustion. The rate of shear of the aircraft engine fuel pump is not sufficient to break down the high molar mass polymer, and the fuel entering the combustion chamber will not atomise and burn effectively. Various high-energy systems, including ultrasonics, have been tried to break down the polymer sufficiently for normal combustion. A multi-stage high-shear pump type degrader is now being produced in the U.S.A., and it is proposed to fly and crash an aircraft, by remote control, fuelled with AMK fuel. There is still much testing to be done on the effectiveness of the degrader in sustained flight, and indeed on the effect of the AMK additive on a long duration flight at very low temperatures and high altitude.

Once again, a fuel can be produced that has excellent safety properties, this time to prevent a serious fire developing quickly from the fuel in a crash situation and so giving the passengers more time to escape from the wreckage. Once again, however, having given it these 'safety' properties it loses its prime property of combustion in the engine. The fuel can be pumped to the engine, but efficient combustion is not possible without an effective degrader. In the gelled JP-4 case, it was not possible to transfer the fuel from the tanks to the engine. If it had been possible, then the energy of the fuel pumps would have produced sufficient shear force to restore the fuel to its normal condition for combustion.

The anti-misting concept for a fuel in a civil airliner is a very valuable contribution to aircraft safety and, if the problems now being encountered could be overcome, this would be a significant step forward in safety. At present, however, a safe solution is not known, and whether it can be achieved or not lies in the future. Even if it can be solved technically, it is questionable whether the high cost of aircraft modification in fitting degraders, and the very high cost of refuelling dispensers together with the extra cost of the fuel, are justifiable on a secondary safety measure. The money may be more effectively spent on primary safety measures such as improving ground proximity warning systems!

7.9.3 Reticulated Foam

Another approach to reducing the fire hazard, in this case for military combat aircraft, is the use of a reticulated foam. The aircraft fuel tanks, usually within the wings, are filled with a plastic honeycomb-like material similar to a rigid plastic sponge. On first sight, these foams appear nearly solid but, in fact, occupy only some 3-4 per cent of the available fuel space, the remainder being very fine pores. The fuel enters these pores and drains down to the bottom of the tank where it can be collected and pumped into the aircraft fuel system. Gunfire strike on the wing, especially of an incendiary nature, will penetrate the wing surface but not meet a mass of fuel nor cause a flow of fuel through the hole, as in a normal tank configuration. The chances of a fire are thus very much reduced. This approach is of particular value when a wide-cut JP-4 type fuel is used.

The system was successful in its fire prevention, but was not without problems. During high-speed refuelling, the fuel entering the tank could compress some foams, forcing a gap between the inlet and the foam which was not restored at the end of loading. When air entered this gap, as occurred in some systems, the conditions for an electrostatic explosion were created. Fuel travelling at high velocity from a filter or filter/separator will be highly charged, and if this sparks across the air gap an explosion will occur. The foam is now strengthened so that the gap does not occur, and is also made semi-conducting in order to prevent a build-up of charge.

7.10 Bibliography

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8 Fuel Combustion Performance

The overall process of combustion of fuel for the generation of power by an open-circuit heat engine comprises the metering of the fuel to the combustion chambers, the preparation of the fuel-oxidant mixture, initiation of ignition, propagation and/or stabilisation of the flame, and subsequent emission of the products. The devices or complete systems used for engine fuel metering represent a separate study, and are covered elsewhere. The remaining topics are determined largely by the type of engine and combustion adopted, and are outlined individually in the following sections.

8.1 Mixture Preparation

In general, fuels burn only in the gaseous or vapour phase, in conjunction with a gaseous oxidant, usually atmospheric oxygen, and thus liquid fuels require prior vaporisation. If the volatility of the fuel is comparable to that of a petroleum-derived gasoline, vaporisation in atmospheric air is so rapid that rudimentary droplet formation only, as in a carburettor, is generally adequate to provide a combustible mixture. The key fuel parameter therefore comprises volatility and, of the three standard laboratory methods of test (distillation, vapour pressure and flash point), the shape and level of the distillation curve provide the most comprehensive indication of vaporisation tendencies over a range of temperature. The distillation curve of a typical aviation gasoline is shown in the upper part of figure 8.1, and particular distillation temperatures can be cross-related to service experience, as discussed in section 9.1. Broadly, the low-temperature recovery limits control starting, warm-up, ice formation and vapour lock, whereas the high-temperature recovery limits control the proportion of heavy fractions which can give rise to maldistribution of mixture within the induction manifold. This problem arises because of the inertia of the unvaporised droplets travelling either in the main stream or along the walls of the manifold, and leads to weak mixtures in some cylinders, which consequently run hot and so knock, and also to rich mixtures in others, which contain excessive concentrations of anti-knock additive. Setting a maximum on the end point also prevents the lubricating oil from being washed from the cylinder walls, and diluted in the crankcase.

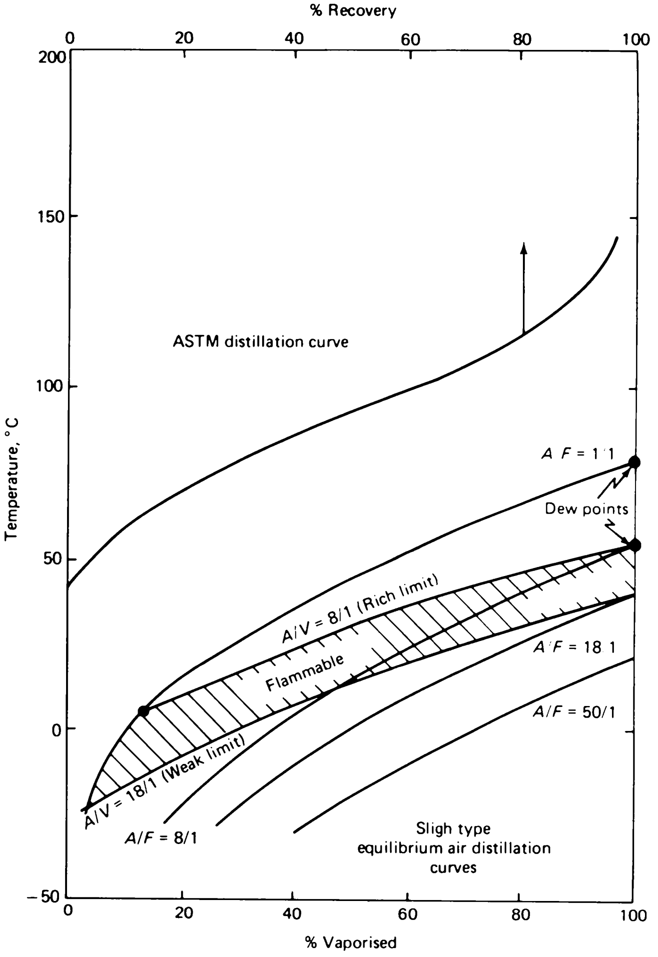


Figure 8.1 Representative ASTM and equilibrium air distillation curves for an aviation gasoline

Although distillation data can be correlated generally with engine performance, as outlined above, the test takes place in the absence of air, which becomes displaced from the flask soon after vaporisation commences, giving an air/fuel ratio of zero. A more fundamental test simulates the behaviour of fuel in an engine inlet manifold by permitting the fuel to vaporise to a condition of equilibrium in a stream of air at constant temperature. This is described as equilibrium air distillation (EAD), and the apparatus is shown schematically in figure 8.2. Measurement of the air and fuel flow rates, and of the unvaporised liquid at the outlet of the apparatus at the end of the test time period, permits the construction of an EAD curve on the basis of temperature *versus* per cent volume

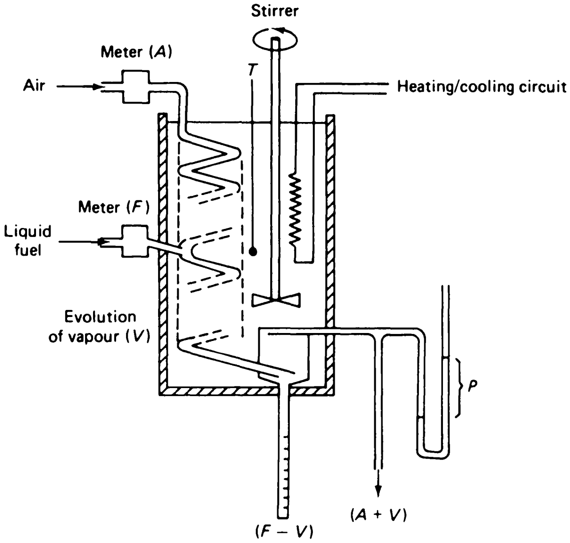


Figure 8.2 Sligh type equilibrium air distillation apparatus

vaporised for the given air/fuel mass ratio supplied. This is related to the ASTM distillation curve, and lies underneath it. A whole family of such curves can be constructed, with values of air/fuel mass ratio varying from zero for the ASTM curve to 50 or more at lower temperatures, as indicated in the lower part of figure 8.1. The temperatures where these curves reach the 100 per cent vaporised ordinate are the dew points for the corresponding mixtures.

Curves can be superimposed on the EAD curves for different air/fuel mass ratio to interconnect points of equal *air/vapour* mass ratio, as follows

$$\text{Per cent vaporised} = 100\left(\frac{\text{vapour mass}}{\text{fuel mass}}\right) = 100\left(\frac{V}{F}\right) = 100\left(\frac{V}{A}\,\frac{A}{F}\right)$$

$$= 100\left(\frac{A/F}{A/V}\right)$$

For example, at $A/F = 1$, it follows that $A/V = 8$ when

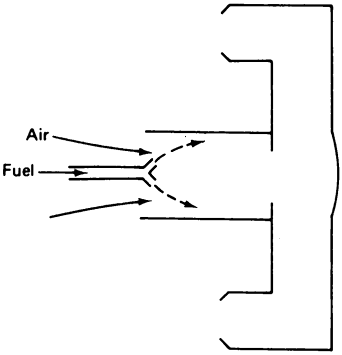
$$\text{Per cent vaporised} = 100\left(\frac{1}{8}\right) = 12.5$$

Curves for air/vapour mass ratios of 8 and 18 have been superimposed on the EAD curves in figure 8.1 since these represent approximately the rich and weak limits of flammability, respectively, for a gasoline. The shaded area in the figure therefore represents the naturally flammable region for the fuel in an air manifold at atmospheric pressure.

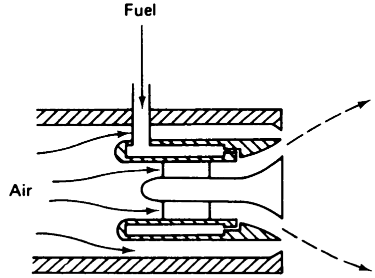
In contrast to the above, the low volatility of the kerosine type fuels used for aero gas-turbine engines is such that carburation, even in moderately heated air, would be too slow for a satisfactory rate of vapour generation. Vaporisation at flame temperature is suitable, however, and the 'walking stick' type of vaporiser tube receives narrow streams of liquid fuel under relatively low pressure, and converts them to vapour within the flame zone of the combustion chamber (figure 8.3). The key property requirement of the fuel is that it should vaporise cleanly without deposition of contaminants or of its own carbon through chemical cracking at the high temperature.

In all other applications to gas-turbine engines, the volatility of the fuel is increased substantially to an effective level roughly equivalent to that of a gasoline by spraying into a large number of very small droplets. This process, loosely termed 'atomisation', gives a massive increase in surface area per unit mass of fuel, and so augments the vaporisation rate by several orders of magnitude. The fuel is also distributed in space such that mixing with air is effected rapidly.

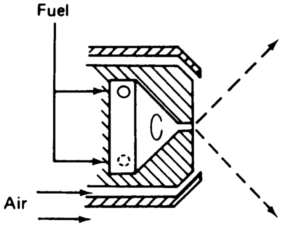
This subdivision of a film of fuel into filaments and droplets is achieved by the shearing action arising from the velocity difference between the fuel film and air. In pressure-jet spraying, the fuel is forced tangentially into a swirl chamber so that it tapers to the orifice and leaves in the form of a rapidly expanding thin



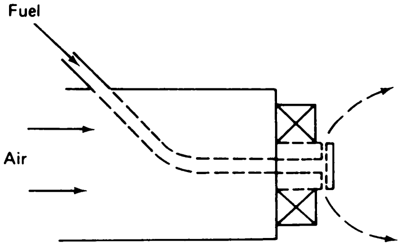
(a) T-type vaporiser



(c) Air-blast atomiser–pre-filming



(b) Pressure-jet atomiser



(d) Air-blast atomiser–plain jet

Figure 8.3 Representative types of fuel vaporiser and atomiser conical sheet. In pre-filming air-blast spraying, on the other hand, the fuel film is established on a solid surface in the vicinity of a rapidly moving air stream. Research is also under way into a simplified system of multiple fuel jets feeding perpendicularly into the air stream.

To a major extent, the size distribution, mean diameter and penetration of the droplets are determined by the design of the injector, fuel pressure and related air geometry, but fuel properties are also significant. Although fuel density alone has little effect on spray formation, viscosity has a direct effect on droplet diameter since it damps out the turbulence induced by the shearing action of the air. Similarly, fuel surface tension has a direct effect on droplet diameter since it resists disintegration although, for the gas turbine fuels, this property varies only slightly between 23 and 26 mN/m.

8.2 Fuel Combustion in Piston Engines

Under normal operating conditions in the spark-ignition engine, a nucleus of burning gases forms rapidly after the igniting spark, and the flame moves radially outwards through the combustion chamber owing to the transfer of both heat and free radicals to each successive layer of unburnt gas until all the mixture is consumed. In consequence, the pressure throughout the combustion chamber rises, owing mainly to the heat release and partly to the increase in the number of gaseous molecules. This pressure rise in turn promotes a rise in temperature of the unburnt gases, but they are consumed by the advancing flame before they can react independently to any significant degree.

However, when conditions are severe, or the gasoline quality is unsuitable, the unconsumed end gases may become sufficiently stressed for a length of time equivalent to their delay period, so that spontaneous ignition of all the unburnt charge occurs before the main flame arrives. This explosive form of combustion is termed *spark knock*, and is most likely to be a high-pressure spontaneous ignition occurring near the end of the combustion period. This phenomenon has also been attributed to such other mechanisms as detonation, involving the propagation of mutually supporting flame-and-shock waves, and also reactions at surfaces of finely divided particles of carbon derived from pyrolysis of the fuel or lubricating oil. However, most evidence appears to support the spontaneous-ignition theory, as represented by the curves in figure 8.4. The upper curves show the variation in minimum spontaneous-ignition temperature (SIT) for a number of individual members of the main hydrocarbon series, as measured by the standard technique of introducing small fuel samples into a heated flask at progressively reducing temperatures, and recording the related ignition delays[2]. The lower curves show corresponding results for the knock-limited compression ratio in a single-cylinder test engine. It is true that the conditions in the flask test relate to atmospheric pressure and therefore have extended delays of several seconds, in contrast to the high pressures and millisecond delays in the engine.

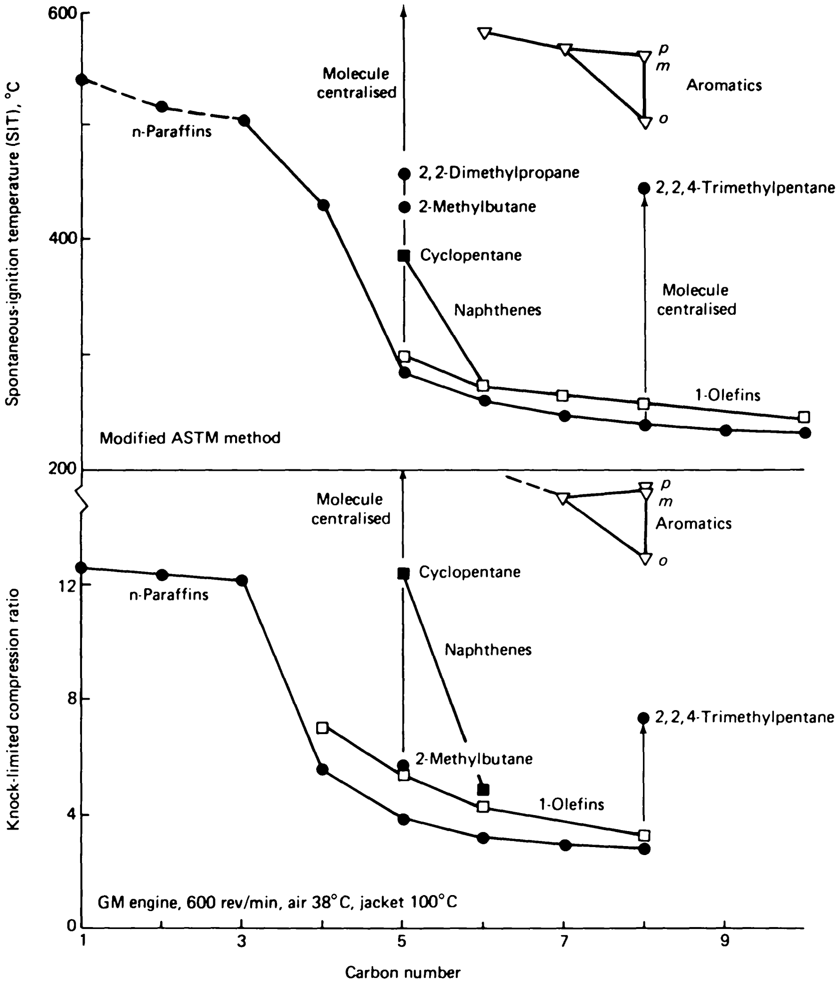


Figure 8.4 Variation of spontaneous-ignition temperature and knock-limited compression ratio with hydrocarbon type (refs 1, 2 and 3)

Nevertheless, the similarity of the three major conclusions is striking, since both SIT and knock-limited compression ratio

(a) reduce generally with increase in molecular carbon number
(b) increase with molecular compactness owing to cyclisation or isomerisation, and
(c) are relatively high for the aromatics and isoparaffins.

Spark knock is promoted by severity in any operating variable that tends to raise the combustion pressure and temperature, or increase the time available for end-gas reactions. It is therefore induced by such engine factors as high inlet manifold (boost) pressure, high compression ratio, excess spark advance, and low engine speed, together with the use of a fuel of inadequate anti-knock quality. It can also result from weak mixture operation which lowers the velocity of flame propagation and with it the conversion of heat to mechanical work. Part of the additional unused heat is retained in the cylinder walls, causing the engine to run hotter and so be more prone to spark knock. With extensive fuel weakening, the flame speed becomes so low that flame is still present when the inlet valve opens for the next admission, leading to blow-back into the inlet manifold.

Spark knock is characterised by violent vibrations of the combustion gases (figure 8.5), with sympathetic vibration of the engine structure causing a sharp metallic noise, and also hot running due to the sudden release of energy. In general, light knock at low speed during acceleration has no adverse effects on an engine of rugged construction. However, sustained heavy knock at high speed can lead to piston-crown erosion, piston seizure and, eventually, piercing of the piston-crown owing to the initial gas vibration, which may reach a pressure level about twice that of the normal peak.

The anti-knock quality of a gasoline is controlled by the blending of such components as *iso*paraffins and aromatics with inherently high resistance to spontaneous ignition, together with the addition of an anti-knock agent such as

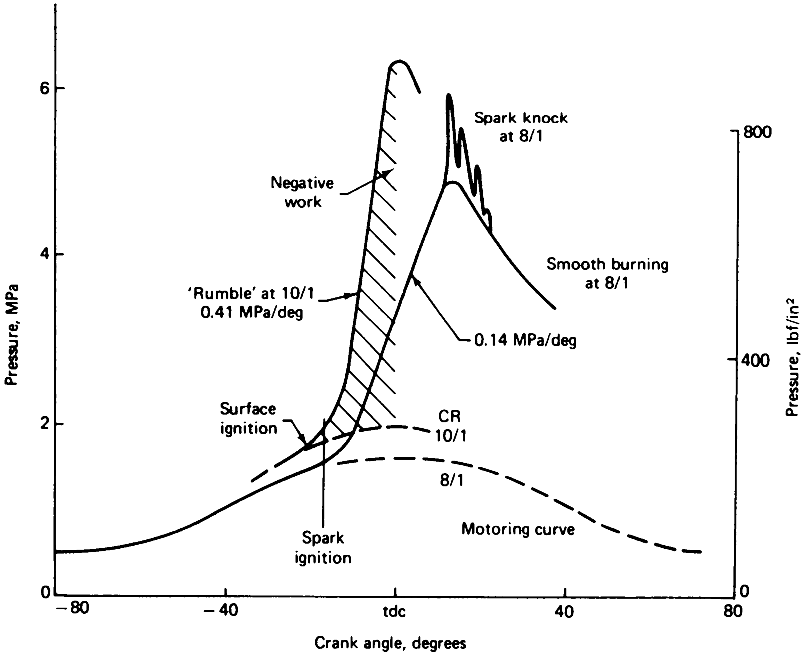


Figure 8.5 Pressure traces for normal and abnormal combustion in spark-ignition piston engine (ref. 4)

lead. The likely anti-knock mechanism of lead lies in its ability to oxidise to PbO_2 during early stages of combustion, and to absorb the excess energy of potentially reactive fuel molecules within the end gas, pending the arrival of the main flame. Although the PbO_2 molecule may be dissociated to PbO in the process, its rapid re-oxidation to PbO_2 implies a capability for the lead atom to inhibit spontaneous ignition repeatedly by recycling with oxygen. In order to ensure adequate lead scavenging during the exhaust stroke, compounds of bromine are included in the lead fluid additive.

One other ignition problem, which can arise under adverse operating conditions, lack of cleanliness in the combustion chamber or inadequate fuel quality, is the uncontrolled ignition of the main charge by the presence of a glowing surface within the chamber. Engine cooling and material selection are such that metallic surfaces are unlikely to reach glow levels of temperature, but combustion deposits build up with time, and the presence of anti-knock additives can depress the glow temperature of the deposited carbon (table 8.1). Since a portion of the charge is caused to burn before it would otherwise have been consumed by the advancing spark-ignited flame, this phenomenon is commonly termed *pre-ignition*. The overall effect is that of an over-advanced spark timing, producing more pressure rise prior to outer dead centre. This in turn tends to stop the engine but, since the piston is forced to continue operating by the action of the other pistons linked to it, a serious self-inducing runaway condition can arise with the generation of a great deal of heat, causing roughness, noise and an occasional spark knock and leading eventually to battered valve springs and melting of the valve heads and piston-crown. Furthermore, an erratic *running-on* or *after-firing* can occur when the electrical ignition is switched off and, since this is liable to reverse the engine rotation suddenly, it is particularly undesirable with engines having a high-speed gear-driven supercharger. For this reason, aero piston engines are shut down by means of a slow-running cut-out to cancel all fuel to

Table 8.1 Approximate glow temperatures of combustion chamber deposits (average values from several sources)

Additives	Deposits	Glow temp. (°C)
Nil	Carbon, C	550
Lead and scavenger	Carbon + lead monoxide, PbO	300
	Carbon + lead dibromide, $PbBr_2$	200
	Carbon + lead oxybromide, $2PbO.PbBr_2$	230
Lead and scavenger + phosphorus	Carbon + trilead diorthophosphate, $Pb_3(PO_4)_2$	460
	Carbon + lead bromophosphate, $3Pb_3(PO_4)_2.PbBr_2$	350
Lead and scavenger + boron	Carbon + lead borate, $PbO.B_2O_3$	340

the cylinders, rather than relying entirely on the switching off of electrical ignition.

Whereas spark knock appears as a gas-phase spontaneous ignition near the end of the combustion process, and thus at a high pressure level, pre-ignition is a forced ignition at low pressure, and is also dependent on the combustion temperature of the previous charges that caused the deposits to glow. Consequently, fuels do not necessarily exhibit comparable resistance to these two phenomena. Thus, although *iso*paraffins resist pre-ignition as well as spark knock, the hot-burning aromatics do not[4]. The problem can be solved largely by restricting the extent of deposition, and also by raising the glow temperature of those deposits that do eventually accumulate. This is achieved by the use of a phosphorus additive, as shown in table 8.1. As a useful side effect, the phosphorus compounds increase the electrical resistivity of the deposits, which restricts misfire due to electrical leakage from the sparking plug electrodes, and consequent fouling of the cold plug.

Clearly such inorganic materials as lead, bromine, chlorine and phosphorus cannot be dissolved directly in a hydrocarbon fluid such as gasoline, however they can be accepted by surrounding each atom of material with hydrocarbon radicals to present an organic molecular exterior to the bulk fuel. In consequence, lead is introduced as tetraethyl lead, $Pb(C_2H_5)_4$, bromine as dibromoethane, $C_2H_4Br_2$, and phosphorus as tricresyl phosphate, $(C_6H_4CH_3)_3PO_4$.

8.2.1 Piston Engine Combustion Emissions

In the piston engine, the working fluid is confined by a solid boundary, and therefore must operate within the mixture range of flammability (compare with continuous combustors), although some overall fuel weakness is possible if the charge is stratified. Figure 8.6 shows the variation with air/fuel ratio over the flammable range of the mass concentrations of those spark-ignition combustion products of greatest environmental concern. Fuel-rich mixtures promote the maximum concentrations of carbon monoxide, particularly at idle conditions, and of unburnt hydrocarbons following deceleration and/or advanced spark. Leaning the mixture as at cruise, acceleration and/or advanced spark gives rise to higher temperatures and thus to peak concentrations of nitrogen oxides, as discussed in section 8.2.

Although the characteristics of spark-ignition engines used in the aviation and automotive worlds are very similar, the light aero engine is usually air-cooled, and so depends more on fuel enrichment for temperature control. The working ranges of air/fuel ratio therefore lie between about 10 to 12 when out of the lean cruise mode, compared with an overall 13 to 16 for automotive engines. Furthermore, the operator controls not only the throttle, as in automotive practice, but also the inlet air temperature and air/fuel ratio, although the ignition timing is usually constant instead of variable with speed and load. Also, maximum power is used for some part of each operation with aero engines, but rarely so with automotive engines. The problem of emissions from aero piston engines there-

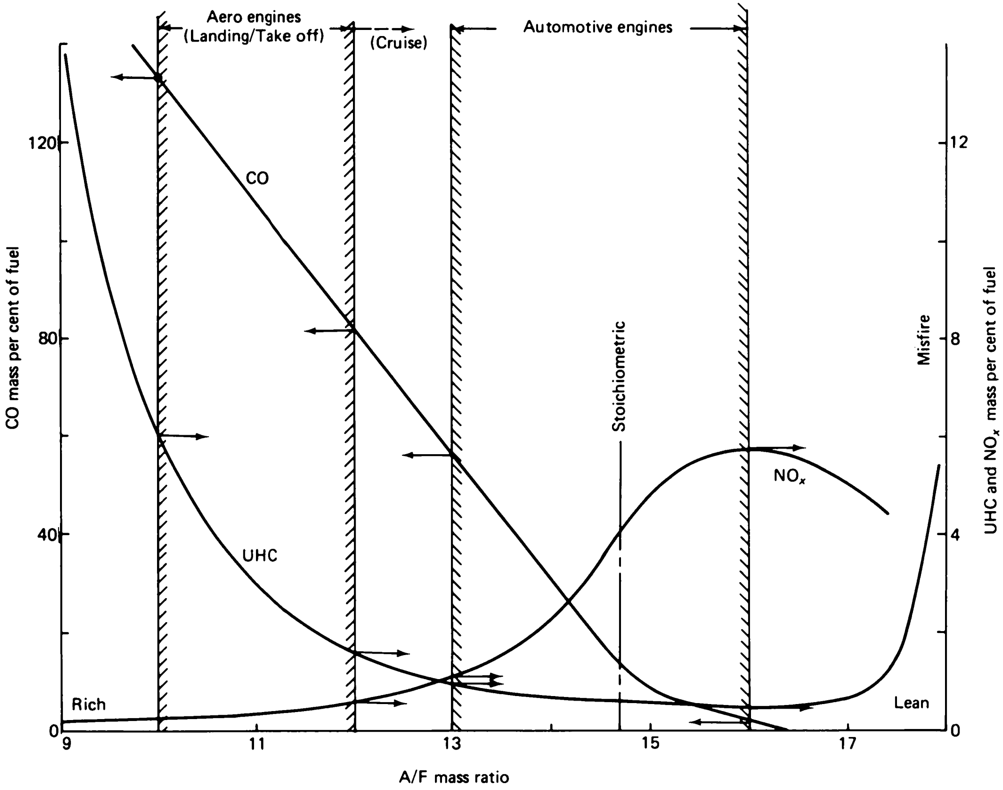


Figure 8.6 Variation of spark-ignition piston engine combustion products with air/fuel ratio (ref. 5)

fore centres on the levels of carbon monoxide, and to a lesser extent of unburnt hydrocarbons and nitrogen oxides, in the vicinity of airports and below altitudes of about 0.9 km, generated by aircraft landing and takeoff movements.

In the test procedures and levels standardised by the United States Environmental Protection Agency in 1973, the emission rates of carbon monoxide, unburnt hydrocarbons and nitrogen oxides are measured over a five-mode landing and takeoff (LTO) cycle consisting of specified periods of time at idle/taxi, takeoff, climbout and approach, but excluding altitude cruise (table 8.2(A)). The maximum permissible emission levels for the cycle are then expressed in terms of the rated power of the engine (table 8.2(B)).

Table 8.2 Aero piston engine combustion emissions
(Derived from references 5 and 6)

(A) EPA five-mode landing/takeoff cycle

Mode name	Mode period (minutes)	Power (%)	Rev/min (%)
Taxi/idle (out)	12.0	*	*
Takeoff	0.3	100	100
Climbout	5.0	75-100	*
Approach	6.0	40	*
Taxi/idle (in)	4.0	*	*
Total period	27.3		

*Manufacturer permitted to specify.

(B) EPA aero piston engine emissions standards

Emittant	lbm/bhp cycle	kg/kW cycle (approx.)
CO	0.042	0.0255
UHC	0.0019	0.0012
NO_x	0.0015	0.0009

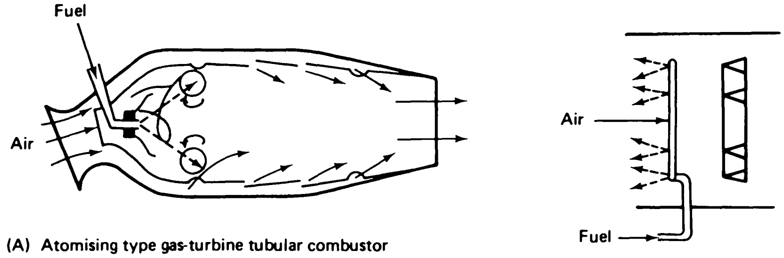
Concepts for the reduction of exhaust emissions include improved fuel injection, heated inlet air, stratified charge, valve overlap control, multiple spark discharge, improved cylinder-head cooling, exhaust air injection and add-on catalytic converters or thermal reactors. Tests show that reduced levels of carbon monoxide during climbout and approach, and of unburnt hydrocarbons during taxi/idle modes, are likely to be achieved more from fuel enleanment by improved mixture management than from subsequent exhaust oxidation.

8.3 Fuel Combustion in Gas Turbine Engines

In contrast to the intermittent flame propagation required across the combustion chamber of a piston engine, combustion in a gas-turbine engine is continuous, and depends on flame stabilisation within a defined region of the combustion chamber. The location of a flame at a fixed point requires a velocity balance between the flame and the approaching mixture. Since the flame velocities of hydrocarbon fuels with air are inherently low (typically 0.5 m/s at atmospheric pressure), a substantial reduction of mixture velocity is essential. This is achieved in two stages:

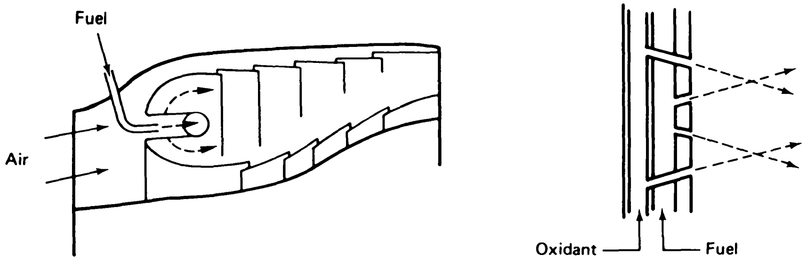
(a) reducing the inlet air mean velocity from about 150 m/s to about 25 m/s by means of diffusion, that is, by increasing the cross-sectional area of the combustor duct, and

(b) reducing, and also reversing, the air flow velocity in the locality of the flame region by means of swirl flow to reduce the pressure in the core of the chamber, together with use of side-entering air jets to strengthen the recirculation (figure 8.7).



(A) Atomising type gas-turbine tubular combustor

(C) Gutter-stabilised upstream injection system for ramjet or gas-turbine reheat combustor



(B) Vaporising type gas-turbine annular combustor

(D) Impinging jet injection system for rocket combustor

Figure 8.7 Flame stabilisation in representative types of continuous-flow combustor

Reduction of the inlet air velocity also serves the purpose of restricting to an acceptable level (about 1 per cent) the fundamental loss of pressure that occurs with the release of heat in a flowing stream.

Again, in contrast to the intermittent nature of combustion in a piston engine, the continuously maintained flame temperature calls for substantial cooling in order to meet the metallurgical requirements of the materials in the hot section. The walls of combustor flame tubes are protected by cooling air which flows externally and is introduced progressively as internal films, whereas the nozzle guide vanes, and particularly the turbine blades which also experience the mechanical stresses of high-speed rotation, are located directly within the main gas stream. For this reason, only about 28 per cent of the air input can be used for combustion, which commences in the primary zone of the chamber at a fuel/air mass ratio close to the stoichiometric value of 0.067. Secondary air is introduced to help stabilise the toroidal vortex derived by the air swirler, and to reduce the combustion temperature to about 1800 K in order to offset the effects of dissociation. Dilution air then enters the flame tube progressively to bring the temperature of the combustion products down to the maximum acceptable level of about 1250 K where the turbine blades are uncooled, and to about 1600 K when the nozzle guide vanes and turbine blades are cooled internally with air bled from the compressor.

Turbine entry temperatures provide a direct indication of the thermal efficiency of the engine, and of the thrust produced. Equally important is the distribution of temperature over the cross-sectional area of the flame tube outlet which should be as uniform as possible in order to maximise the mean outlet temperature, and to avoid hot regions at the turbine blade disc. The temperature traverse factor, TTF, defined as

$$\mathrm{TTF} = 100\left(\frac{\text{maximum outlet temperature} - \text{mean outlet temperature}}{\text{mean outlet temperature} - \text{inlet air temperature}}\right)$$

is, in fact, an indirect measure of temperature uniformity, since a *lower* value indicates *greater* uniformity. Despite fuel residence times of a few milliseconds only, TTF values of 30 per cent are typical, with combustion efficiencies in excess of 99 per cent, under most conditions except at idling.

A gas-turbine combustion chamber is required to operate satisfactorily over specified ranges of overall fuel/air mass ratio (0.0077 to 0.0222) and air mass flow rates in order to meet the requirements of idling, cruise, takeoff and dash. Although a fuel spray of uniformly small-sized droplets would appear to give the desired rapid and complete combustion, the optimum fuel-air matching would apply over a relatively narrow range of chamber conditions, leading to poor performance at extreme ends of the operating spectrum, with the possibilities of flame-out, following rapid movements of the throttle. Some degree of spray heterogeneity is therefore useful in widening the mixture range of the combustor stability loop, as shown in figure 8.8.

The oxygen in the chamber cooling and dilution air is, of course, unconsumed, and therefore available for subsequent combustion downstream of the turbine in a reheat chamber. This provides additional thrust for such purposes as aircraft takeoff, combat or transonic operation. However, the thermal efficiency of the engine is reduced since the reheat combustion occurs at a pressure lower than that in the main chamber. Typically, a reheat chamber comprises a relatively simple V-type gutter baffle system for air recirculation, and is therefore generally similar to a ramjet combustion chamber.

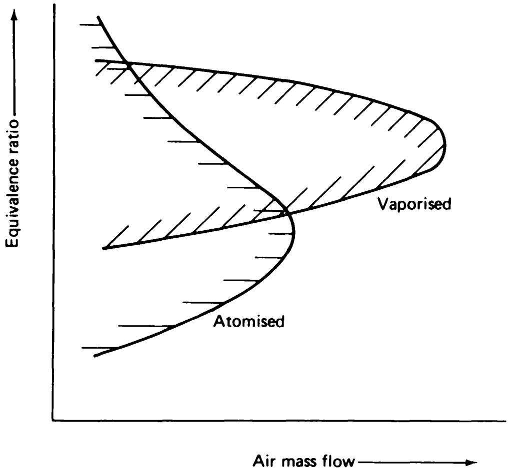


Figure 8.8 Stability loops for gas turbine combustion chambers

In the tubular design of main combustor, the geometry of fuel flow is well matched with both primary and secondary air flows, and development work can proceed on a single chamber in the absence of the complete engine air flow, but the engine diameter and mass tend to be high. Annular chambers, on the other hand, permit lower aerodynamic pressure losses, but give poorer matching of fuel and air flows with consequent adverse effects on the outlet temperature profile. High buckling loads are also exerted on the outer flame-tube walls. The hybrid tubo-annular design combines the tubular advantages of good flow matching and ease of development with the lower engine diameter of the annular design, while losing some of its aerodynamic advantage.

Combustors designed for a stoichiometric primary zone achieve a high flame temperature which assists the rate of heat release and combustion efficiency, with little carbon deposition, smoke, flame luminosity or partially burnt products. They do, however, give a high rate of heat transfer to the flame tube. Reduction in air flow rate to give a rich primary zone eases ignition and promotes good flame stability, but the formation of excess carbon leads to deposits, smoke and flame luminosity, with a poor outlet temperature traverse. A weak primary zone resulting from additional air, on the other hand, gives no carbon, with a low-temperature non-luminous flame, and therefore low heat transfer to the flame tube, with a good outlet temperature traverse. However, ignition performance and flame stability are affected adversely.

8.3.1 Influence of Fuel Composition on Combustor Performance

With the impending decline in crude oil availability, a general reduction in fuel quality is expected as refiners face a diminishing choice between types of crude feedstock. A record of major fuel properties compiled in the U.S.A. during the

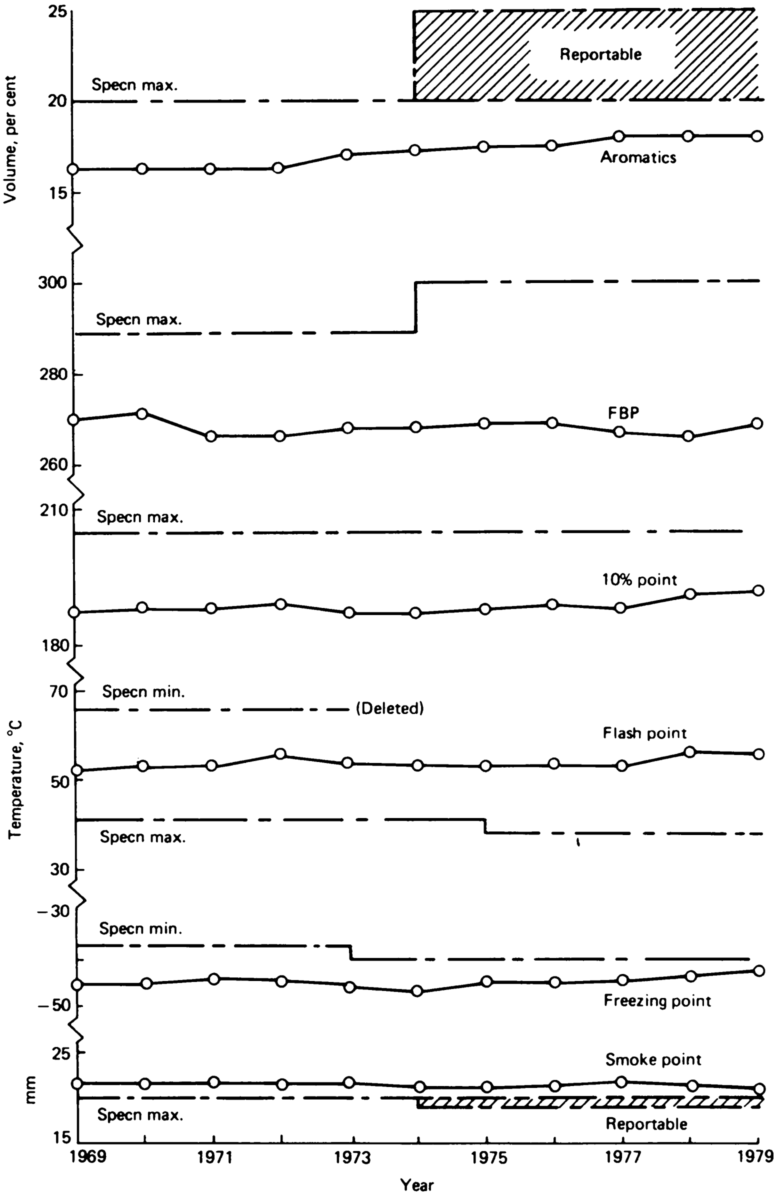


Figure 8.9 Variation of Jet A fuel properties, 1969–79 (ref. 7)

period from 1969 to 1979 is illustrated in figure 8.9, and summarised in table 8.3. This period incorporates the OPEC fuel embargo of 1973, following which continued supplies of aviation turbine fuels were maintained in the U.S.A. by the adoption of Emergency Specification ES-2-74, which permitted temporary waivers to maximum aromatic content (20 to 25 per cent volume, or 22 per cent in the cases of Jet A-1 and Jet B), and in maximum final boiling point (288 to 300°C), with corresponding reductions in minimum smoke point (20 to 18 mm, or 19 mm in the cases of Jet A-1 and Jet B) in conjunction with a maximum of 3 per cent volume naphthalenes, and reduction in minimum flash point (40.6 to 37.8°C). The original limits were re-imposed on return to a more stable pattern of crude oil supplies, but these relaxed limits tend to be written in to the latest specifications.

In table 8.3, a sample is defined as 'near-specification' when the relevant property lies within the range of test reproducibility precision from the specification limit, the figures shown applying to those samples that exhibited 'near-specification' values for the stated property *only*. In many cases, samples exhibited such values for more than one property. Furthermore, a 'near-specification' property is defined as 'controlling' when it is either the only such property for the given sample, or when it is the closest to its specification limit for several such properties; the determination of 'closest' between properties of different units, for example, °C, mm and per cent volume, is not clear, but freezing point, smoke point and aromatics content are listed in arbitrary order of preference. Overall increases were also noted with these three dominant properties as controlling.

Table 8.3 Overall changes in U.S. aviation turbine fuel properties, 1969–79 (reference 7)

Property	Change	Reproducibility	% of samples	
			Near-specification	Controlling
Aromatics, % vol.	+ 1.9	3.2	9.9	25.2
Smoke point, mm	– 1.0	3.0	11.2	31.1
Freezing point, °C	+ 2.1	2.6	5.6	14.5
10% point, °C	+ 4.5	4.4	–	1.0
fbp, °C	–	10.5	1.5	1.5
Flash point, °C	+ 3.5	2.2	–	0.5
Mercaptans, % mass	+ 0.00041	0.0006	–	2.8

The general conclusions, therefore, point to a steady rise in aromatics content, together with rises in freezing point and flash point, and a reduction in smoke point. However, these data are from the U.S.A., whereas in Europe and parts of the Far East during the late 1970s, the freezing point of – 50°C for avtur/Jet A-1 became critical and limiting, leading to fuel 'allocation' (rationing) at major airports. Avtur, then Jet A-1 and IATA Guidance Materials specifications were revised by raising the freezing point from −50°C to −47°C, so enabling the European Joint Fuelling Check List Jet A-1 specification to follow suit. This greater flexibility for refiners (potentially allowing approximately 10 per cent more production from a given volume of crude) eased the situation, and currently there is no supply problem for avtur/Jet A-1 to meet the −47°C freezing limit.

8.3.2 Fuel Aromatics Content and Related Properties

In view of the growing concentrations of aromatics in aviation turbine fuels, and the likely continuation of this trend with supplementation from non-petroleum sources, a comparison of some relevant properties of individual paraffinic and aromatic hydrocarbons is made in figure 8.10, including those for conventional avtur. These curves show that, with avtur derived by distillation over the current specification temperature range of 150-300°C, any increase in aromatics content tends to:

(a) depress the hydrogen/carbon atomic ratio (and thus the hydrogen content)
(b) increase the density (and thus the energy density), and
(c) raise the freezing point if the aromatics concerned are of the polycyclic (naphthalene) type.

With regard to the first conclusion, no precise relationship can be derived between the contents of aromatics and hydrogen owing to the differing natures both of the aromatic and non-aromatic components within different fuels. Nevertheless, a number of relationships have been reported in the literature, as shown in appendix 2, and these average out to give the following as broadly representative of petroleum-based aviation turbine fuels

$$\text{Hydrogen per cent mass} = 14.9 - 0.0638\ (\text{aromatics per cent volume})$$

over the ranges of 11-15 per cent hydrogen and 0-65 per cent aromatics.

A more comprehensive relationship is given in ASTM D3343[8], incorporating terms for fuel density and the average of the 10, 50 and 90 per cent distillation temperatures. The fact that this relationship holds closely for a 96 per cent concentration of tetralin, which is largely aromatic but enriched with hydrogen, indicates that its application is wide.

8.3.3 Fuel Hydrogen Content and Related Properties

For aviation turbine fuels, the reproducibility (different operator with similar apparatus) of measuring aromatics content is in the region of 3.5 per cent volume. With the development of the nuclear magnetic resonance technique, however, hydrogen content can now be measured with a reproducibility down to 0.11 per cent mass. This raises the question of the extent to which aromatics content can be replaced by hydrogen content as a useful and reliable indicator of handling characteristics and combustion performance. Since the hydrogen/carbon atomic ratio is often quoted in the literature as an alternative to hydrogen

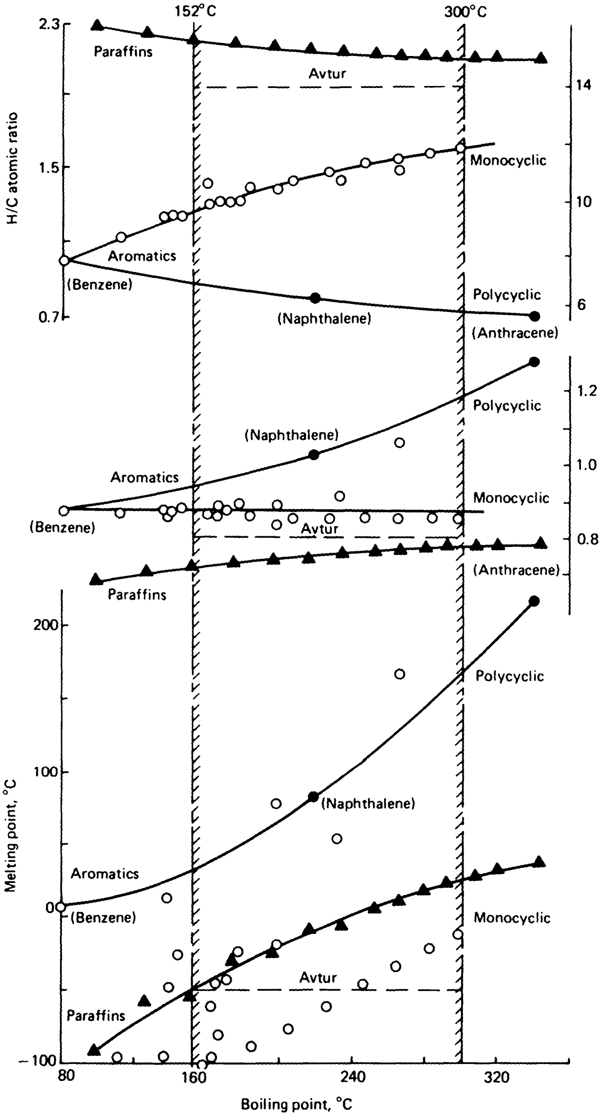


Figure 8.10 Influence of aromatics on hydrogen content, density and freezing point of avtur

per cent mass content, the relationship between the two is also shown in appendix 2.

The first step in answering this question is an appraisal of the influence of hydrogen content on the laboratory-measured physical and chemical properties of a hydrocarbon fuel. A collation of such data is presented in figures 8.11 to 8.15 which show that an increase in hydrogen content tends to:

(a) Reduce the density of the petroleum fuels with a fairly clearly defined linear relationship, whereas the reduction from aromatic to paraffinic hydrocarbons is less steep (figure 8.11).

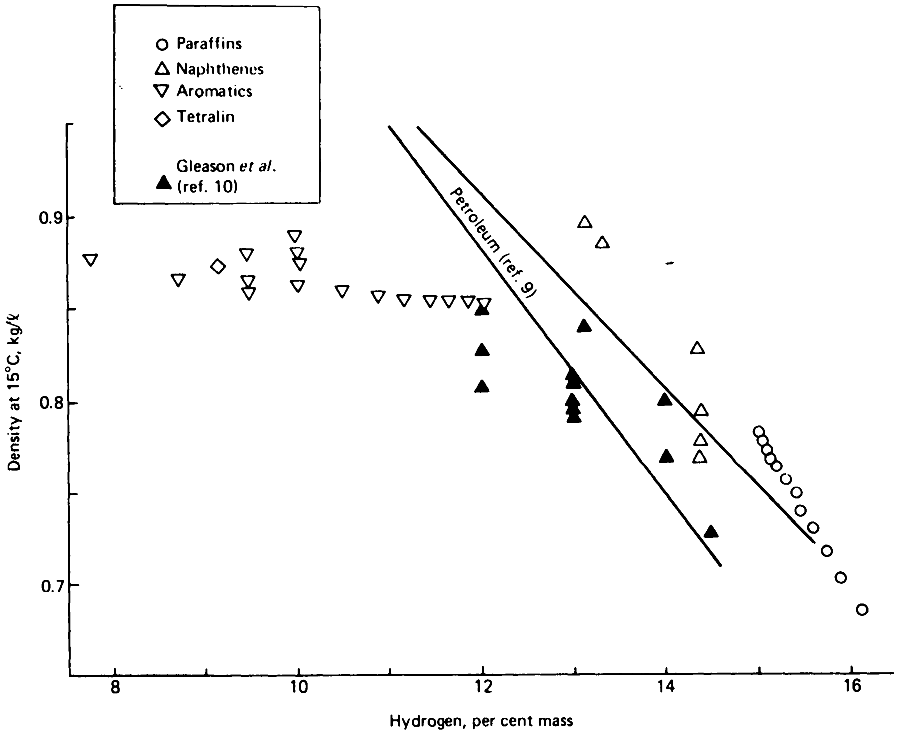


Figure 8.11 Relationship of fuel hydrogen content with density

(b) Reduce both final boiling point and viscosity of the petroleum fuels in a non-linear manner, whereas no clear relationship exists for the individual hydrocarbons (figures 8.12 and 8.13).
(c) Increase the net specific energy with a clearly defined linear relationship for the petroleum fuels, with a similar but less marked effect for the individual hydrocarbons (figure 8.14).
(d) Increase the smoke point of the petroleum fuels with a clearly defined non-linear relationship (figure 8.15).

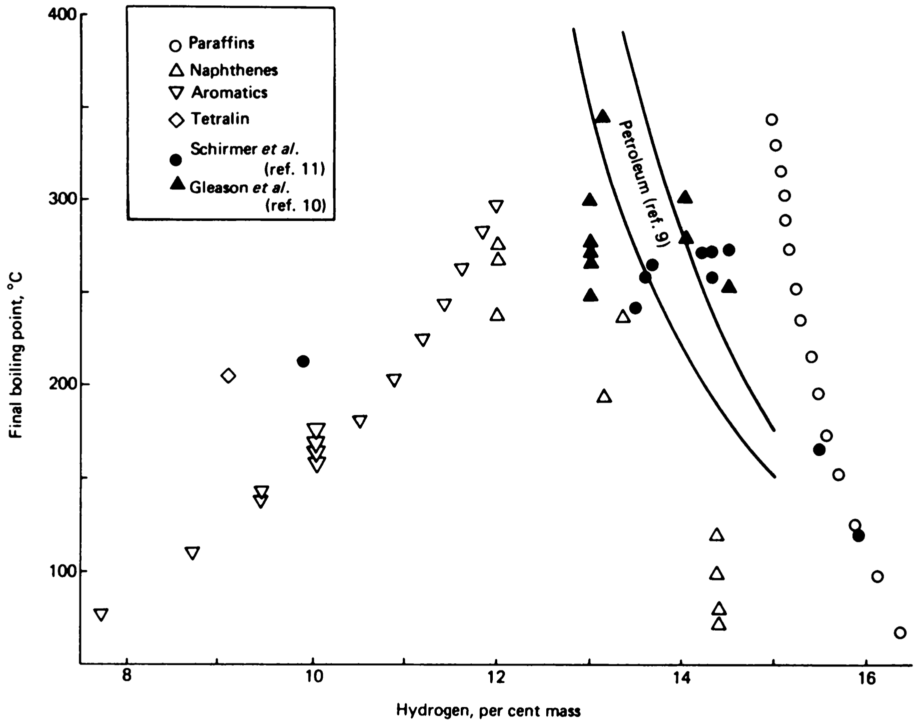


Figure 8.12 Relationship of fuel hydrogen content with final boiling point

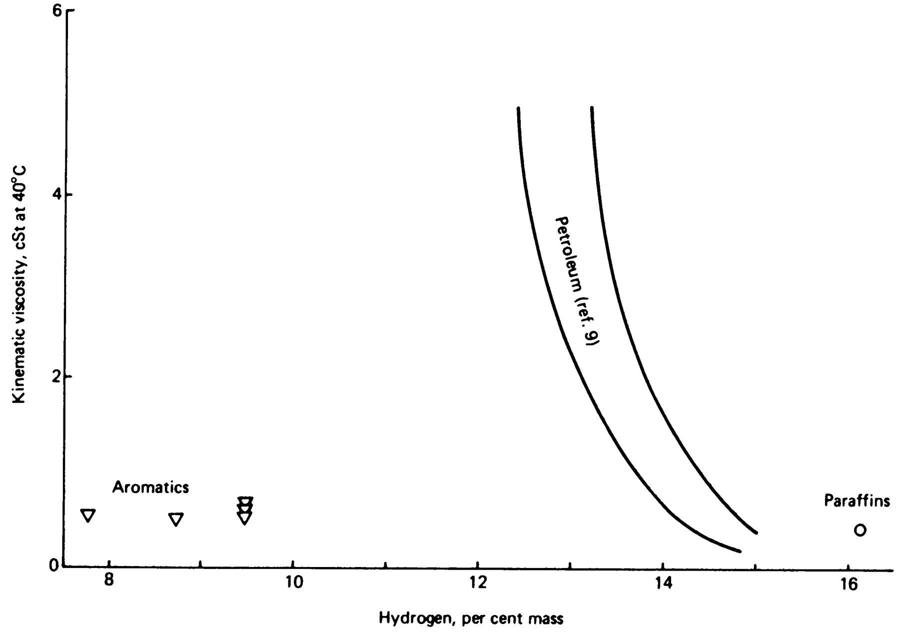


Figure 8.13 Relationship of fuel hydrogen content with kinematic viscosity

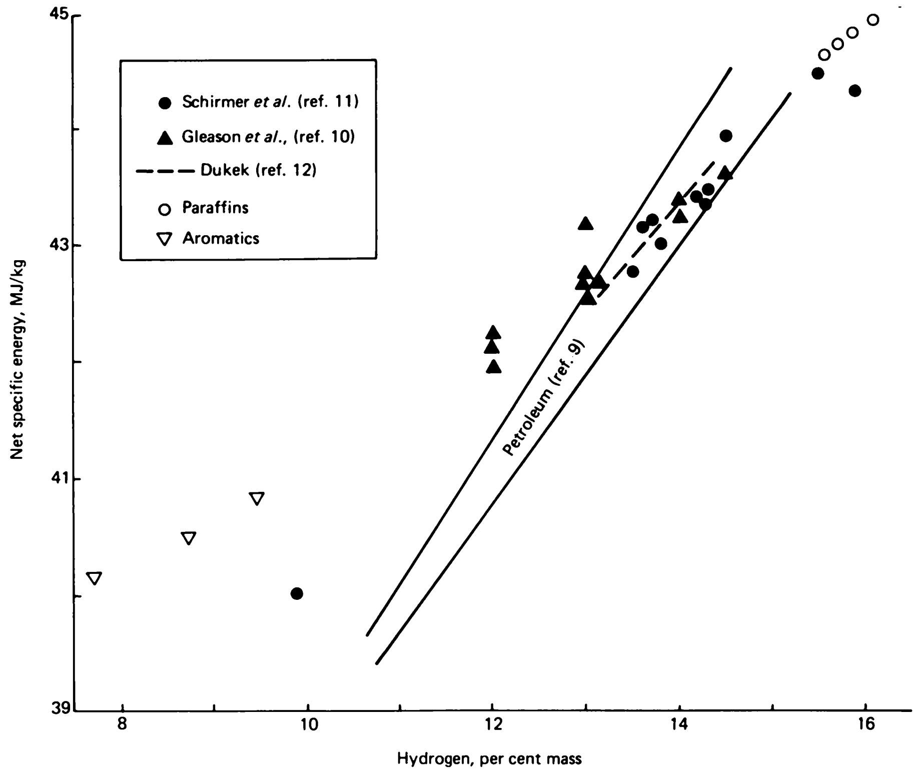


Figure 8.14 Relationship of fuel hydrogen content with net specific energy

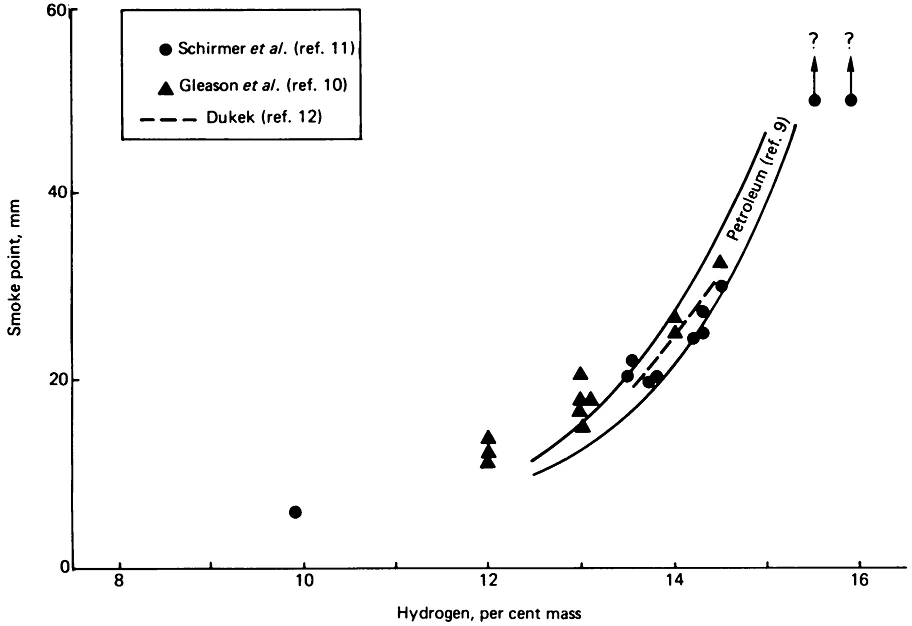


Figure 8.15 Relationship of fuel hydrogen content with smoke point

The effects of the expected fall in hydrogen content with future degradation in aviation turbine fuel quality may therefore be summarised broadly as increases in density, boiling level and kinematic viscosity, and reductions in net specific energy and smoke point, although these effects may be less marked if the quality degradation is due largely to a change from paraffinic to aromatic type components.

8.3.4 Fuel Hydrogen Content and Related Combustor Performance

In recognition of the falling level of hydrogen content, a Broad-Specification Fuels Combustion Technology Program was devised by NASA to assist in tackling the related performance, durability and emissions problems. The first experimental referee broad-specification (ERBS) fuel was devised in 1977, with a hydrogen mass content reduced from the typical 14 per cent to 12.8 per cent by raising the aromatics content from 20–25 per cent to about 35 per cent volume, as shown in table 8.4. Since then, ERBS fuels of 12.3 and 11.8 per cent hydrogen mass have also been devised so that the extended trends in combustion performance with varying hydrogen content can be assessed[13].

The aim is to prescribe a fuel with properties representing a reasonable range based on expected fuel trends to the year 2000, in order to give the manufacturers of aircraft, engines and components an opportunity to test their products against the expected deterioration in fuel quality. In Europe, a comparable programme has been initiated by AGARD with a research fuel (ARF) of relatively low hydrogen content and correspondingly high freezing point and viscosity.

Tests have been conducted with a variety of fuel blends ranging from JP-4 (wide-cut gasoline) to No. 2 diesel (gas oil) with and without different types of paraffinic and aromatic blending agents, and also with some individual hydrocarbons. The 19 fuels used by Butze and Smith[14] ranged from 0 to 63.5 per cent volume aromatics and 11.0 to 15.3 per cent mass hydrogen, however, the detailed properties are not reported here since the plotted points were not identified with the fuel numbers. The main component concentrations of the test fuels used by Schirmer *et al.*[11], Gleason *et al.*[10], Schirmer and Quigg[15] and Naegeli and Moses[16] are in the ranges shown in table 8.5. The full-scale combustors tested included tubular, tubo-annular, annular with lean primary, and tubo-annular with rich primary, using either pressure-jet or air-blast systems of fuel injection. Included are results from the Phillips 5.08 cm diameter tube rig.

In the full-scale chambers, an increase in fuel hydrogen content increased combustion efficiency very slightly over the average 90 or 94 per cent levels at idle condition, but had no effect on the 99.9 per cent level common to cruise and takeoff conditions. However, other combustion parameters were influenced significantly, as discussed in the following sections.

8.3.4.1 Flame Radiation

The extent of radiation from a flame is determined by the emissivity, which is a function of both the temperature of the flame and the concentration of solid

Table 8.4 Main differences between aviation turbine fuel specifications

Property	Wide-cut gasoline			Aviation kerosine					High-flash kerosine	
							Experimental			
	Avtag DERD 2454	Jet B ASTM D1655	JP-4 Mil-T-5624 L	Avtur DERD 2494	Jet A/A-1 ASTM D1655	JP-8 Mil-T-83133 A	ERBS 1 (NASA)	ARF (AGARD)	Avcat DERD 2452	JP-5 Mil-T-5624 L
Aromatics, % vol. max.	25	20, 22*	25	22	20, 25* (A) 20, 22* (A-1)	25	35**	R	25	25
Hydrogen, % mass, min.	13.8**	–	13.6	13.8**	–	13.5	12.6–13.0	13.0–13.4	13.8**	13.5
Freezing point, °C max.	–58	–50	–58	–47	–40 (A) –47 (A-1)	–47	–28.9	–30	–46	–46
Viscosity, cSt max.										
at –23.3°C	–	–	–	–	–	–	12	–	–	–
at –20°C	–	–		8	8	8	–	12	8.8	8.5

*Purchaser to be advised.

**Representative but not specified.

R Reported, but limit set by other requirements.

Table 8.5 Composition ranges of representative experimental fuels

		Reference	Per cent volume					Per cent mass hydrogen
			Aromatics		Naphthenes	Paraffins	Olefins	
			Total	Polycyclic				
5.08 cm	full scale	11	0-94	0-94	?	?-100	0-3.2	9.9-15.9
		10	10.9-53.4	0.3-24.6	13.6-39.1	25.7-62.4	0.5-2.7	12.0-14.5
	tube	15*	0-17.3	?	0-67.2	24.7-100	0	7.74-16.38
		16	22.9-35.9	?	?	62.5-75.4	1.2-1.7	12.8 common

*Plus representative hydrocarbon members of the normal paraffinic, *iso*paraffinic, naphthenic, olefinic and aromatic series.

particulates within it. A comparison has also been made, therefore, of the combustion temperature, calculated on an isobaric (related to non-work steady flow) adiabatic basis for the individual hydrocarbons in stoichiometric mixtures with air, allowing for dissociation to CO, H_2 and O_2 only (that is, ignoring atomic and radical species). The curves in figure 8.16 for standard conditions of 1 atmosphere, 298 K initial temperature and stoichiometric air-fuel mixture (except where stated) show that an increase in hydrogen content also tends to:

(e) Reduce the level of combustion temperature of the individual hydrocarbons, irrespective of the direction of molecular size and mass, despite the relatively high value for elemental hydrogen in comparison with elemental carbon (as graphite).

(f) Limit such temperature differences because the increase in heat release is counteracted by a corresponding (and slightly greater) increase in heat capacity of the larger proportion of combustion-generated water.

Normally, carbon particles are released during the initial stages of combustion, but are then consumed within the flame, provided that the mixing patterns with the air are suitable. However, during their existence, the hot carbon particles radiate to a much greater extent in comparison with the hot gases, and so intensify the heating of the inner surface of the combustor liner. Radiation in the luminous range appears to represent about 1 per cent only of the total and, at atmospheric pressure, the carbon particles appear to be too small to radiate appreciably within the significant infrared region. At high pressure, on the other hand, the carbon particles can grow to radiate severely as black bodies. Hence, flame radiation increases directly with combustion pressure, as well as with inlet temperature.

The fraction of liner heating at high pressure attributed to flame radiation has been found to vary from 40 per cent with a paraffinic fuel to 80 per cent with an

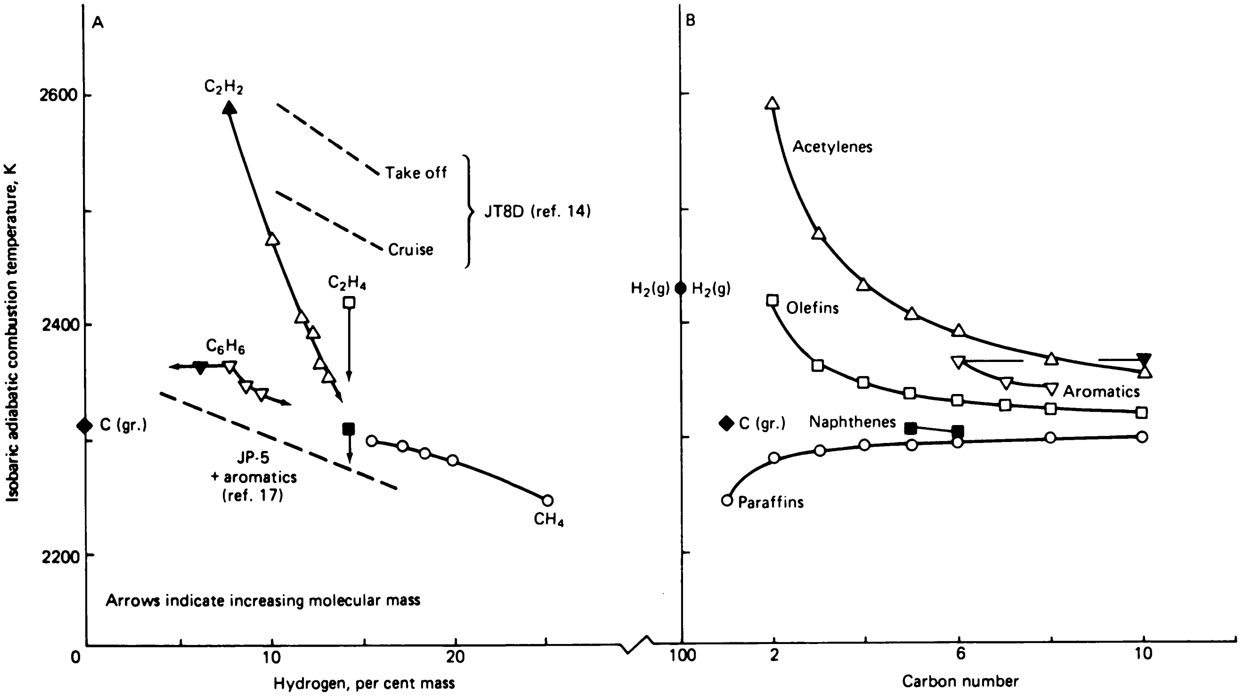


Figure 8.16 Variation of combustion temperature with hydrocarbon fuel type

aromatic fuel, the remainder resulting from convection of the highly turbulent gas stream[11]. Values of flame radiation in the J57 combustor are plotted against aromatics content in figure 8.17A, and against ASTM-calculated hydrogen content in figure 8.17B. These curves for the full-scale chamber show that the level of flame radiation rises with increased concentrations in the fuel of total aromatics and of polycyclic aromatics (naphthalenes). They also show a reduction in flame radiation with increased fuel hydrogen content, the overall correlation appearing closer than that for total aromatics content, but with a less marked influence of naphthalene content. This inverse effect of hydrogen content on flame radiation was also noted in the Phillips tube rig[15], but at a rate dependent on operating conditions and with no clear influence of aromatic type. When fuel hydrogen was maintained constant[16], on the other hand, flame radiation was found to be markedly higher with substantial concentrations of polycyclic aromatics, although radiation correlated more closely with smoke point than with total aromatic content or aromatic ring carbon.

8.3.4.2 Combustor Liner Temperature

The direct relationship expected between flame radiation and consequent liner temperature is exemplified in figure 8.18 for the averaged values from the J57 combustor operating at a simulated altitude pressure of 4.75 atm. The peak liner temperatures correlated equally well at a level some 100-200°C higher. Liner temperatures were also found to vary directly with inlet air temperature and with combustor pressure, at reported rates of 1.13 K/K and 4.7 K/atm. respectively.

Peak liner temperature rises are shown for the J57, JT8D, J79, F101 and some advanced combustors under cruise conditions in figure 8.19, for the J79 under idle and takeoff conditions in figure 8.20(A), and for the J79 and F101 under conditions averaged for cruise/takeoff/dash in figure 8.20(B). These results show that the extent of peak liner temperature rise increases with higher concentrations in the fuel of aromatics and of naphthalenes. They also show a reduction in extent of peak liner temperature rise with increased fuel hydogen content, the overall correlation appearing closer than that for aromatics content, but with a naphthalene content influence no less marked.

As shown in ref. 20, the rise in emissivity with pressure not only approaches unity but is counteracted by a corresponding rise in convective heat removal, consequently changes in fuel properties have little influence on liner temperature at high chamber pressure. This fact is borne out by the disposition of the peak liner temperature rise curves in figure 8.21, plotted relative to a standard fuel of 13.975 per cent mass hydrogen, which show the sensitivity of peak liner temperature to fuel hydrogen content to *increase* directly with combustor pressure up to a level of about 8 atm, and then to *disappear* at about 10 atm. This sensitivity is substantially reduced (and sometimes reversed) for the staged type of advanced combustor, even at pressure levels *below* 10 atm.

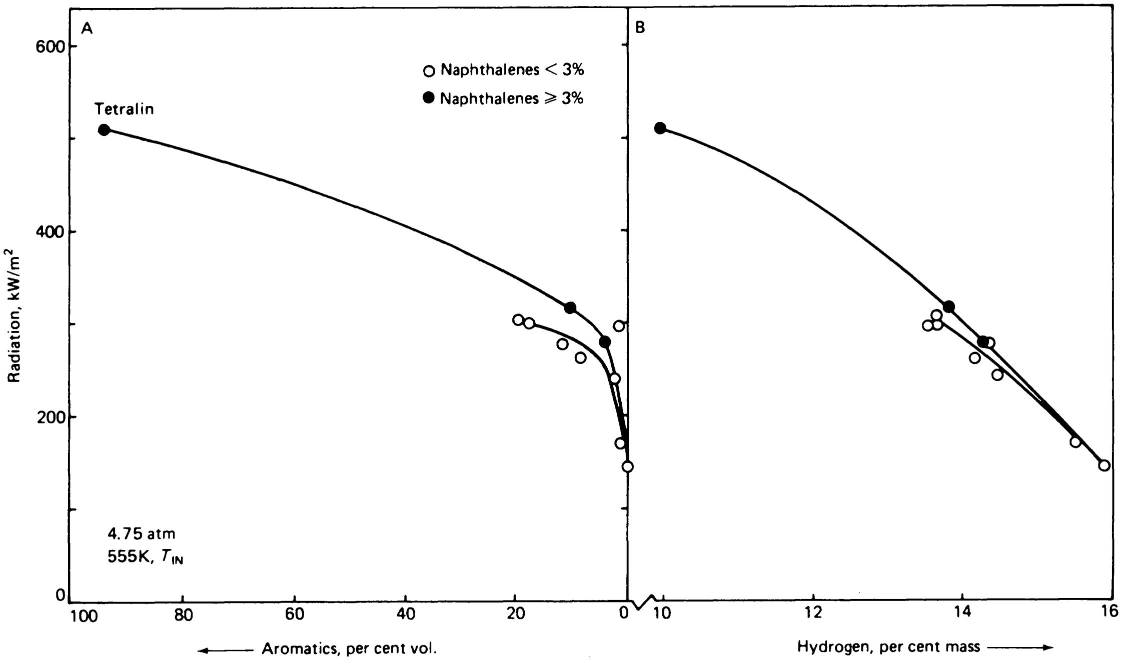


Figure 8.17 Variation of flame radiation with fuel aromatics and hydrogen contents (ref. 11)

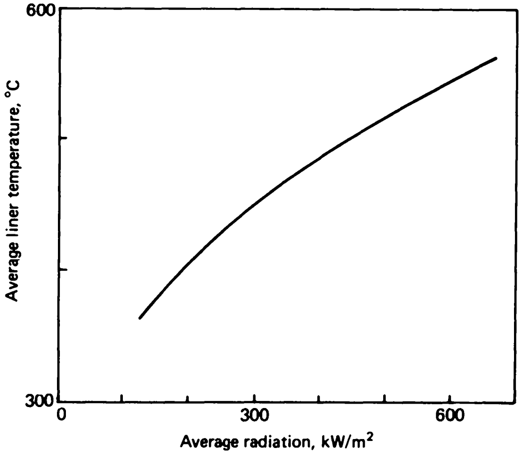


Figure 8.18 Relationship between flame radiation and liner temperature (ref. 11)

8.3.4.3 Gas Turbine Engine Combustion Emissions

Traces of carbon monoxide and unburnt hydrocarbons persist as combustor emissions owing to incomplete combustion, and reach maximum values at the lower-power conditions of idle and cruise, where the inlet temperature and combustor pressure are minimal. Nitrogen oxides and smoke, on the other hand, are generated by combustion at high temperature, and so reach maxima at high power. Nitrogen oxide emissions are increased when appreciable quantities of fuel-bound nitrogen are involved, as with shale-derived kerosine. The curves for carbon monoxide, unburnt hydrocarbons and nitrogen oxides therefore tend to follow those of the piston engine in figure 8.6, with air/fuel ratio in the abscissa replaced by engine thrust. The smoke number (determined from the intensity of staining of a filter paper sampling a pre-determined volume of exhaust products) also follows the general trends of nitrogen oxides.

The high-power pollutants are particularly obnoxious since nitric oxides are toxic and increase when the combustion temperature is raised in an effort to eliminate the unburnts, whereas particulates appear as smoke and serve as condensation nuclei for smog. Although pollution by jet aircraft represents a small proportion only of the total emissions within a metropolis, that within the immediate vicinity of an airport is comparable to an industrial environment and amounts, for example, to about 4000 tonnes of particulates emitted annually per airport. Nevertheless, the sum of the emission indices (g pollutant per kg fuel) for aero jet engines is less than 1 per cent of the equivalent sum for aero piston engines[24].

As discussed above, carbon particulates are formed early in the combustion process, and then consumed progressively during subsequent traverse of the

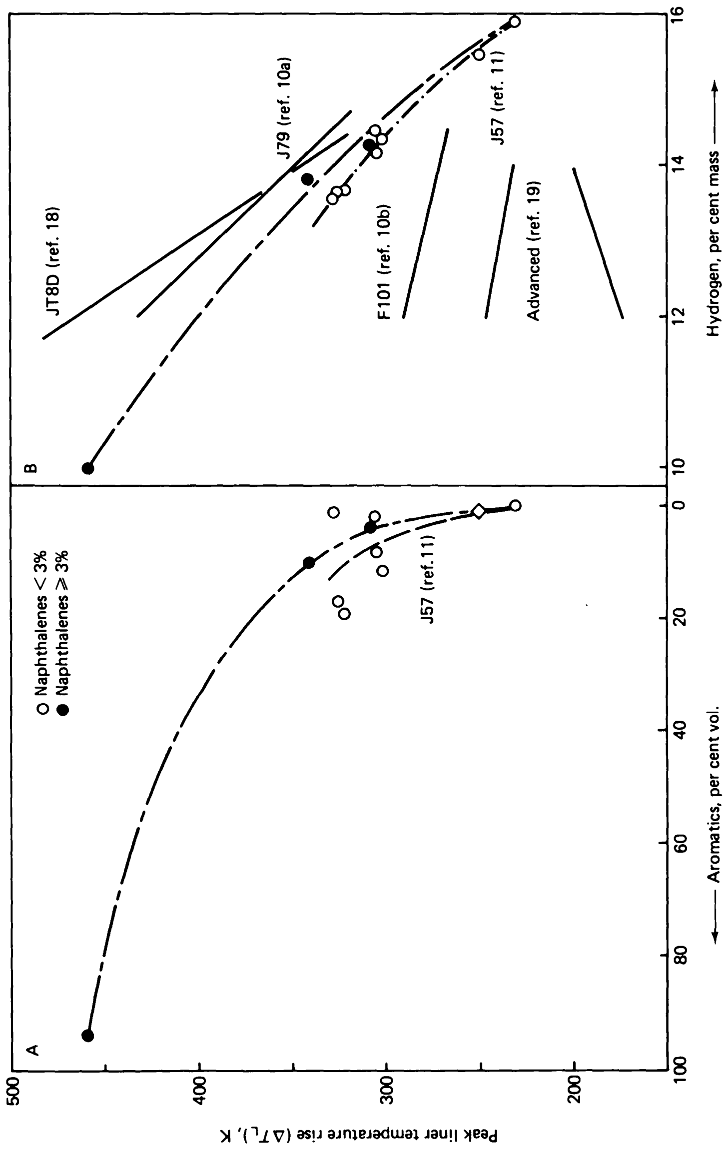


Figure 8.19 Variation of peak liner temperature rise with fuel aromatics and hydrogen contents

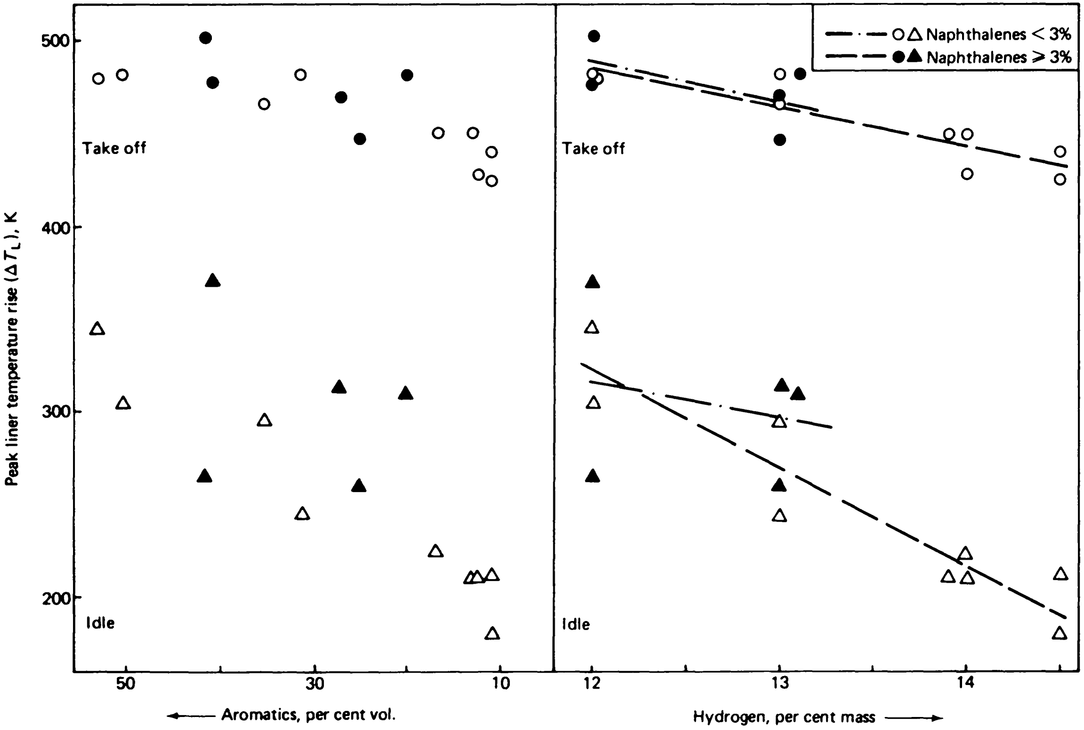
flame. Those persisting beyond the flame are emitted as smoke. The curves in figure 8.22 show that smoke number, which varies directly with fuel input rate, increases with higher concentrations in the fuel of total and of polycyclic aromatics. They also show a reduction in smoke number with increased fuel hydrogen content, the overall correlation appearing closer than that for aromatic content. With fuel hydrogen content held constant, the Phillips rig results show that smoke number increases with concentration of polycyclic aromatics above about 20 per cent, including those that are partially hydrogenated, such as tetralin. This is to be expected if smoke generation follows the postulated rapid route through the condensation of aromatic rings to polycyclic aromatics, rather than the slow route through the fragmentation reactions of monocyclic aromatics to open-chain components. At this stage, this leads to an overall conclusion that fuel hydrogen content represents a satisfactory combustion predictor for petroleum, and possibly shale and tar-derived, aviation fuels with moderate concentrations of polycyclic aromatics, but may not do so for any future fuels derived from coal if they contain appreciable quantities of polycyclic aromatics.

Smoke point, despite its determination via a wick-fed laminar diffusion flame which is unrepresentative of the turbulent spray-stabilised combustion in practice, is generally considered to give a reasonable prediction of tendency to smoke emission in gas-turbine engines. Attempts have been made to refine the test by measurement of radiation and flame temperature rise, as discussed in chapter 5, but the resulting 'luminometer' test methods have not been adopted widely. Both peak liner temperature rise and smoke number are therefore plotted against smoke point in figures 8.23 and 8.24 for the J79 combustor, the curves showing that an increase in smoke point (that is, a cleaner burning fuel) reduces the peak liner temperature rise, particularly at idle (figure 8.23), where the correlation is superior to that with hydrogen content. At all other test conditions, correlation with hydrogen is superior. Increase in smoke point also reduces smoke number, particularly at idle, but its correlation is generally superior to that with hydrogen at all conditions. The correlation with carbon monoxide concentration is generally superior with fuel hydrogen content, but concentrations of hydrocarbons and nitrogen oxides sometimes correlate better with smoke point.

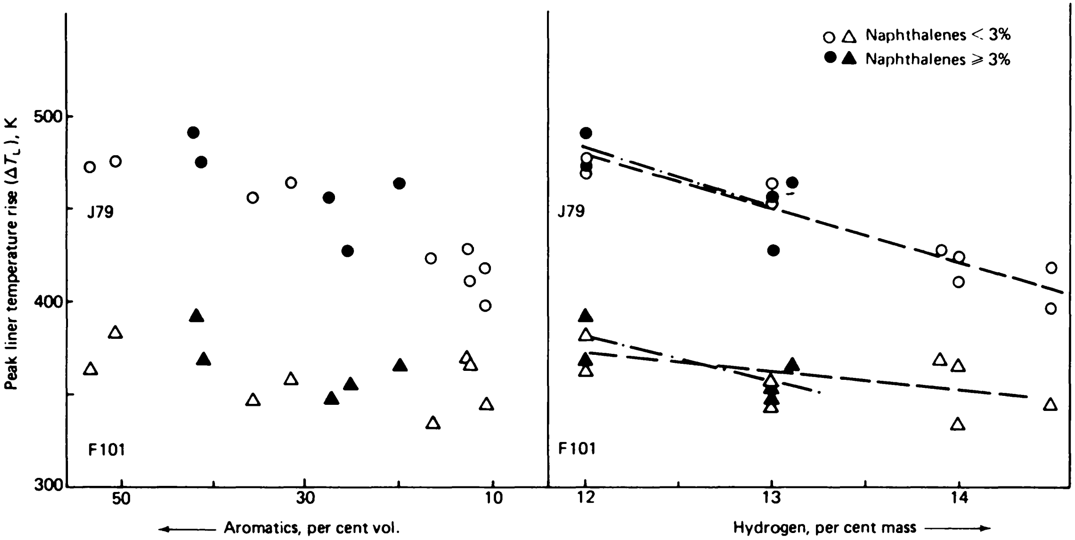
Research continues into alternative methods of correlating combustion performance. One approach is to use some form of Gibbs function, since free energy relates directly to the chemical potential for reactions to occur, however any improvement over hydrogen content appears to be marginal[25].

Comparable to the legislation regarding piston engine emissions discussed in section 8.2.1, the Environmental Protection Agency, United States Air Force and other bodies have standardised the test procedures and maximum permitted levels of pollutants for different engine types, examples of which are shown in table 8.6.

Concepts for the reduction of exhaust emissions from aero gas turbine engines include modifications to the fuel and air flow patterns, improved fuel injection by air-blast carburation, staged fuel injection coupled with sector burn-


○△ Naphthalenes < 3%
●▲ Naphthalenes ⩾ 3%
Peak liner temperature rise (ΔT_L), K
500
400
300
200
Take off
Idle
Take off
Idle
50
30
10
12
13
14
Aromatics, per cent vol.
Hydrogen, per cent mass

(A) J79 engine



(B) J79 and F101 engines
Average cruise/takeoff/dash

Figure 8.20 Variation of peak liner temperature rise with fuel aromatics and hydrogen contents (refs 10a, b): (A) J79 engine; (B) J79 and F101 engines

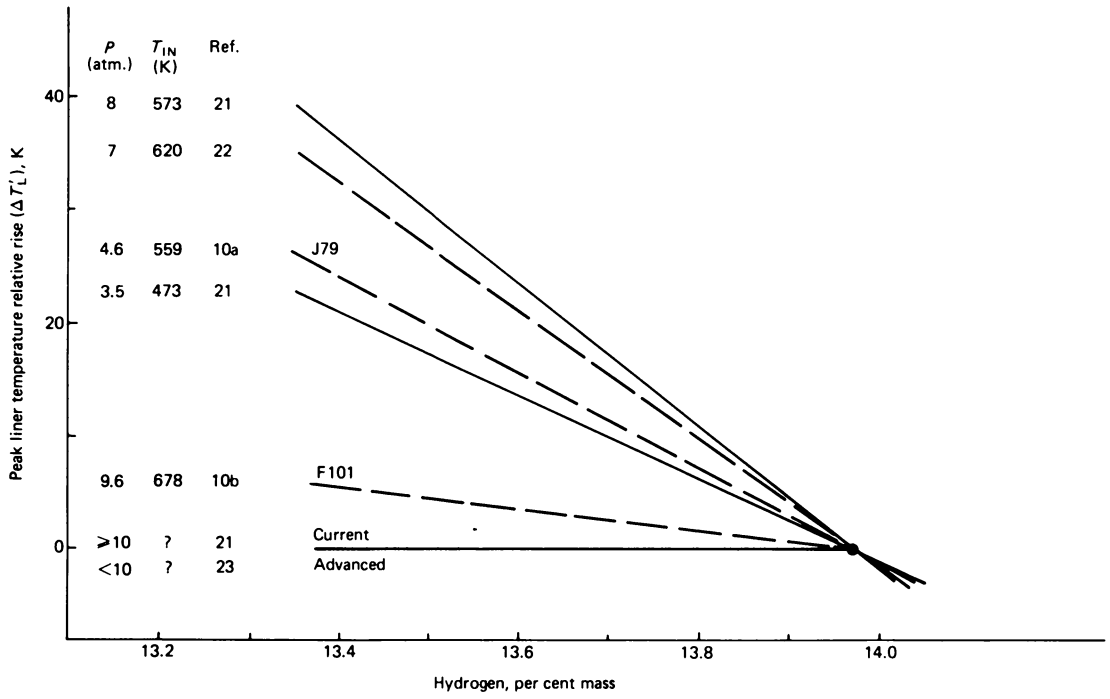


Figure 8.21 Effect of pressure on sensitivity of peak liner temperature to fuel hydrogen content

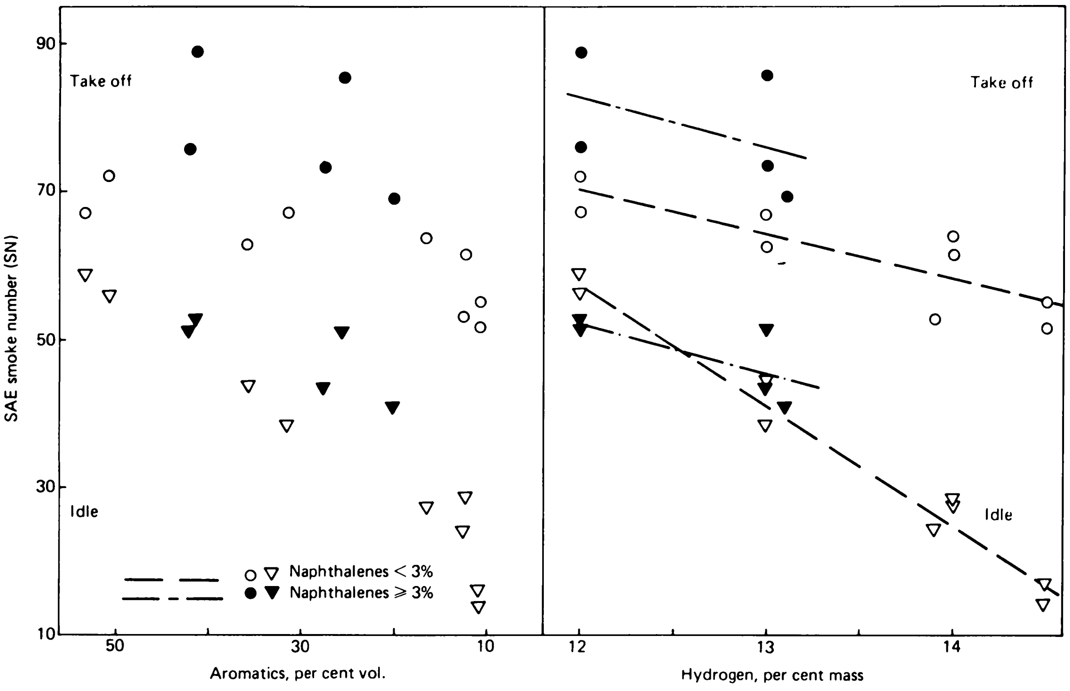


Figure 8.22 Variation of smoke number with fuel aromatics and hydrogen contents for J79 engine (ref. 10b)

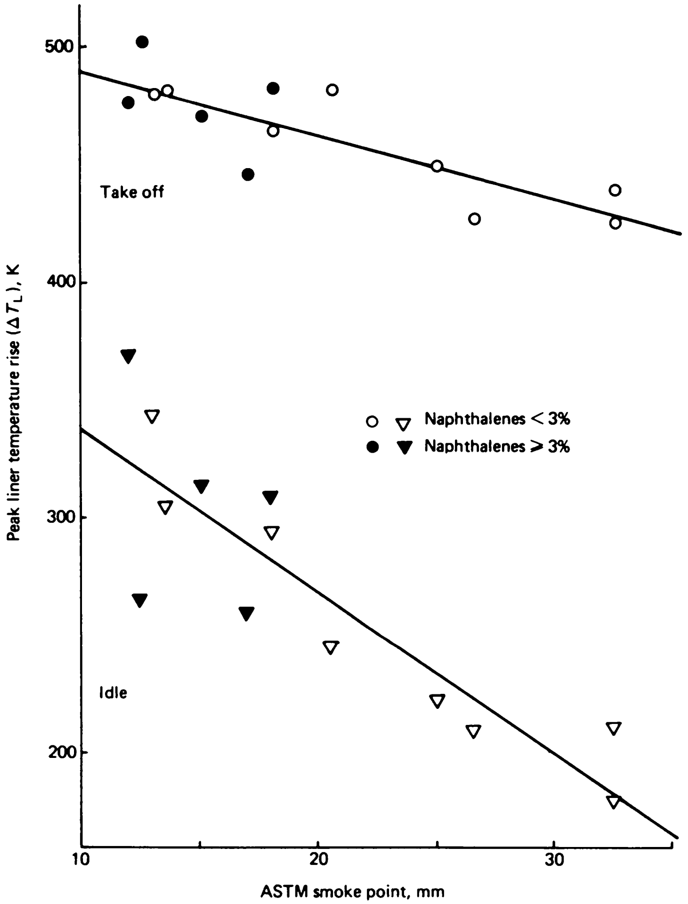


Figure 8.23 Variation of peak liner temperature rise with fuel smoke point for J79 engine (ref. 10a)

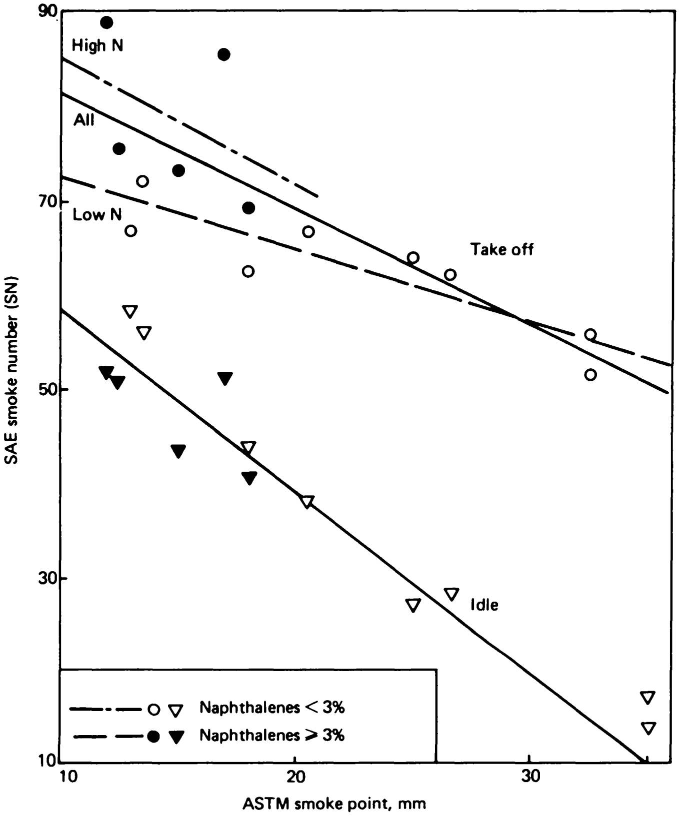


Figure 8.24 Variation of smoke number with fuel smoke point for J79 engine (ref. 10a)

Table 8.6 Aero turbine engine combustion emissions
(Derived from references 26 and 27)

(A) EPA five mode landing/takeoff cycle for P & W JT9D engine

Mode name	Mode period (minutes)	Power (%)
Taxi/idle (out)	19.0	*
Takeoff	0.7	100
Climbout	2.2	85
Approach	4.0	30
Taxi/idle (in)	7.0	*
Total period	32.9	

*Manufacturer permitted to specify.

(B) Representative EPA aero turbine engine emissions standards (thrust > 35 kN)

Emittant	lbm/1000 lbf thrust hour cycle	kg/kN thrust hour cycle
CO	3.0	306
UHC	0.4	41
NO_x	3.0	306
Smoke No.	20	20

ing control, pre-vaporised and pre-mixed systems, increasing idle fuel/air ratios by compressor air bleed, limiting combustion temperature by water injection, increased combustion temperature at idle by reduction of compressor efficiency, variable geometry combustors, and catalyst hybrid techniques.

8.4 References

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9 Development of Specifications

The history of aviation fuel specifications, both gasoline for piston engines and turbine fuel for gas turbine engines, is based on operational need and on petroleum technology to supply the quality and quantity required.

9.1 Aviation Gasolines

The original engines for aircraft of the 1903 to 1910 period operated on the lightest and most volatile material available, as it was noticeable that 'heavy' fuels resulted in hot running, and what was called 'pinking', a first observation of spark knock. To obtain this fuel, a 'high test' gasoline was demanded, which implied a low gravity. The first U.S. government specification appeared in 1907 as Navy Specification 24 G.5, and was for 'high grade refined gasoline free from all impurities, having a gravity of 70° Be, and requiring that no residue be left in a platinum dish after one hour in boiling water.'

The first World War saw dramatic advances in aircraft and engines, but fuel lagged behind. The British and French were using gasoline derived from crude oils from the Dutch East Indies and Borneo. These were aromatic crudes with up to 30 per cent of aromatics in the gasoline fraction. This fortunately had a high anti-knock value and so did not limit engine development. When the main aviation gasoline source moved to the U.S.A., after they had entered the war in 1917, aircraft engines were supplied with Grade X fuel, specified simply as having an end point of between 160 and 190°C, and consequently ran into problems with serious overheating and piston failures. The reason, not then understood, was that the British and French aviation fuels had an octane rating of 65 to 70, whereas the American fuel, mainly from Pennsylvania and Oklahoma crudes, was only 45 to 55 octane. To keep flying, the immediate remedy was to blend in up to 20 per cent by volume of benzole.

In 1918, the U.S. government issued another specification covering three grades of fuel. As before, distillation only was defined but, by 1922, the specification covered distillation, acidity of residue, copper dish corrosion, colour, Doctor test, water and sediment, and unsaturates.

In the U.K., knocking in motor vehicle engines had been noted in 1906, and was being actively investigated by Professor Bertram Hopkinson and his young assistant Harry Ricardo at Cambridge University. The understanding of the knock mechanism and of the role played by the fuel had a significant effect on aviation fuel and specifications. Ricardo went on to investigate spark knock in a single-cylinder supercharged engine of his own design, and Professor A. H. Gibson at the Royal Aircraft Factory (now Establishment) in 1915 investigated the effect by determining the minimum specific fuel consumption to cause spark knock. The discovery of the effect of air/fuel ratio on spark knock was made much later (1940) and led to the plotting of what became known as the 'Rich mixture response curve'. Work by Ricardo on variable compression-ratio engines, together with that of Midgley on his 'bouncing pin' instrument to detect differences in the intensity of knock pressures, and also his work on additives to suppress knock, culminated in the discovery of tetraethyl lead (TEL) which has remarkable anti-knock properties.

By 1930, the U.S. issued an aviation gasoline specification, including octane rating and requiring the use of TEL, and the first British specification for avgas was issued as DTD 134. This limited cracked spirits to a trace only, and stipulated that the anti-knock value be equal to a 50/50 mixture of benzene and hexane in a standard single-cylinder engine at 900 rev/min (equivalent to an octane number of 74). Benzole was limited to 20 per cent by volume because higher percentages caused freezing in carburettor jets. In 1933 this specification was replaced by DTD 224, which raised the octane level to 77. In the same year DTD 230 was issued, requiring 87 octane and permitting the use of TEL up to 4 ml/Imperial gallon for the first time. The octane number was determined in the Ethyl knock test engine.

In 1937, the U.K. Air Ministry issued its first provisional specification for 100 octane fuel. In 1938 a new test method, the rich-mixture rating, was introduced and this, as well as a lean-mixture rating, was incorporated in U.K. specifications for 100 octane fuel. It had been noted that fuels of the same lean-mixture rating behaved differently when tested under supercharged or rich-mixture conditions, and the sensitive fuels giving higher maximum power under rich conditions were preferred. The 100 octane fuel had to meet the performance of *iso*octane plus 1 ml TEL/U.S. gal when tested in a supercharged CFR engine under rich-mixture conditions. This *iso*octane plus TEL comparison became the basis of the Performance Number scale, the rating scale used above 100 octane. In 1942, the rich-mixture rating was also specified by the U.S. Army, and the grade became known as 100/125. The rich-mixture rating was then upgraded to *iso*octane plus 1.25 ml TEL/U.S. gal, and the grade became 100/130. The figure of 130 was based on the Performance Number (PN) scale, where a PN of 100 matches pure *iso*octane in a supercharged engine, and a PN of 130 would permit 130 per cent of the power available from *iso*octane alone at the mixture strength for maximum power with *iso*octane.

In July 1944, a new specification, AN-F-33, was issued for a grade 115/145, however this was not produced in quantity until 1945 when demand for 100/130 eased. By 1945, therefore, aviation gasoline had become fully developed. It could have gone higher in the PN scale, but engine development programmes now concentrated on the new gas-turbine engines, heralding a new fuel development programme. The specification starting from 'high test' grade had become sophisticated to suit the engines. Volatility was carefully controlled by Reid Vapour Pressure (RVP), together with the 10, 50 and 90 per cent evaporated temperatures and a final boiling point to cover start, warm-up, carburettor icing and vapour lock conditions, as shown in figure 9.1. RVP is the best single control for vapour lock, which occurs when sufficient fuel vaporises in the fuel system to interfere with normal fluid flow. Dissolved air in the system also contributes to vapour lock when changes in conditions reduce the solubility of the air. The 10 per cent point needs to be low for cold starts but not too low to cause vapour lock. The 90 per cent point should not be too high or power output and fuel economy will be reduced, and mixture distribution to individual cylinders will be adversely affected. The 50 per cent point needs to be low enough to ensure good fuel distribution but not so low that it aggravates ice formation in float

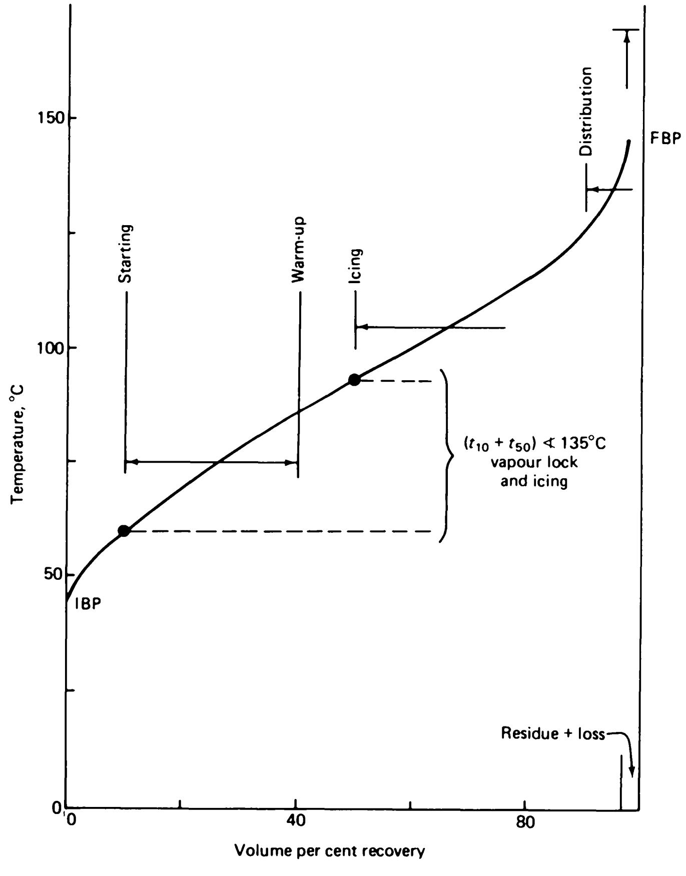

Figure 9.1 Distillation curve for aviation gasoline showing related engine performance factors

type carburettors. The sum of the 10 and 50 per cent points is kept fairly high as a carburettor icing control.

Corrosion is controlled by a low copper strip value and a low total sulphur content, and a low freezing point is necessary to prevent filter clogging and carburettor icing at the very low temperatures encountered at high altitude. Water tolerance, or the solubility of water in the fuel, must be low because water will tend to come out of solution on cooling and settle in the bottom of the tank. If this became excessive it could either be supplied to the engine in place of fuel, or freeze and prevent fuel flow. Also, since water has no energy output, its presence in the fuel lowers the specific energy of the mixture.

Gum contents are controlled because gums may deposit in intake ports or on intake valves and cause sticking. Existent gum, that is the gum already present in the fuel, is also a sensitive control check on product contamination. Potential gum is that which may be formed during extended storage, mainly by the oxidation of unstable hydrocarbons. This should ensure reasonable storage stability against oxidation and lead precipitation. Oxidation inhibitors are used in aviation gasoline to achieve storage stability by preventing gum formation.

The net specific energy of the fuel is very important for it defines the energy available for use. Heavy spark knock in aero engines causes overheating, leading to burnt valves and sticking piston rings. As described above, much time and effort from the early days have gone into means of determining this criterion, and the knock rating system with lean and rich mixtures is used to control this.

Modern specifications for aviation gasoline have not changed significantly since 1945. The number of grades available has been reduced as demand itself reduced, and the 1970s saw the phasing out of the 80/87 grade with 0.5 ml TEL/U.S. gal and the introduction of a new grade 100 called grade 100 LL. This low-lead grade meets the 100/130 specification but limits the total amount of TEL to 2 ml/U.S. gal (0.56 g Pb/litre) as opposed to the 4.6 ml TEL/U.S. gal (0.85 g Pb/litre) of the original grade 100/130. Owing to problems of sticking and burning valves, and of cracked cylinder heads in engines of light aircraft designed for grade 80 but using grade 100 LL, the grade 80 has been re-introduced into the DERD 2485 specification. Details of the current specifications for aviation gasoline are given in chapter 3.

9.2 Aviation Turbine Fuels

As the original aero piston engine operated on the gasoline that was then available, so the early gas-turbine engines were developed on a burning oil or kerosine that was then available. It was stated by one of Whittle's team in the U.K. that the gas-turbine engine was non-critical to fuel, and could run on anything from coal dust to candle ends. Although industrial gas turbines have been designed to run on heavy fuels, and attempts made to run on pulverised coal, the weight-critical aero gas turbine is also fuel-critical but in a very different way from the piston engine. It does not need a high octane fuel as its combustion is continuous with no opportunities for premature spontaneous ignition but, as the engine has developed in efficiency by increasing the pressure level in the combustor and so raising the inlet air temperatures, it has become sensitive to fuel quality.

The first effect was that these higher temperatures restricted the use of high boiling fuels which would be liable to thermal cracking with the deposition of coke in the system. Later, the fuel heat exchangers were liable to have deposits formed in them, reducing heat transfer, and this led to a need to control thermal stability. As yet, however, no firm decision had been taken on exactly what type of fuel would be used with gas turbines, and the choice was between gasoline, kerosine or gas oil. Gasoline was too volatile, causing vapour lock and boil-off at altitude, while gas oil had too high a freezing point to be used safely without the use of fuel heating. From a technical viewpoint, kerosine was a good compromise for aviation gas turbines since it had a low vapour pressure, reasonably high flash point (38-40°C), and acceptable freezing point characteristics. This type of fuel was, therefore, adopted as the main fuel for civil aircraft. The military also developed a wide-cut fuel, combining low-boiling fractions from gasoline with kerosine to increase the quantity available from a barrel of crude oil.

The history of the development of the major aviation turbine fuel specifications is shown in table 9.1. Since 1960, these have been amended several times to fit into the requirements of a changing situation, but today they are still basically those which had been developed by the late 1950s. The U.S. military adopted the use of the JP grades to denote their gas-turbine fuels. A list of these with their specification names and year of introduction is given in table 9.2. In the U.K. the government, via the appropriate ministry (originally the Ministry of Aviation and now the Ministry of Defence) has always issued specifications, and since 1947 has used a coding (originally D.Eng.R.D., but now DERD) to denote its specifications. A list of these, with year of introduction and type, is shown in table 9.3.

The original DERD 2482 in 1947, and its amendment in 1948, is shown in table 9.4, while table 9.5 shows the original DERD 2486 specification of 1951. It is interesting to compare these with the current DERD 2494 specification, which replaced DERD 2482, and the current DERD 2486 specification. The RDE/F/KER 210 fuel is also worth noting. It was a wide-cut fuel meeting DERD 2486 but restricting certain parameters thought to be critical for engine test and development type fuels. For example, the amount of aromatics was restricted to the upper end of the specification, as were the vapour pressure and total sulphur content. It is also interesting to note that the vapour pressure parameter for RDE/F/KER 210 later became, and still is, the required specification limit in DERD 2486.

As the systems developed with time, the specification, which combines engine and airframe requirements, became more critical. The specific gravity, now density, became limited. The main reason for this is that the controls in the fuel system for fuel flow are designed so that the required air/fuel ratio is achieved in the combustor. Air/fuel ratio is based on mass, but the flow controls are volu-

Table 9.1 Aviation turbine fuel development

1943	U.K. issued first specification, RDE/F/KER, with freezing point −40°C
1944	U.S. issued first specification, AN-F-32a, with typical kerosine flash point 43.8°C, but freezing point −60°C as avgas (in 1950, became JP-1 in Mil-F-5616)
1945	U.S. AN-F-34 issued, wide-cut fuel JP-2. Viscosity was restrictive, and RVP of 14 kPa gave potential explosion hazard, vapours being flammable from −7 to 27°C.
1946	U.S. evaluated two prototype fuels: Fuel A, a combination of avgas and kerosine (maximum availability on crude = 48%) Fuel B, with 38°C flash point similar to JP-1 (maximum availability on crude = 13%)
1947	U.S. Fuel A became AN-F-58A and superseded JP-2 (in 1950 became JP-3 in Mil-F-5624A) U.K. issued first avtur specification DERD 2482
1950	U.S. wide-cut fuel JP-4 in Mil-F-5624 JP-5 high-flash kerosine for Navy
1951	U.K. wide-cut fuel DERD 2486
1952	U.K. DERD 2488 high-flash kerosine for Navy (avcat)
1957	U.K. DERD 2494, as −50°C freezing point version of DERD 2482
1958	*ASTM Tech J.* published commercial specification ASTM D-1655 Grades: Jet A kerosine with −40°C freezing point Jet A-1 kerosine with −50°C freezing point Jet B wide-cut gasoline
1980	U.K. DERD 2494 freezing point raised to −47°C

Table 9.2 Grades of U.S. military fuels

Name	Specification	Year introduced	Type	Status
JP-1	AN-F-32a (Mil-F-5616 1950)	1944	Low freezing kerosine, 76°F (−60°C)	Discontinued
JP-2	AN-F-34	1945	Wide-cut gasoline	Discontinued
JP-3	AN-F-58a (Mil-F-5624 1950)	1947	Wide-cut gasoline (avgas–kerosine blend)	Discontinued
JP-4	Mil-F-5624	1950	Wide-cut gasoline	USAF/NATO
JP-5	Mil-F-5624	1950	High-flash kerosine	Navy
JP-6	Mil-F-25656	1956	Light kerosine	Obsolete
JP-7	Mil-T-38219	1965	High-flash, low-aromatic kerosine	Special fuel
JP-8	Mil-F-83133	1968	Kerosine similar to Jet A-1, −50°C freezing point	Partially replaced JP-4

Table 9.3 U.K. aviation turbine fuel specifications

Specification	Year introduced	Type	Status
RDE/F/KER	1944	Kerosine, −40°C freeze	Discontinued
DERD 2482	1947	First avtur specification, −40°C freeze	Replaced by DERD 2494, −50°C freeze
DERD 2486	1951	Wide-cut avtag	Now issue 9
RDE/F/KER 210	1951	Type test development wide-cut fuel	Discontinued
DERD 2488	1952	High-flash kerosine, avcat, −40°C freeze	Replaced by DERD 2498
DERD 2494	1957	Avtur, −50°C freeze	Now issue 9, −47°C, freeze
DERD 2498	1960	High-flash kerosine, avcat, −48°C freeze	Amended in 1966
DERD 2498	1966	High-flash kerosine, avcat, issue 3, freeze to −46°C	Now issue 7
DERD 2453	1967	Avtur/FSII	Now issue 4
DERD 2454	1967	Avtag/FSII	Now issue 4
DERD 2452	1979	Avcat/FSII	Now issue 2

Table 9.4 First avtur fuel specification, DERD 2482 (issued 1.4.47, amended 1.11.48)

Property	Min.	Max.
Water tolerance, ml		2.0
Specific gravity at 60/60°F		Not limited, but must be determined
Total sulphur, % wt		0.1
Corrosion (copper strip)		Slight discoloration
Flash point, °F	100	
Viscosity, cSt at 0°F		6
Freezing point, °C		−40
Aromatic content, % vol.		20
Heat of combustion, net Btu/lb	18 300	
Existent gum, mg/100 ml		6
Distillation, fbp, °C		300
% evap. at 200°C	20	
Total acidity, mg KOH/g		0.10

The following inhibitors may be used:
2,6-ditertiary-butyl-4-methyl phenol
N,N′-di-secondary-butyl-*para*-phenylenediamine
2,4-dimethyl-6-tertiary-butyl phenol.

Table 9.5 First avtag specification, DERD 2486 (RDE/F/KER 210 additions shown in parentheses)

Property	Min.	Max.
Acidity, mg KOH/g		0.1
Aromatics, % vol.	(15)	25
Bromine No.		3
Copper strip corrosion		No evidence of corrosion, and not more than a slight discoloration of the strip
Distillation, 10% recovered at °F		250
90% recovered at °F		400
FBP, °F		550
Vapour pressure, psi	(2.0)	3.0
Freezing point, °C		−60
Gum, existent, mg/100 ml		10
accelerated, mg/100 ml		20
Heat of combustion, net Btu/lb	18 400	
Specific gravity at 60/60°F	0.739	0.825
Total sulphur, % wt	(0.2)	0.4
Mercaptan sulphur, % wt		0.005 Doctor sweet accepted
Water tolerance, ml		2

metric. To keep the settings accurate therefore, it is necessary to limit the density.

The mercaptan content, coupled with the copper strip corrosion test, was required to protect the hot turbine section from corrosion, and also the elastomeric coatings in the fuel system. Later on, as a result of a field problem discussed in chapter 7, a silver strip corrosion test was added to some specifications to protect silver-plated parts of the fuel system from trace amounts of H_2S and elemental sulphur, which are so small that they do not affect the copper strip. A viscosity limit is set to ensure pumpability at low temperatures plus the ability to vaporise the fuel at low temperatures for a cold start or relight.

For some years a potential gum requirement was included in specifications. This was supposed to predict the gum level that would be achieved in storage with time. A series of tests was carried out in the Middle East to guarantee high average ambient temperatures in a storage tank. The fuel was held static for 5 years, being tested regularly for gum and potential gum contents. The results showed that the original potential gum determinations had no correlation with the gum content found with time. As a result the potential, or accelerated, gum content requirement has been deleted from most aviation turbine fuel specifications.

Smoke point has for many years given a correlation, not too precise but adequate, with radiant heat emissions from the fuel in the combustor. A more sophisticated method based on smoke point has also been used in the U.S. specifications. This is the luminometer number, by which the emissivity of the flame is measured and then converted into a scale which correlates with radiant heat in the combustor.

The aromatics content of fuel has had a varied career. In kerosines, it has been set at 20 per cent maximum by volume, whereas in wide-cut fuels up to 25 per cent by volume is allowed. The main reason put forward for an aromatic content control is as part of the emissivity measurement or luminosity of the flame in the combustor. This in turn is a measure of the radiant heat impinging on the walls of the combustor. The real combustion controller is the hydrogen/carbon ratio of the fuel, but until recently it had not been possible to determine this factor accurately and quickly. Now, with a simple-to-operate NMR method, the hydrogen content of the fuel may be determined in less than 10 minutes. If this method, which has been standardised jointly by ASTM and IP, were put into all specifications, an accurate knowledge of hydrogen/carbon ratio would be available which would obviate the need for aromatic content and indeed smoke point. At present the implementation of this test in specifications is being held up by objections from a U.S. aero engine manufacturer.

As discussed in chapter 7, the freezing point is a fuel characteristic affecting fuel flow from the wing tank through heat exchangers and the fuel control system on into the engine. In civil aircraft, the possibility of ice crystals, formed from water that comes out of solution as the fuel cools, entering and clogging the engine fuel filters is remote since fuel heaters are fitted which heat the fuel before it enters the filter. To keep the weight down in military aircraft, however, fuel filters are not fitted with heaters, and so an anti-icing additive is included in the specification. Anti-icing additives are fully compatible with all parts of the airframe and fuel system as well as with any other additive permitted for use in aviation turbine fuels. They function by dissolving any free water present, and depressing its freezing point. In the avtag/JP-4 and avtur/JP-8 fuels, the additive used is ethylene glycol mono-methyl ether, EGME. A few years ago this was also introduced into avcat/JP-5 fuels but has since been changed to di-ethylene glycol mono-methyl ether, di-EGME. The reason for this is that these are high flash point fuels, with a minimum value of 60°C, whereas the addition of EGME additive at the specified concentration of 0.10–0.15 per cent volume in the fuel would reduce the flash point by some 2–3°C. This meant that the refiner had to cut an even higher flash point material to meet the specification. The yield on crude oil of this product is low, and this extra restriction made its production almost impossible. The di-EGME additive has a flash point above 60°C, and so the problem is overcome. Apart from the difference in flash point, these two additives are very similar and have the same anti-icing properties.

10 Relaxation of Specifications

Specifications, as stated in chapter 5, are formed by balancing the demands of satisfactory performance, production availability and cost control that arise from the combined experience of fuel production, intermediate handling and use. As long as crude oil was readily available at reasonably low cost, the fuel quality tended to be a performance specification.

10.1 Aviation Gasoline

With aviation gasoline, the engine and fuel quality were developed together, particularly from the mid-1920s to the mid-1940s when development effectively ceased owing to the advent of the gas-turbine engine, and the specification still reflects this quality. Aviation gasoline is a special product which can only be produced from a limited number of blending components, and its specification has remained almost unchanged since 1945. Because of its special requirements, only a limited number of refineries can produce it, and as the demand reduced so the number of refineries producing it also reduced, as did the number of grades. The only significant change in specification comprised this reduction in grades, with the introduction of the 100 LL grade to replace grades 80 (80/87) and 100 (100/130). This is not a true specification relaxation since it has not changed any performance criteria. Owing to the very low volume usage, it was uneconomic to tie up tankage at refineries, depots and airfields with two grades of fuel when one would suffice. To overcome this, it was decided to remove the grade 80 (80/87), which allowed 0.5 ml TEL/U.S. gal, and replace it with grade 100 LL (100/130) with a maximum lead content of 2.0 ml TEL/U.S. gal, half the maximum permitted in grade 100.

Releasing tankage for other use, generally for aviation turbine fuel at airfields, and eliminating a grade for production and testing at refineries, has helped to keep the cost of aviation gasoline down. Its actual cost, compared with motor gasoline for example, is still high, and hence the demand from clubs and small operators to be permitted to use motor gasoline in light aircraft. Its high cost relates to the special components required to produce it, and its very low volume requirement compared to other refinery products together with its special handling needs.

10.2 Aviation Turbine Fuels

The decline in consumption of aviation gasoline has been completely overshadowed by the tremendous volume growth of aviation turbine fuel. In the U.K. alone, aviation turbine fuel consumption was some 0.4 million tonnes/year in 1955. By 1967 this had risen to 2 million tonnes/year and, in that same year, it was estimated to reach 8 million tonnes/year by the early 1980s. However, the 1973 oil crisis halted this rapid increase in volume consumption rate. Since then, even with the new more efficient engines and with fewer civil flights using larger aircraft, aviation turbine fuel consumption in the U.K. was 4.5 million tonnes in 1982. To put this in perspective, it must be realised that by 1973 the U.K. was processing just over 100 million tonnes/year of crude oil, and that by 1982 total processing was less than 80 million tonnes. That is, in spite of a reduction of over 20 per cent in crude oil refining, aviation turbine fuel is still growing in total consumption though nowhere near as high as was predicted in the late 1960s.

How does this affect specifications? Firstly, the total off-take of aviation turbine fuel per barrel of crude oil processed is rising and, with current specifications, it has a limit. Secondly, both gasoline, which is above kerosine in the distillation range, and diesel fuel, which overlaps it and is lower, are also increasing in volume. This means that transportation fuels are competing for the same section of the barrel.

If one considered aviation turbine fuel in isolation, how could the volume produced from a fixed volume of crude oil be increased? The answer is to decrease the flash point and/or increase the freezing point. In this way the boiling range, now typically 150-250°C, could be increased to, say, 130-270°C, or even 120-290°C depending on the changes made to the two parameters. This would greatly increase the volume of aviation turbine fuel available, but at what cost?

10.2.1 Flash Point

In the above approach, the first step is to decrease the flash point, that is, to lower the temperature at which the fuel can be ignited by a flame. This parameter has been introduced for safety reasons, since a lower flash point implies that fuel handling becomes more hazardous. Safety regulations in fuel storage facilities are written around flash point minima; go below these limits and tank location and construction methods change. This increases storage and handling costs as well as making the product more hazardous. The increase in hazard can become particularly significant on the many large civil airports throughout the world where aircraft are refuelled on the apron with the aircraft docked at the boarding bay, relatively close to the passengers. At the same time that refuelling is taking place many other functions, all involving people, are carried out, for example, passenger baggage being loaded and off-loaded, passenger food and drink supplies being restocked, passenger cabins being cleaned, etc. With the current specification minimum of 38°C, and with all the precautions of bonding the aircraft and refuelling system, not allowing smoking and restricting the area to essential personnel only, the operation is safe. In the U.K., even in the summer, the fuel at the time of loading is most unlikely to rise above 38°C, but this is not so at some other airports in the world. In the Mediterranean area in mid-summer, the air temperature can exceed that figure, and the fuel temperature be some 30-35°C depending on where and how the fuel has been stored. So, on safety grounds alone, should the flash point be reduced to increase the volume of fuel available? This is still the subject of much debate. There is a small section of opinion that believes that the flash point does not affect airport safety, but the majority opinion believes that it does. To what extent could a 'safe' reduction in flash point be carried out? A reduction to 35°C or even to 32°C minimum could probably be made without increasing the hazard, but it is very difficult to prove conclusively. What is known is that the present 38°C is a safe level, and that any reduction is unlikely at present, since it is not restricting production.

On the other hand, relaxations in flash point and freezing point are the most effective ways of increasing fuel availability. Studies of the fuel available, and the specification needed to meet the demand for the year 2000 and beyond, show that a decrease in flash point to 32°C would permit the current specification to be maintained in all other respects. A reduction to 35°C would increase availability by some 10 per cent, and go a long way to meeting future volume demands. It is suggested that a research programme be carried out to ascertain the effects on safety of a reduction of 3°C in flash point.

This is by far the simplest way to increase the volume availability of aviation turbine fuel. Other ways are an increase in the freezing point and the use of additives as discussed in section 10.2.2, or the incorporation of processed stocks at the refinery. At present, only virgin stocks are used in aviation turbine fuels. Both of these measures could produce the volume of fuel required in the future but, before they could be adopted, larger research programmes would be needed to ascertain their effect on combustion, combustor life and fuel systems handling equipment. Could existing equipment be modified to cope, and what effect will this have on future engine design?

10.2.2 Freezing Point

In the avtur/Jet A-1 specification, the freezing point level has been at − 50°C for many years without a problem. After the 1973 oil crisis and the resulting change in product demand pattern, however, it was predicted that the avtur/Jet A-1 grade of aviation turbine fuel was likely to be in short supply if no relaxations to the specifications were allowed. It was also shown that a small variation in the freezing point specification could significantly affect the volume of product available from a barrel of crude oil. For every 1°C relaxation in the freezing point, the volume available increases by some 3 per cent. At first, major airlines opposed any relaxation in freezing point, stating that this would restrict their operation on a world-wide basis, although the main concern was the North

Atlantic, especially for carriers who flew from Europe to Vancouver, San Francisco, Los Angeles and other points deep into the U.S.A. and Canada. It was later realised that there were very few data on minimum fuel temperatures, and that these went back mainly to a survey in 1958 on Comet aircraft! From a personal visit to the flight deck over the Atlantic, it was discovered that the aircrew had no fears of the fuel freezing during flight. IATA did start to collect data, and in the U.S.A. serious studies were instituted by NASA to determine what flight temperatures were, and what effect they had on fuel flow.

In this way, the low-temperature properties of aviation turbine fuels were being correlated, together with their consequent behaviour in aircraft undertaking long-range flights of several hours duration. Under these conditions of long cruise time at high altitude, the fuel would chill to a point where phase separation could occur. This is the critical condition, and the freezing point test defines the freezing point as 'that temperature at which crystals of hydrocarbons formed on cooling disappear when the temperature of the fuel is allowed to rise', that is, the end of the phase separation as the last wax crystal disappears. The test name is unfortunate since many people think that it is the point at which the fuel goes solid; in fact this would be closer to the pour point, a parameter not specified for aviation turbine fuels. The reason that the freezing point is so defined is because once phase separation occurs in an aircraft fuel system the wax crystals are likely to cause filter blockage which will, in turn, cause fuel starvation and engine flame out.

Following the IATA survey on flight temperatures, and a deeper survey by ASTM Technical Division J on Aviation Fuels covering the aviation and petroleum industries on the actual raising of the freezing point of Jet A-1, ASTM held a Symposium on Jet Fuel Low Temperature Requirements in December 1976 which highlighted the problem.

In the summer of 1978, civil airline fuel to −50°C freezing point did become in short supply and had to be 'allocated' to airlines, a form of rationing. This caused ill-will between certain customers and suppliers as the supply situation was not consistent and varied between locations and suppliers. This shortage undoubtedly helped the acceptance of a freezing point relaxation.

In 1978/79, both the U.K. MOD and the ASTM relaxed the freezing point of avtur and Jet A-1 respectively from −50 to −47°C. This has given the refiner the flexibility needed and, at present, this parameter does not limit supply nor have there been any operational restrictions.

In 1977, NASA held a workshop at its Lewis Research Center on jet aircraft hydrocarbon fuels technology to look beyond the then availability limitations. One of the recommendations to come out of this workshop was to investigate experimentally the freezing behaviour in a fuel tank to determine whether two-phase flow could be tolerated. Subsequently NASA let contracts to Lockheed and Boeing to study the cold flow behaviour of fuels in a simulated wing tank. The first tests were carried out by Lockheed, and the follow-up contract with Boeing was to see if the results obtained could be confirmed in a different tank simulator. Fuels for these tests were supplied by the CRC and selected from paraffinic and naphthenic crude oil sources. The CRC also carried out a variety of laboratory tests on the fuels that could be used to describe low-temperature handling characteristics. Both simulators were based on the outer wing fuel tank of a modern commercial jet aircraft, the Boeing version being constructed of material and dimensions representative of a 747 outboard main tank, whereas the Lockheed version was representative of the outer wing fuel tank of a L-1011 Tristar.

Each test tank had viewing ports, cooling panels on the upper and lower surfaces, and insulation on the other surfaces to ensure that heat transfer was confined to the upper and lower surfaces only. Provision was also made for sloshing and vibration. Thermocouples were mounted on vertical racks inside the tanks, and spaced to provide a temperature profile of the fuel. They were also attached to the upper and lower outer skins. There were certain differences in the internal arrangements of these two tanks which might affect heat transfer rates.

Ranges of different tests were carried out on both rigs. Both gave comparable results, the main points of interest being as follows:

1. A very steep thermal gradient exists between the skin and the first few centimetres of fuel, hence bulk fuel temperature lags behind skin temperature owing to the low thermal conductivity of the fuel.
2. Wax separation occurs at the fuel boundary layer as it goes below the freezing point of the fuel.
3. Slosh and vibration decrease the difference between skin and bulk fuel temperatures.
4. The approximate average of the freezing and pour points of the fuel best predicts fuel hold-up.

Future work is planned to extend the knowledge to accepted commercial flight model atmospheres, and to obtain detailed in-flight temperatures to correlate with simulator data. Another important step was to see if flow-improver additives can reduce the level of hold-up in the low-temperature boundary layer of fuels, and to investigate the optimum technique for adding heat to the fuel to avoid unacceptable hold-up during cruise conditions.

Yet another critical step, which could influence future specifications, is the desire to develop a small-scale laboratory test device with temperature gradients in the fuel sample similar to those observed in the wing tank simulators, and from this to establish the relationship to or effect of the fuel properties on hold-up.

At present, the specification test used to control low-temperature flow is the freezing point but, with the changes envisaged, is this the best form of control? Are there other methods that are less restrictive or better suited and that can assure safe aircraft operation at very low temperatures? The current standard tests available are the freezing point (D2386/IP16), pour point (D97/IP15) and cloud point (D2500/IP219). Then there is the Shell cloud/pour analyser, an automatic instrument that predicts cloud and pour points, and also the Shell cold flow test that runs a fuel from one compartment to another in a finite time.

By repeating the test at lower temperatures, the minimum temperature is found at which all the fuel will drain to the lower compartment.

The cold filter plugging point test, CFPP (IP309), cools the fuel at a rate of 40°C per hour to the test temperature, and then at 1°C intervals draws it through a 45 micrometre wire mesh filter, using a 200 mm water gauge vacuum. The CFPP is the highest temperature at which the fuel either will not flow through the filter, or requires more than 60 seconds for the passage of 20 ml.

The Enjay fluidity test (EFT) consists of two graduated plastic cylinders connected together to form two compartments separated by a brass capillary. A fuel sample is put in the lower compartment, and cooled at 4°F per hour to the test temperature. The tester is then inverted, and the volume of fuel in the lower compartment measured after 3 minutes. This test is repeated at lower temperatures until 80 volume per cent of the fuel is recovered in the lower compartment.

The Setapoint Detector (D4305) uses a small volume of fuel (6 ml) contained in a sample chamber set in an aluminium block. The fuel is circulated at 1 ml per second at 10 mm Hg pressure through a 400 mesh (33 micrometre) stainless steel filter. The aluminium block temperature is controlled by compressor refrigeration and thermoelectric cooling. The temperature at which the filter plugs or, if used manually, when the first crystal is observed, can be used to define the low temperature operating limit.

When the true relationship between fuel hold-up in wing tanks and fuel properties has been established, then will be the time to define the means of controlling this most important property. In no way must the safety of the aircraft be put at risk, but it may be that our simple and well-tried freezing point is not the most suitable test for the future to maintain safety and yet have the maximum volume of fuel available. On the other hand, it may prove to be so!

In the long term, therefore, it is necessary to establish which is the best test to define and control safely low-temperature fuel properties before predicting what the future limit should be. If the present test remains, it is likely that in some 10 years time there will be great pressure to raise the current avtur/Jet A-1 freezing point from its present -47°C to -45°C or even as high as -40°C. At -40°C, some long-distance civil aircraft would require some form of fuel heating, assuming the fuel to have the same composition that it has today. On the other hand, if flow improvers/wax crystal modifying additives prove to be successful in aviation turbine fuels, and not cause filter blockage or other problems, then the additive approach to overcome the low-temperature fuel problem could be the answer. If this were the chosen route, then the test method for predicting the low-temperature operating regime must be changed from the current freezing point test.

10.2.3 Thermal Stability

Internationally, there are still two methods of determining the thermal stability of aviation turbine fuels, the CRC fuel coker (D1660) and the Jet fuel thermal oxidation test (JFTOT), (D3241/IP323). The preferred method is the JFTOT, but ASTM still allows the fuel coker to be used in its Jet A-1 specification. In time, it is assumed that the JFTOT will be the only permitted method, together with a test temperature of 260°C.

A serious problem is created when considering relaxation of this parameter. Firstly, from a long-term manufacturing viewpoint, it would be advisable to reduce the severity of the test by reducing the test temperature. For example, the AGARD Propulsion and Energetics Panel Working Group 13 on Alternative Jet Engine Fuels has suggested a test fuel ARF (AGARD Research Fuel) which has a JFTOT thermal stability with a maximum tube temperature of 230°C. It must be explained that this is a research fuel specification and *not* a recommendation for a marketed fuel. This research fuel is recommended by the Working Group to be adopted as a baseline fuel to ensure a consistent data base among participating researchers.

Secondly, from an engine designer's viewpoint, a more advanced energy-efficient engine means higher pressure ratios and this, in turn, means higher engine temperatures. To maintain or improve on the present long life of the engine, a fuel thermal stability of current quality or even better will be required.

It is in an attempt to resolve these two differing viewpoints that the AGARD Working Group on Alternative Jet Engine Fuels has suggested using the ARF in order to see what actually happens when these new improved engines are designed and run on a fuel of controlled quality but lower in standard, with respect to thermal stability, than the current fuels.

It is not considered that the JFTOT itself will be replaced in the near future, but it could be modified. Research on new engines with specified test fuels could indicate a different trend in thermal stability. The more efficient engines could, for example, be more critical on burner nozzle fouling than overall thermal stability. This might be controlled by introducing the already available mini heated reservoir (MHR) on the JFTOT into the test standard. This involves a means of heat-soaking the fuel for 1 hour at a temperature of up to 200°C before carrying out the standard test. This pre-heat thermal stress on the fuel could help to eliminate those fuel species liable to crack easily under thermal stress and form coke on the burner nozzles. If this were so, it is directionally the way to proceed to alter, rather than relax, the specification to make it acceptable to both fuel producer and fuel user, as well as engine manufacturer.

10.2.4 Combustion Parameters

At present, the combustion parameters are controlled by specific energy, smoke point, aromatics content and naphthalene content of the fuel. As fuel becomes more scarce, the tendency is to relax the freezing point which, in effect, makes the fuel heavier by allowing more of the higher molecular mass molecules to be included. This tends to lower the specific energy and smoke point, and raise the aromatics and naphthalene contents of the fuel. None of these changes is appreciated by the airline operators and engine manufacturers who claim that this will either reduce engine life or the time between overhauls, or both. In each case this means increasing the running costs. The only airline that has carried out an in-depth study of the effect on its engines of increasing total aromatics from 20 to 22 volume per cent is United Airlines, and they have found no significant difference in operating costs and engine life since the change-over. This revives the old argument 'is the measurement of total aromatics relevant and meaningful?' The majority of aromatics in aviation turbine fuels, as presently produced, comprise some 75-80 per cent of single ringed branched-chain components which are very stable.

It is widely believed that a far better combustion parameter is the hydrogen content of the fuel. Until a few years ago, a speedy, reliable and accurate method for the determination of this parameter was not known, and so no serious attempts were made to introduce it into specifications. This situation has been altered completely by the advent of the simple-to-use nuclear magnetic resonance (NMR) apparatus, developed and produced by Newport Instruments, to determine the hydrogen content of liquid fuels.

In future, the major parameter for controlling combustion may well be the hydrogen content as determined by this NMR method. This will make total aromatic content and smoke point determinations obsolete. The specific energy will still be required since the energy available must be known. It may also be wise to include one other test to control the amount of polycyclic aromatics present in the fuel. As the number of aromatic rings in the molecule increases, so the stability decreases. The total amount of these polycyclic aromatics should, therefore, be controlled. At present there is a control on the naphthalene content, up to 3 per cent maximum. This is a very adequate test, and simple to carry out, and in all probability is all that is needed, along with the hydrogen content, to control the combustion parameter. The 3 per cent maximum could become limiting but test fuels with some 3 and 5 per cent naphthalenes have shown no deleterious effect on engine performance. Not until the 12-15 per cent level of naphthalenes was reached did adverse effects appear. It would seem, therefore, that a relaxation to 5 or 7 per cent is possible.

All of this, of course, would also depend on the lower level of hydrogen content being permitted in the specification. Current U.S. military specifications allow 13.6 and 13.4 weight per cent hydrogen, but figures for the future down as low as 13.0 weight per cent have been suggested. At present, typical hydrogen content figures for aviation turbine fuels in Europe are 13.9 weight per cent, and so the pressure to reduce below 13.6 weight per cent has not yet arrived.

10.2.5 Volatility

In discussing the possible ways of relaxing requirements for the current aviation turbine fuels, the over-riding theme was to broaden the specification. This is effectively done by reducing the flash point and increasing the freezing point, as currently defined. This, of course, will affect the volatility. At present, apart from the flash point, the only control on the avtur/Jet A-1 type of fuel is the 10 per cent maximum recovered at 205°C. This is unlikely to change, as a significant reduction in the current flash point is unlikely on safety grounds. The only other control point is the final boiling point, set at 300°C maximum. At present, with a −47°C maximum freezing point, it is difficult to achieve a final boiling point in excess of 260/265°C and so it will be a long time, if ever, before there is a need to revise this specification point. If it were to be raised, it would only be by a small amount, and a maximum of 325°C has been suggested.

With current thinking, it is most unlikely that there will be a change in the volatility specification, certainly not for the remainder of this century.

10.3 Bibliography

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F. J. Stockmer, *Experimental study of fuel heating at low temperature in a wing tank model*, NASA CR 165391, August 1981

11 Aviation Fuels from Alternative Sources

Since the earliest days of powered flight, aviation fuels have invariably been derived from petroleum, hence both the continuity of petroleum supply, and the subsequent availability of suitable alternative sources, are of concern for the long-range future of aviation itself. The events of 1973 and 1979 brought sharply into focus the finite extent of fossil fuels, together with the vulnerability of extraneous sources of supply. The fuel embargo of 1973 did, in fact, give rise to shortfalls in suitable crudes, and supplies of commercial aviation turbine fuels were maintained only by the adoption of temporary waivers, as discussed in chapter 8 which, in the event, showed no significant differences in combustion chamber liner temperatures or smoke formation[1]. These waivers were then seen to be incorporated in the subsequent specifications.

It is difficult to forecast accurately the remaining lifetimes of a non-replenishable commodity such as a fossil-based fuel in view of the many unknowns and uncertainties in the technological, economic and political futures. For resources in quantity exploitation, however, a useful comparative benchmark is given by the life index representing the years that current known resources could support current annual consumption, given by the ratio (proved reserves)/(annual consumption rate). Inaccuracies in excluding the likely increases in both reserves and consumption tend to self-cancel to some extent. It is salutary to note from figure 11.1 that currently this index for petroleum is no more than about 33 years and, apart from recent upturns, may already be in an overall decline. In the event, the actual resource lifetime of crude oil will also be influenced by the extent to which the various schemes of enhanced oil recovery (EOR) from presently producing fields are adopted, and by the suitability of existing deposits of very heavy crudes.

The diminution in resource quantity will inevitably affect product quality, as outlined in chapter 8, since the refiner will face greater restrictions on crude oil selection. This suggests an increasing need for energy-intensive cracking and reforming, both thermal and catalytic, of the heavy fractions to meet the growing demands for the lighter distillates. The depressed levels of octane quality of gasoline due to the higher proportions of unstable olefin components will lead to more severe methods of processing, particularly with the phasing down of lead additive, whereas the higher levels of aromatic content of aviation turbine

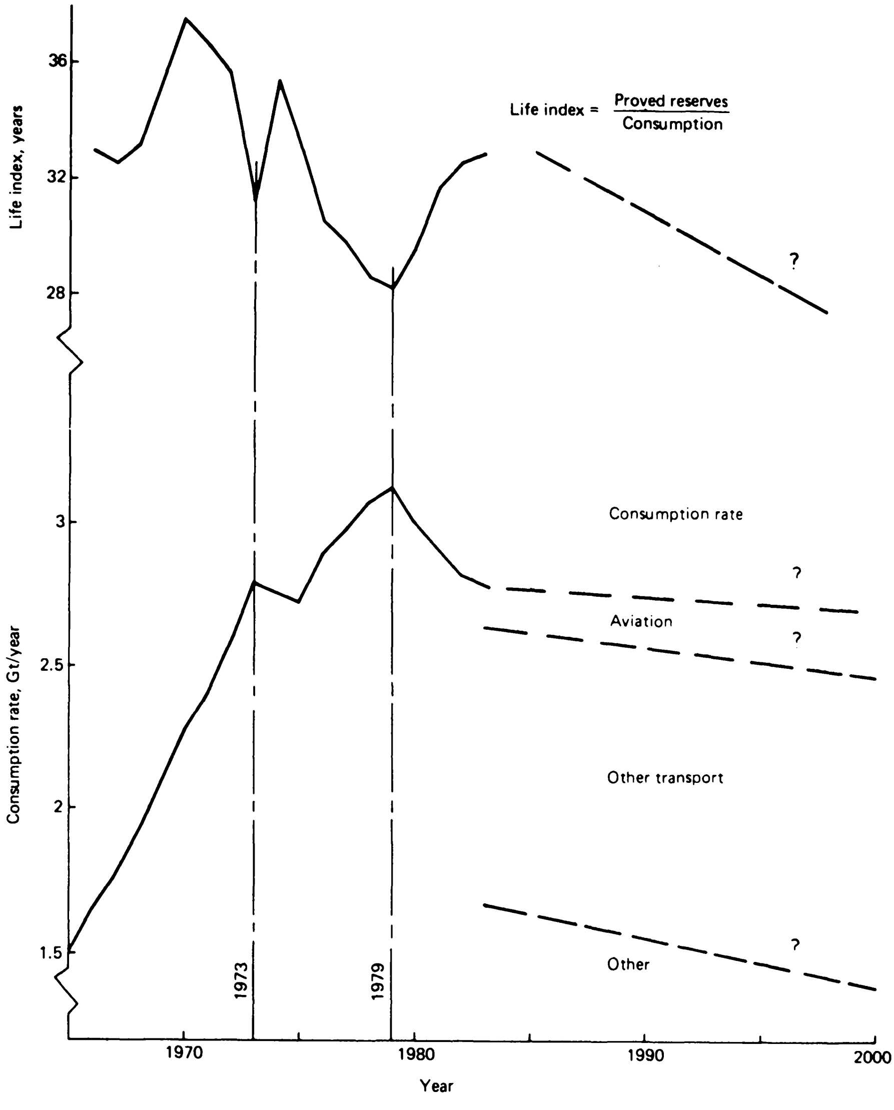


Figure 11.1 World oil annual consumption rate and life index (derived from ref. 2 and other sources). Gt = Gigatonnes = tonnes × 10^9

fuel will accentuate the handling and combustion problems discussed in chapter 8. Clearly, a demand for petroleum replacements can be expected in the not too distant future.

Crudes derived from non-petroleum feedstocks are already accepted by some refineries for blending with petroleum feedstocks, but future refineries could no doubt be designed solely for these alternative crudes. Ideally, the non-petroleum products will match the conventional fuels to such a degree that they will be completely miscible, and can be blended with them. For this reason, the non-petroleum sources and their products may be described as 'supplemental' since they supplement the pool of the conventionals. This title might be stretched to include products whose properties, although close, differ from those of the conventionals to the extent that they are not miscible with, but can be used in lieu of, with minimal changes in fuel system materials and design, or engine performance and control.

In selecting resources for such supplementals, the clear objectives are extensive resource life, together with ease of winning and economy of product production plus, of course, satisfactory combustion performance. The first objective is quantified broadly by means of the life index discussed above. The alternative resource of closest similarity to petroleum is shale oil, followed by tar, but neither of these is being exploited fully at this time. Coal, on the other hand, has long been in quantity production, and its life index of about 300 years is not only attractive but compares favourably with that of petroleum itself. The estimated reserves for all four resources are shown in table 11.1.

Table 11.1 Estimated world energy reserves, consumption and life index values
(Derived from references 2–6)

Source	Reserves (EJ)		Annual consumption (EJ)		Life index (years)
	Proved	Ultimate	1983 (%)	2000 (%)	
Natural gas	3500	11 000	56 (17)	80 (13)	63
Petroleum	3900	15 000	118 (36)	190 (31)	33
Oil shale	2000	23 000	–		
Tar sands	3000	10 000	–		
Coal	24 000	300 000	89 (28)	150 (25)	270
Uranium	11 000	3×10^8	12 (4)	100 (16)	920
*	$> 10^{12}$	$> 10^{17}$			
Renewables	–	–	50 (15)	90 (15)	–
World total	–	–	325 (100)	610 (100)	–

*Breeder reactors.

EJ = Exajoule = $J \times 10^{18}$.

Life index = (Proved reserves)/(Annual consumption).

11.1 Shale Oil

Deposits of oil-bearing shale are widespread throughout the world, and may represent the most abundant resource of hydrocarbons[7]. Large deposits with commercial potential, for example, exist in the Green River Basin of Colorado, in Alaska and in Brazil. Apart from some bitumen, which is soluble in organic solvent, the main organic content of oil shale is kerogen, a solid mixture of hydrocarbon compounds, which is found either mixed or combined with the mineral marlstone rock of the shale. Kerogens are considered to have been formed in pre-Cambrian times (600 million years ago) by anaerobic bacterial action on marine algae[8], and to have converted slowly to petroleum-like liquids under the action of very high pressures at temperatures up to about 125°C.

The industrial extraction of shale oil began in the mid-nineteenth century, and is based mainly on the acceleration of the kerogen-oil conversion by retorting at raised temperatures, coupled with the separation of the liquid oil from the solid shale. The three main techniques used are as follows:

(1) Direct above-ground retorting. The shale is mined, broken and ignited in a retort, the liquid products being condensed by cooling with fresh shale (for example, Union, and USBM).
(2) Indirect above-ground retorting. The shale is mined, broken and heated by means of an externally heated gas stream (Paraho), or by mixing in a rotating drum with hot solid balls of ceramic acting as a heat transfer medium, the liquid being condensed out, and the solid balls retrieved by sieving (for example, Tosco).
(3) *In situ* retorting. Access to the underground shale is achieved by fracturing from the surface (true *in situ*) or by mining and accurate blasting (modified *in situ*), followed by retorting conducted by top-initiated combustion, or by the supply of steam or hot gases. Some of the vaporised oil transfers at about 500°C to the surface, leaving a residue of carbon which serves as fuel for further combustion, the remaining oil condensing and being pumped from the base of the retort (for example, Garrett, USBM, Occidental & Tenneco, and Rio Blanco[9]).

The properties listed in table 11.2 show that, in comparison with petroleum crudes, shale oils tend to have higher densities, viscosities, pour points and nitrogen contents.

In general the shale oils retorted rapidly at the surface are heavier, and have higher boiling levels, less carbon, hydrogen and oxygen compared with the oils retorted slowly *in situ* which contain less residuum and thus have lower viscosities and pour points, with less sulphur, nitrogen, arsenic and iron[12].

The oil yields of shales are commonly determined by means of the Fischer Assay, in which 100 g of shale sample is heated to 500°C in 40 minutes, and held at this temperature for a further 40 minutes, the resulting vapours being condensed to oil. The method is used primarily for evaluating the resource rather than

Table 11.2 Representative properties of petroleum, shale oil and tar-derived crudes
(Derived from references 7, 10, 11, 18 and 19)

Property	Petroleum crude	Kerogen	Shale oil	Tar	Tar-derived crude	Coal	Coal-derived crude
Density kg/l at 15°C	0.84		0.92	0.94	0.88	1.35	0.99
C mass %	84.2	78.2	83.7			85.2	85.0
H mass %	12.7	10.4	10.9	10.7	12.6	5.4	9.3
O mass %	1.2	7.6	2.6			6.7	4.7
N mass %	0.1	2.6	1.9	0.2	0.03	1.8	0.6
S mass %	1.8	1.2	0.9	2.8	0.08	0.9	0.4
Viscosity, cSt at 40°C	5.1		21	3000	3.0		6.5
Pour point, °C	−7.5		14		45		17

the most appropriate extraction process. For the latter purpose, such alternative techniques as laser pyrolysis chromatography, thermal chromatography, pulsed nuclear magnetic resonance, and correlation with organic carbon or shale density, are under investigation. The oil yield averages at about 90 l/tonne, but can reach 230 l/tonne, and approach 1000 l/tonne in the highest grades of shale in New South Wales. One of the major problems involved with shale retorting is that the dense parent rock reduces to fine powder, occupying about double the initial bulk volume and complicating subsequent disposal of spent shale. This represents an advantage for the *in situ* process, but control is more difficult, and the oil yield lower. However, this may constitute the only process feasible for thick strata at very deep locations. A further problem is posed by high viscosity and pour point which makes pumping difficult at moderate temperatures.

A number of alternative methods are available for subsequent processing of the shale-derived oil. Immediate refining at the retort site permits independent control of each process, with ease of transfer of hot oil between plant units. However, the size of such plant is inevitably below optimal, and the availability of skilled manpower, as well as process water, may be difficult. The handling of small amounts of several products would be costly, and the products might not be compatible with conventional fuels. Hydroprocessing would improve the quality of the shale oil, but the hydrogen requirements would be costly. Pipeline transport to a petroleum refinery is attractive since the additional feedstock provides greater utilisation of plant. An insulated pipeline would restrict the temperature loss to about 3°C per km, and a small quantity of the oil itself could be utilised for reheating. This problem could also be eased by an initial lowering of the pour point, effected by distillation to remove the heavy asphaltenes which may then be cracked to lighter liquids, together with mild thermal cracking of the shale oil itself to break the large n-paraffin molecules, similar to the visbreaking process.

A wide-cut gasoline derived from shale by hydrogenation in a fluid catalytic bed has been found to possess properties broadly similar to those relating to the conventional oil-derived JP-4, the major differences in the former being higher concentrations of nitrogen but much lower concentrations of aromatics, olefins and sulphur[13]. Results from the copper corrosion and JFTOT tests were also promising, the more extensive hydrotreatment raising the breakpoint from about 200°C to the required level of 260°C, with reduction in the nitrogen content by an order of magnitude, and a low concentration of naphthalenes[14]. The performance characteristics of the shale-derived fuel in a test engine were comparable, with identical combustor liner temperatures.

In the U.S.A., a shale-derived aviation turbine fuel is also under test in a Pratt and Whitney F100 engine, and an accelerated test, equivalent to 1000 hours of flight, is announced in a P-W TF30 engine, together with flight tests and introduction to service use[15]. However, the most likely short-term development appears to be reduction of the pour point at the retort site to enable pipeline transfer to a petroleum refinery, followed by hydrotreatment to remove nitrogen, oxygen and sulphur, and blending of the distilled products with comparable products from the petroleum feedstock.

11.2 Tar

Tars (asphalts, pitches or bitumens) are usually found in the form of a semi-solid phase enveloping particles of water-coated sand. Extensive deposits of early Cretaceous age have been found in north-eastern Alberta, Canada, at Wabasca, Cold Lake, Peace River and Athabasca[16,17]. The last named were first reported in 1788, and explored systematically in 1897, the small plants proliferating from 1936 and leading to the start of large-scale production in 1967. The Athabasca deposits extend over an area of about 4 million hectares, and range in thickness up to about 50 m. The oil sand is primarily quartz with varying quantities of silt and finely divided clay. The mass percentage oil saturation ranges from lean (2 to 5), through intermediate (5 to 10) to rich (10 to 18), and represents some 120×10^9 tonnes of oil in place. The estimates in table 11.1 show the worldwide reserves of tar to be comparable with those of conventional petroleum.

Some deposits are exposed at the surface, but others are covered by layers up to 600 m thick, comprising scrub spruce, muskeg (organic soil), and an overburden of shale and lean sand, the tar being too viscous to migrate upwards, in contrast to petroleum. For moderately deep deposits, winning proceeds by clearing the vegetation, and ditch-draining the muskeg ready for stripping when frozen sufficiently solid to support the equipment, but not too solid to dig. The extraction process is based on separation of tar and sand by hot water[18]. The raw sand is conditioned by mixing into a slurry with hot water and steam plus sodium hydroxide for pH adjustment, in a rotating horizontal drum at about 85°C. The tar then separates by froth flotation with air, the sand and water being removed as a tailings stream. The froth is then steam-heated and diluted with naphtha in order to reduce the density and viscosity before centrifugal separation of solids, the water and the diluent naphtha being removed by distillation. The tar is then cracked thermally by a delayed coking process at about 500°C, causing deposition of coke containing the metals and part of the sulphur, the coke being used as a cracker fuel. The liquid product streams are hydrogenated to remove most of the nitrogen and remaining sulphur, and then recombined to form a derived crude stock ready for pipeline transfer to petroleum refineries for conventional processing.

Associated problems include the unavailability for recycling of much of the process water owing to the slow settling rate of the small clay particles, increasing volume of tailings sludge owing to swelling of clay in water, the presence of a film of tar on the water in the tailings pond, and the disposal of the excess coke and recovered sulphur. Typically, 65 per cent of the tar is convertible to a crude feedstock, and 5 per cent to coke, each barrel of crude representing some 2.5 tonnes of parent sand and overburden.

Since no more than about 10 per cent of tar sand deposits are sufficiently close to the surface to permit open-cast mining, long-term recovery is likely to be on an *in situ* basis. Methods of *in situ* recovery reduce the viscosity of the tar to permit its flow to the surface[19,20]. In the thermal recovery method, air is injected into the formation, and the tar is ignited by means of a subsurface heater. The combustion heat lowers the viscosity of the remaining tar, and also gives rise to some coking which upgrades the fluid collected by the production wells. Alternatively, high-pressure steam may be used on a cyclic basis, first to fracture the formation and *stimulate* the tar by heating, followed by injection of steam down one well to *displace* the hot tar-water emulsion up through a second well. Displacement may also be effected by means of an air-water drive. Other methods proposed for reducing the viscosity include the use of solvents, and of the waste heat from nuclear reactions.

The molecules of tar are of large scale, which promotes very high levels of viscosity, as shown in table 11.2, and with high proportions of both polycyclic aromatic and naphthenic rings incorporating atoms of sulphur and nitrogen. Following the initial cracking and hydrogenation treatment described above, the tar-derived crudes, which are generally free of residuals, show viscosities similar to those of petroleum, the high aromatics content, low wax content and severe hydrogenation treatment giving respectively higher densities, lower pour points and low concentrations of sulphur and nitrogen. A substantial proportion (47 per cent) of the components boils in the middle-distillate range, but only a small proportion in the ranges of gasoline and wide-cut gasoline jet fuel. Furthermore, these light fractions result from molecular cracking, and contain only limited quantities of aromatics (6 per cent) which, together with the normal structured paraffins, provide a relatively low octane number. The kerosines resulting from tar-derived crude, on the other hand, differ from the conventional petroleum-based kerosines through lower hydrogen content, specific energy and smoke point, and higher density and aromatics content (32 per cent). Nevertheless, the aromatics are almost entirely monocyclic in nature, owing to the cracking reactions, and the wax content is low, consequently the freezing point is not higher; in fact, it is typically some 10°C lower[21,22].

In these early stages of exploiting tar sands, the derived crude reaching the refinery could be mixed up to about 30 per cent with petroleum crudes to be processed for kerosines meeting the aviation specification, but some reports suggest that this proportion may be raised to 65 per cent, and that future refineries could be designed solely for these derived crudes. Such developments entail more complexity and flexibility with increased capabilities for cracking and hydrotreating. More upgrading of the tar-derived crudes may also take place on site prior to transfer to the refinery.

11.3 Coal

Coal is an organic sedimentary rock, with some inorganic materials (minerals) in admixture, formed by bacterial, chemical and geological actions on the remains of land-based vegetation. The microscopical examination of transparent slices of coal reveals the cell structure of the parent vegetation, together with fossilised fragments (macerals) of primitive tree ferns and club mosses in the case of the 300 million year old Carboniferous coals, and of more developed trees in the later 100 million year old Cretaceous coals. The former coal types are distributed widely over the Earth's surface, and therefore more closely match the regions of high consumption, whereas the latter are more limited.

The process of coalification of the original wet carbohydrate materials results in a reduction in the concentrations of hydrogen, oxygen and water, with progression through humic acid, peat, sub-bituminous and bituminous coals of increasing maturity, to anthracite of a relatively high density and carbon content. With such a variety in original source material and geological history, individual coals show variations in composition and properties, but systems of classification have been devised to identify broad types, as shown with their representative analyses in table 11.3. In view of the variable concentrations possible in ash and water, composition analyses are generally conducted on a *dry ash-free* (DAF) or *dry mineral-matter free* (DMMF) basis. Alternatively, the sample may be stored at specified temperature and humidity, and then analysed on an *air-dried* basis.

More precise methods of classifying coals include Seyler's chart of per cent mass carbon plotted against per cent mass hydrogen, the point for each sample relating to many other properties superimposed on the chart, and also the Rank Number System of the United Kingdom National Coal Board[26], and the related International System based on volatile matter and specific energy, with more detailed subdivisions. Coals are further classified according to their ability to coke (that is, to soften, swell and resolidify with shrinkage and caking), and to cake (that is, to adhere on heating). The bituminous coals with good coking properties are required for metallurgical purposes but many of the remaining hard coals, excluding anthracite, together with the less mature brown coals, are suitable for liquefaction. The liquefaction constraints appear to be minimal concentrations of 40 per cent volatile matter and 5 per cent hydrogen, with

Table 11.3 Representative composition of solid fuels by rank
(Derived from references 22, 23, 24 and 25)

Fuel	Lump density kg/l	Per cent mass DMFF						Air dried 60% RH	
		C	H	O	N	S	Volatile matter	H_2O	Ash
Wood	0.5–1.1	48.1	6.0	45.0	0.6	0.3	80	12.5	
Peat	1.2	58.3	5.7	34.0	1.4	0.6	62.7	21.7	5.5
Lignite/ brown coal	1.28	68.0	5.5	24.2	1.6	0.7	53.3	18.3	10.0
General-purpose sub-bit. coal	1.3	76.9	5.3	15.4	1.6	0.8	39.3	13.3	7.5
High volatility bituminous coal	1.35	82.6	5.0	10.0	1.5	0.9	31.7	5.3	5
Low volatility bituminous coal	1.45	89.4	4.8	3.6	1.5	0.7	19.2	1.0	4
Anthracite	1.55	92.7	3.0	2.4	1.2	0.7	7.0	2.2	3
Coke	1.88	94.1	1.4	2.3	1.4	0.8	6.5	2	7

maximum levels of 82 per cent carbon and, preferably, 10 per cent ash[27].

In structure, coal comprises platelets of carbon atoms arranged in predominantly C_6 rings, which are cross-linked by straight chains of carbon atoms. For a representative molecular platelet comprising some 27 fused rings, of which 25 are C_6 and 2 are C_5, about 9 of the C_6 rings would be partly hydrogenated with the H atoms augmented to H_2. About 2 of the rings would each incorporate an atom of nitrogen. The atomic groups bonded externally to the rings would include 4 methyl radicals, 4 hydroxyl radicals, and 4 double-bonded oxygen atoms. One or more atoms of sulphur may be bonded internally or externally.

The size and complexity of the platelets are such that the chemical bonding forces that extend beyond the molecular boundaries are relatively strong, and hold the molecules together as a solid structure with a comparatively high density. The highly aromatic nature of the carbon rings, which ranges from about 50 per cent for a sub-bituminous coal to over 90 per cent for anthracite, implies an inherently low content of hydrogen. Breaking the molecules down into smaller configurations of atoms reduces the intermolecular forces, so permitting internal movement as a liquid and, at the same time, a less dense packing and thus a reduction in density. The provision of extra hydrogen also permits the saturation of the carbon rings from aromatic to naphthenic.

The variation of hydrogen content with density for both liquid and solid fuels in figure 11.2 indicates the two fundamental steps necessary to convert a solid coal into a liquid fuel of the gasoline or kerosine type. These steps are:

(a) Rupture the very large polycyclic components of the carbon platelets of the coal structure into small molecules with weaker intermolecular bonds, permitting a liquid physical state and a reduction in density from about 1.4 kg/l to the required 0.72 or 0.8 kg/l.

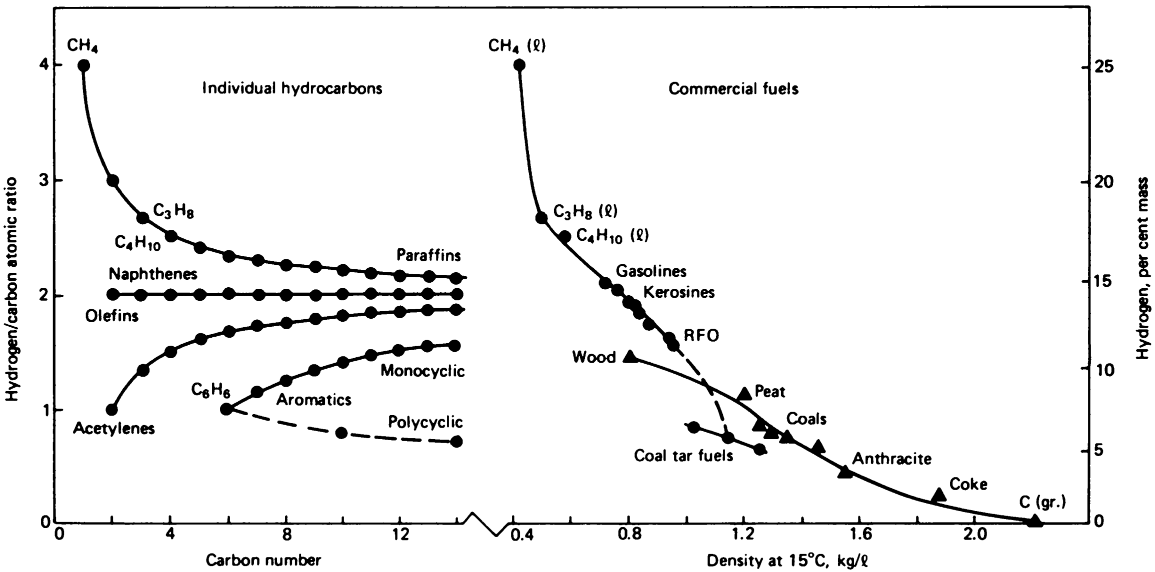


Figure 11.2 Hydrogen content of hydrocarbons and commercial fuels

(b) Increase the hydrogen mass content from about 5 per cent to the required 14-15 per cent by the addition of hydrogen and, possibly, the rejection of some carbon as char.

In the current commercial method of coal liquefaction by gasification and synthesis, and in the many alternative processes under development, these two distinct steps can generally be recognised. The relationship between these steps is understandable from the breaking of the methylene $-CH_2-$ cross-link by saturation to a methyl radical $-CH_3$.

The early German method of coal liquefaction comprised a drastic reduction in molecular size by gasification to hydrogen and carbon monoxide by heating in the presence of steam and oxygen, followed by synthesis to the molecular size and complexity appropriate to the product required. This 'indirect' system has been adopted and developed further by SASOL (South African Coal, Oil and Gas Corporation), the additional hydrogen derived from the added water permitting a product of high paraffinic content. The later methods employ a less drastic degradation of the coal platelets by heating or solution, aimed at a more direct and therefore more efficient conversion to the molecular size required. The extra hydrogen needed may be supplied during the coal decomposition (hydrocarbonisation) or during the subsequent refining of the liquid product (hydrogenation). Since many of the cyclic components of the original coal platelets endure, the resulting products tend to retain their aromatic character, depending on the extent of hydrogen added. Although the higher hydrogen content of the gasolines implies a correspondingly lower concentration of aromatics, these compounds are beneficial in relation to anti-knock quality. With kerosines, however, aromatics can give rise to problems of combustion and fuel system freezing, as outlined in chapter 8.

Molecular rupturing can be achieved either by heat or by solvent action using one of the coal-generated liquids for the purpose. The resulting products appear as mixtures of tars and pitches in the form of viscous liquids or low-melting solids. Being somewhat akin to crude oils, they are described as synthetic crudes, or syncrudes, and are then distilled and refined in the usual manner, with incorporation of the additional hydrogen. The various methods of liquefaction are outlined in table 11.4, and recent developments are discussed in reference 28.

11.3.1 Gasification plus Synthesis

The gasification-synthesis process of coal liquefaction is indirect in the sense that the large coal molecules are first reduced to their elemental components which are subsequently to be rebuilt into the required compound structures, smaller than the original. In the Lurgi process of coal gasification, coal particles down to about 3 mm diameter containing up to 30 per cent ash are heated in a slow moving, mechanically stirred chamber with steam and oxygen. Conditions are optimised, with a shift reaction, to maximise the yield of liquid products rather than char. The raw synthesis gas is then cleansed of tar, sulphur, ammonia, phenols and carbon dioxide, and its composition adjusted to give a

Table 11.4 *Coal liquefaction processes*

	Method	Examples	p (atm.)	T (°C)	%*	Yield (l/tonne*)
1. Indirect	Gasification with H_2O and O_2 to $(CO + H_2)$. Catalytic synthesis to liquids	Lurgi Fischer–Tropsch	3 30	980–1930	40	125–300
2. Direct	Catalytic carbonisation to tar, then hydrogenation with H_2 gas	Cerchar Coed Tosco Garrett	1–200	300–870	58	125–225
3. Direct	Hydrocarbonisation	Coalcon H-coal Synthoil	40–270	450–540	56	370–520
4. Direct	Liquid solvent extraction, then hydrogenation	NCB NCB supercritical	20–200	400–500	73 65	400–460
5. Direct	Combined liquid solvent extraction and hydrogenation	SRC	20–270	260–465	68	225–450
6. Direct	Hydrogen-donor liquid solvent extraction	Exxon CSF	11–200	370–480	65	270–330

*Values dependent on conditions, hence not necessarily comparable directly.

2/1 volumetric ratio of hydrogen to carbon monoxide. Initially, synthesis took place by the German Arge fixed bed process in the presence of pellets of iron-oxide–cobalt catalyst to provide normal paraffinic components for gasoline, gas oil, fuel oil, waxes and alcohols. However, increasing use is now being made of an entrained iron catalyst in the American Synthol fluid bed process (figure 11.3) which produces gaseous methane and ethene, together with a liquid similar to a light crude oil consisting largely of *iso*paraffins and light olefins, but free of the contaminants that normally accompany crude oil. In the SASOL plant, the Synthol process has been optimised for gasoline production, but could be adapted for a kerosine yield of about 30 per cent containing no more than 5 per cent aromatics.

Methane represents a viable by-product in the event of a local market for natural gas, otherwise it is reformed and returned to the synthesis input which improves the yield but reduces the overall efficiency of the process. Coals of low grade are acceptable as feedstock. A more efficient and less complex method for the conversion of coal to gasoline comprises an intermediate stage of production of methanol from synthesis gas employing well-established technology, followed by the highly selective conversion by dehydration to gasoline using a zeolite catalyst developed by Mobil[31].

11.3.2 Carbonisation plus Hydrogenation

The well-established techniques for carbonising coal to coke provide coal tar fractions as by-products. Hydrogenation then results in saturated mono- and bi-cyclic hydrocarbons which show promise as components for aviation fuels and, in comparison with standard aviation kerosine specifications, the Cerchar fractions, with zero aromatic content, showed higher flash point (53°C compared with 38°C), higher density (0.89 kg/l compared with 0.80 kg/l), lower freezing point (−60°C compared with −47°C) and much lower sulphur content (50 ppm compared with 2000 ppm)[32].

11.3.3 Hydrocarbonisation

In the Coalcon process, carbonisation takes place in an atmosphere of hydrogen gas at high pressure so that the two stages of coal liquefaction can occur together. The products leave the reactor in the gaseous phase, and are then cooled to condense as heavy oil which is distilled to yield light and heavy fractions. The hydrogen required for the process is obtained by cryogenic distillation of the gases, and by gasification of the char. Part of the gaseous and char products provide the process energy.

In the H-Coal process, the pulverised coal is slurried with recycle oil and then agitated violently with hydrogen gas by ‘ebulliation’ in a fluid bed of catalyst. In the Synthoil process, reaction occurs with a fixed catalyst bed. The production of lighter fractions is favoured by higher pressures and longer reaction times. Decompression assists in the removal of solids, and distillation provides the

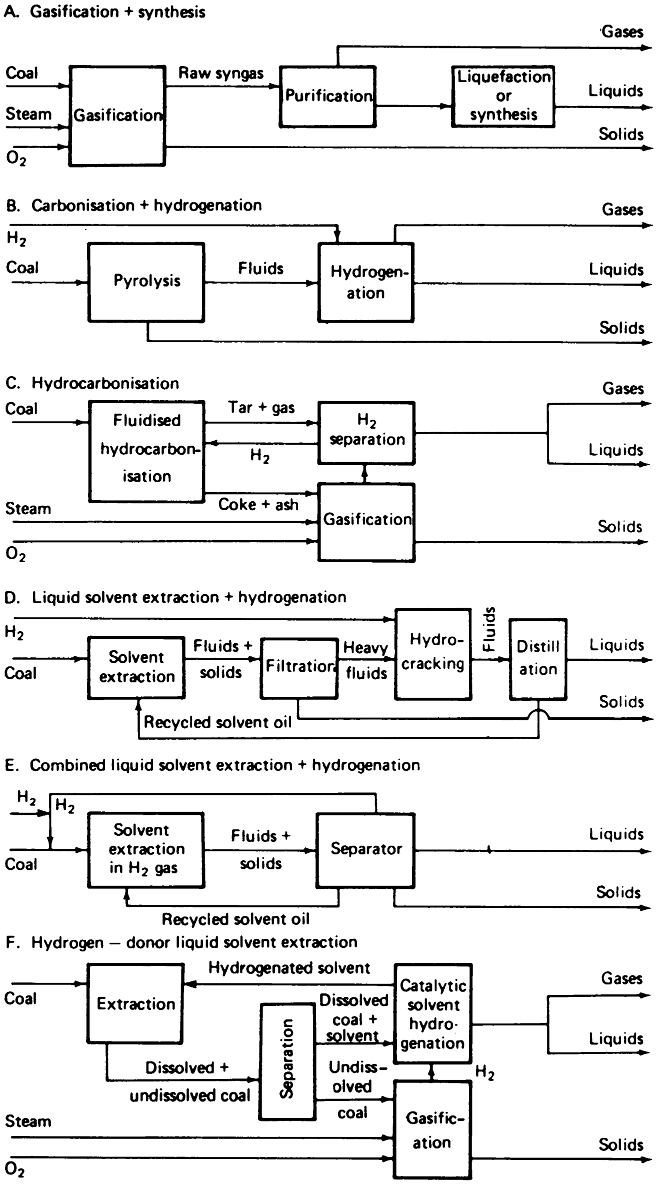


Figure 11.3 Schematic of processes for coal liquefaction (derived from refs 29, 30 and other sources)

required fractions. The remaining coal solids are mixed with fresh coal and gasified to provide the process hydrogen.

11.3.4 Liquid Solvent Extraction plus Hydrogenation

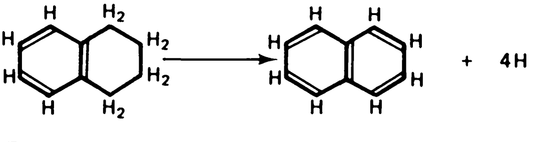
In the liquid solvent extraction process of the United Kingdom's National Coal Board, the coal is dissolved in oil, and the ash separated by filtration. The ash-free liquid is then cracked over catalysts in the presence of hydrogen to produce an oil similar to crude oil, so that standard refinery techniques can then be utilised for fractionation into transport fuels. The process is self-sustaining with regard to solvent oil, and a pilot plant to handle 2½ tonnes of coal per day is planned for operation in 1987. In a development of this process, the solvent reaction takes place at supercritical conditions which eliminates the need for filtration since condensation and release of solids occur when the pressure is reduced in a separator vessel.

11.3.5 Combined Liquid Solvent Extraction and Hydrogenation

In the Solvent Refined Coal process, the pulverised coal is slurried with a recycle oil in the presence of hydrogen gas. The coal dissolves in the oil and, at the same time, combines with the hydrogen. The solids are then filtered out, and the liquid fraction distilled to give the required products and the recovered solvent for recycling. If required, further hydrogenation can be used over a fixed catalyst bed.

11.3.6 Hydrogen-Donor Liquid Solvent Extraction

In these processes, the solvent oil is enriched with the required hydrogen before reaction with the coal charge. This technique is adopted in the Consol Synthetic Fuel process, which also incorporates secondary hydrogenation of the liquefied coal in order to produce distillate type oils. In the Exxon process[33], the separated solid residue from the main reactor is transferred to a delayed coker to improve the liquid yields. Materials suitable as donor solvents include the hydroaromatics tetralin (tetrahydronaphthalene) and hydrogenated anthracene, which dehydrogenate in the reaction to the normal polycyclic aromatic form, as shown.



Tetralin, $C_{10}H_{12}$ Naphthalene, $C_{10}H_8$

11.3.7 Coal-Derived Aviation Fuel Properties and Performance

The intrinsically high aromatic content of the gasoline fraction of the liquid fuels derived from coal is attractive since this imparts a high resistance to spark knock.

The early recognition of this feature is evident from the reference in a 1933 edition of *Hansard* to the full-scale experiment in which one home defence squadron of the Royal Air Force was flying solely on gasoline extracted from British coal[34]. Currently, its potential lies in supplementing aviation turbine fuels, and it is of interest to compare the aromatics contents with the specification limit. In fact, the aviation turbine fuels produced by the various liquefaction processes under study generally show levels of aromatics content lower than those in conventional fuels, as indicated in table 11.5. This is due to the adoption of two stages of hydrogenation in order to meet the requirements for smoke point and thermal stability. In general, the thermal stability breakpoint temperatures are found to meet the usually accepted value of 260°C at a hydrogen mass content of 13 per cent, and to increase with hydrogen content.

Table 11.5 Property differences between supplemental and conventional aviation turbine fuel fractions (comparable distillation ranges)

Property	Fuel source		
	Shale oil	Tar	Coal
Density	–	High	High
Aromatics	Low	High	Low
Naphthalenes	–	Low	Low
Olefins	Low	–	Low
Sulphur	Low	Low	Low
Hydrogen	–	Low	Low
Flash point	–	–	High
Freezing point	–	Low	Low
Smoke	–	Low	Low

An aviation kerosine derived from hydrogenated coal tar has been evaluated on a test bed and in a Mirage fighter aircraft[32], whereas a high-flash kerosine produced by the Sun Oil Company from a COED syncrude has been tested successfully by the U.S. Navy Air Propulsion Test Center using a T63-A-5A engine at sea-level conditions[35].

11.4 Resource-to-Propulsion Energy Economy

The estimated reserves of the non-petroleum fossil sources are of such magnitude as to generate considerable interest as potential sources of supplemental aviation fuels. Starting with a quantity of such an alternative source, the overall efficiency of energy conversion to aircraft propulsion appears as a product of the individual efficiencies of each process along the particular route of conversion, and these processes can be grouped as

Stage 1: resource to aircraft tanks
Stage 2: aircraft tanks to propulsion.

In stage 1, the conversion efficiency is defined as the ratio

$$\left(\frac{\text{specific energy of aviation fuel}}{\text{energy of parent resource plus refining input}}\right)$$

Table 11.6 shows these values to be roughly similar for the resources shale oil and coal. For the AiResearch-Lockheed-NASA studies discussed in chapter 12, the utilisation of the fuel energy is given in terms of kJ/seat km, and is therefore common for all three cases since aviation kerosine applied throughout. The overall efficiency from source to propulsion can then be represented inversely by the mass of parent resource required for the mission. From these values, both shale oil and coal appear as feasible replacements for crude oil, the former being more attractive on an energy economy basis.

Table 11.6 Resource-to-propulsion energy economy for aviation turbine fuel (subsonic aircraft, 400 seats, 10 190 km range)
(Derived from references 10, 36 and 37)

	Fuel source		
	Crude oil	Shale oil	Coal
Resource-to-ATF conversion efficiency, %	90	56	54
ATF-to-propulsion energy utilisation, kJ/seat km	759	759	759
Resource mass required for mission, tonne	80	140	206

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12 Aviation Fuel Substitutes

Previous chapters have indicated that petroleum, the main source material for aviation fuels, must be expected to approach exhaustion within the next few decades, and that comparable fuels may well be derivable from such alternative sources as shale, tar and coal. Much development work awaits completion before these 'alternative-source' fuels become available in sufficient economic quantities to supplement effectively the conventional aviation gasolines and kerosines. Furthermore, the price differential will clearly remain unfavourable until quantity production is established and, probably, conventional fuels continue to become more expensive.

The development of new processes to supplement conventional fuels raises the additional question of processes for *new* fuels, and this chapter reviews those materials which may be described as 'substitute fuels' in that they appear as potential replacements of conventional fuels but are virtually independent of them in terms of properties as well as source. Included in this category are any existing materials, such as methane, which are already established as conventional fuels but for some other applications. The requirements to be met by a substitute fuel concern its availability, handling qualities, combustion performance and price. Large-scale, or preferably renewable, availability is clearly desired, otherwise the evil day of eventual fuel shortage can be neither postponed significantly nor eliminated. Ideally, handling should be no more difficult or hazardous than at present, but special arrangements may be worthy of consideration. Again, comparable combustion performance is sought, but some reduction may be traded against availability and price.

The main feature of conventional aviation fuels is that, being naturally formed compounds of highly energetic hydrogen and much less energetic carbon, they exist as carbon hydrides in the form of liquids with generally good handling convenience and combustion quality. A move to methane, for example, secures a higher hydrogen content, but the normal gaseous state demands liquefaction to limit the requirement of on-board storage volume, and the high flammability both outside the combustor as well as within it draws attention to fire safety. The chemical fuel of ultimate gravimetric energy is, of course, hydrogen itself, but the handling considerations outlined above for methane apply with much greater severity, and are discussed later in this chapter. Of immediate interest are other hydrides that also contain oxygen, nitrogen or both and that, although releasing less combustion energy as a result, may offer reasonable performance with acceptable handling and good availability.

The following materials therefore offer potential as substitute fuels:

Liquefied hydrocarbon gases
Hydrogen
Hydrocarbon oxygenates; alcohols, ethers, biofuels
Nitrogen compounds of hydrogen or hydrocarbons; ammonia, hydrazine, nitromethane

12.1 Substitute Fuel Production

The primary requirement for a substitute fuel is that it should be available in adequate quantity on a long-term basis (table 12.1). This is particularly important in cases where the substitutes are derived currently from fossil sources which are themselves, of course, subject to exhaustion.

Table 12.1 Substitute fuel sources

Substitute fuel	Formula	Resource		
		Short term	Medium term	Long term
Hydrogen	H_2	NG Crude oil + H_2O	Coal + H_2O	H_2O
Methanol	CH_3OH	NG + H_2O or O_2	Coal + H_2O	Biomatter (inc. SMW)
Ethanol	C_2H_5OH	Crude oil	Coal	Biomatter (inc. SMW)
MTBE	$CH_3OC_4H_9$	Alcohols + *iso*butane	→	
ETBE	$C_2H_5OC_4H_9$			
Vegetable oils		Biomatter	→	
Ammonia	NH_3	$N_2 + H_2$	→	
Nitromethane	CH_3NO_2	NG + HNO_3	→	

NG = natural gases.
SMW = solid municipal wastes.

12.1.1 Liquefied Hydrocarbon Gases

The lightest hydrocarbon gas, methane (CH_4), comprises the major component of the various natural gases deposited worldwide either as free gas or in association with petroleum. Useful quantities can also be derived from the degassing of coal. Having evolved from organic deposits, natural gases also contain some higher hydrocarbons together with traces of inert nitrogen, carbon dioxide and/

or hydrogen sulphide, depending on the geological location and history. Natural gases from fields within the North Sea, for example, contain relatively small proportions of higher hydrocarbons (4.6 per cent) with no hydrogen sulphide, and are consequently categorised as 'dry' and 'sweet'. In comparison with methane itself, the small quantities of higher hydrocarbons, nitrogen (1.8 per cent) and carbon dioxide (0.3 per cent) together give an increase in density of 8 per cent, and in energy density of 4 per cent, with a reduction in specific energy of 4 per cent.

Other natural gases range in composition from almost pure methane (99.5 per cent, Ravenna, Italy), through the wet gases (27.8 per cent C_xH_y, Kuwait), the high nitrogen-content gases with correspondingly low energy density (14.3 per cent N_2 and 29 MJ/m^3 net, Groningen, the Netherlands) and the high carbon dioxide-content gases (44 per cent CO_2, Kapuri, New Zealand), to the sour gases (15 per cent H_2S, Lacq, France). The treatment of natural gas comprises the separation of the higher hydrocarbon condensates and water, first at the well head and subsequently by refrigeration treatment or desiccants to give appropriate dew points. Carbon dioxide and hydrogen sulphide may be removed by alkaline scrubbing or adsorption, or the latter sweetened to innocuous organic disulphides, the nitrogen usually being left untreated. Alternatively, carbon dioxide may be converted to methane and water by a process of methanation using hydrogen. Supplies of natural gas can, in fact, be supplemented by the processing of other hydrocarbon feedstocks, as with the steam reforming of light hydrocarbons, hydrogasification of middle distillates and partial oxidation of residual oils and coal to give supplemental natural gas (SNG)[1]. Methane may also be derived from solid municipal waste, and from biomatter generally. Extensive quantities of methane, mostly of non-fossil origin, are postulated in the form of ice-like solid hydrates within the molecular cavities of water, representing a volume storage potential six times that of methane gas, and a supply resource for some 30 000 years. A theory is also being explored for the existence of vast deposits of methane gas from below the biogenic depths of the Earth's mantle which promote an outgassing leading to earthquakes, mud volcanoes and giant tidal waves, and could be of sufficient magnitude to sustain the present rate of hydrocarbon consumption for about a million years[2].

In order to condense methane to the liquid phase required for storage and transport applications, cooling is necessary to the boiling point of −161°C at 1 atmosphere. In general, liquefaction of gases is effected by several cycles of compression, cooling and expansion but, in the case of methane, the required levels of pressure and of volume for the vaporisation of the refrigerant would be excessive. The more satisfactory approach is to cool the methane in stages by means of a cascade of refrigerants, typically propane, ethene and methane gas, which are themselves chilled by compression, water-cooling and vaporisation, following expansion through throttling valves within closed circuits. With natural gas, the heavier hydrocarbons accompanying the methane may themselves be condensed from the feedstock in a modified cascade, and used as refrigerants for cooling the methane[3].

The two heavier hydrocarbons, propane (C_3H_8) and butane (C_4H_{10}), are generally described as petroleum gases since they exist as components of crude petroleum. The principal treatment of petroleum gases comprises the removal or sweetening of mercaptans in order to eliminate both obnoxious odour and corrosive potential. Since the critical temperatures are well above ambient, both fuels exist as vapours at atmospheric temperature, and can be liquefied by compression, the vapour pressures at 15°C being 780 and 290 kPa (7.7 and 2.9 atm.) for propane and butane respectively. Commercially they are marketed as Liquefied Petroleum Gases (LPG) either as propane, butane or mixtures of the two, the last named being popular as bottled gas for cooking since, in cold weather, butane alone will not vaporise readily enough to supply the volume rate needed.

12.1.2 Liquid Hydrogen

In the laboratory, small quantities of hydrogen gas may be generated by simple reactions of certain metals with acids or bases of suitable reactivity, or with steam. In industry, however, hydrogen gas can be released from methane by decomposition, jointly from hydrocarbon fuels and water by steam reforming or partial oxidation, or from water alone by reaction with iron oxide, or by decomposition using electricity, heat or solar radiation (table 12.2). Where catalysts are involved, prior desulphurisation of the fuel is necessary to prevent catalyst poisoning, and is achieved by adsorption on activated carbon, or by conversion to H_2S and absorption in hot zinc oxide.

The decomposition of methane is effected in the presence of a heated catalyst. The resulting carbon deposits on the surface of the catalyst, which is transferred to a regenerator where the carbon is burnt off, in a similar way to the practice of catalytic cracking. The regenerated catalyst, which is raised to the temperature level for reaction by means of the combustion heat, is then returned to the reaction vessel for further duty. In the steam reforming of methane or naphtha, using a nickel catalyst, the endothermic heat required for decomposition is provided by burning part of the feedstock externally, and the resulting carbon monoxide co-product is then converted with further steam to additional hydrogen and carbon dioxide, the latter being removed by liquid countercurrent scrubbing and, finally, methanation. A substantial proportion of the resulting hydrogen is derived from the steam, as follows

Methane, CH_4 $\quad CH_4 + 2\,H_2O \rightarrow 4\,H_2 + CO_2$

Naphtha (CH_2 empirically) $\quad (CH_2) + 2\,H_2O \rightarrow 3\,H_2 + CO_2$

In the partial oxidation of light fuels catalytically at low temperature, or of a wide range of gaseous to less reactive solid fuels at high temperature without catalysts, the required heat is evolved within the reactor by partial combustion of the feedstock with oxygen in the presence of steam to produce a mixture of hydrogen and carbon monoxide (syngas) as in the reforming process. The water gas reaction and carbon dioxide scrubbing then follow, as before. Autothermal equilibrium is achieved by balancing the exothermic oxidation with the endo-

Table 12.2 Production of hydrogen
(Derived from references 4-8)

Reactant	Process	p (atm)	T (°C)	% H_2 from H_2O	H_2 purity	η (%)
NG	Thermo/catalytic decomposition	1	950-1000	0	95	
NG to naphtha + H_2O	Catalytic steam reforming	25	900-1000	50-65	98	75
NG to naphtha + H_2O + O_2	Catalytic partial oxidation	25	1200-1300	52		
NG to RFO, coals, coke, char + H_2O + O_2	Non-catalytic partial oxidation	Any	700-2000	60-83	98	60
CO from above reaction + H_2O	Water gas shift reaction			100		
CO + H_2O + Fe	Steam-iron thermal decomposition	15	1500-2000	100	99	65
H_2O	Electrolytic decomposition	1		100	99.8	57-72*
H_2O	Thermal decomposition	1		100		50
H_2O	Photolytic decomposition	1		100		
H_2O	Photobiological decomposition	1		100		

*Approximately 27% overall, including efficiency of electrical generation at power station.

thermic steam reforming reaction, and the overall reaction appears as in the following examples

Residual fuel oil ($CH_{1.8}$ empirically)

$$(CH_{1.8}) + 0.51\ O_2 + 0.98\ H_2O \rightarrow 1.88\ H_2 + CO_2$$

Coal ($CH_{0.8}$ empirically)

$$(CH_{0.8}) + 0.7\ O_2 + 0.6\ H_2O \rightarrow H_2 + CO_2$$

In the steam-iron process, hydrogen is released from the steam by oxidation of iron to FeO and to Fe_3O_4, both of which are then reduced with carbon monoxide to the original states plus carbon dioxide. The carbon monoxide itself is derived with additional hydrogen from the gasification of coal in steam and air. Since the oxidation and reduction take place in separate zones within the reactor, the product hydrogen contains only traces of carbon monoxide, carbon dioxide and nitrogen, and no shift reaction is necessary. Furthermore, the thermal energy remaining in the reducing gases can be utilised to generate electricity, but the process depends on the handling of two solids, coal and iron oxide.

Water alone may be decomposed by providing the quantity of energy that will be released by subsequent combustion in service. This energy input may be derived by electrolytic, thermal, photolytic or photobiological means. In electrolysis, a direct current is passed between two electrodes separated by a water-based electrolyte which must have a high ionic conductivity. This can be achieved by adding an acid (sulphuric), base (potassium hydroxide) or possibly a salt (sodium chloride) as an ionisable solute to augment the relatively few ions (H^+ and OH^-) arising from water itself. In practice, a concentration of about 30 per cent potassium hydroxide is preferred in order to avoid corrosion, with electrodes of nickel-plated mild steel or platinum-plated nickel, the surface areas of which are increased by sintering, finning, perforating or chemical roughening. Advanced designs incorporate water-saturated solid polymeric electrolytes comprising acidic resins, with electrodes of tantalum or gold. Hydrogen gas collects at the cathode, and oxygen at the anode, mixing of the two gases being prevented in the aqueous cells by a woven asbestos separator which is porous to the electrolyte and the passage of ions.

As indicated above, the energy required for electrolysis is equal to the enthalpy of reaction of $H_2(g) + \frac{1}{2} O_2$ (g) to H_2O (g), which is also equal to the enthalpy of formation of water vapour, that is

$$\Delta H_r^0 . H_2\ (g) = \Delta H_f^0 . H_2O\ (g) = -\ 241.83\ kJ/mol$$

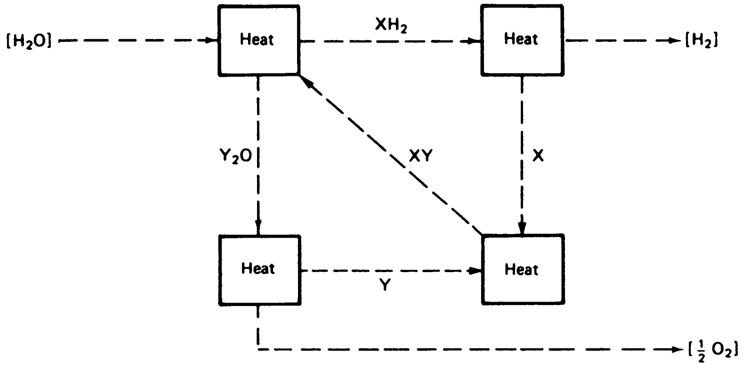
However, only the portion of this quantity represented by the Gibbs free energy of formation, given by

$$\Delta G_f^0 . H_2O\ (g) = -\ 228.59\ kJ/mol$$

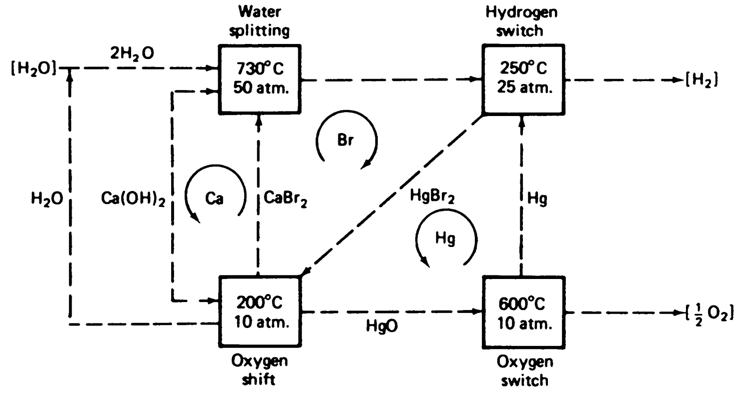
is required to be supplied as electrical energy, the remainder deriving as heat either from the environment or from the electrical losses within the cell itself. Theoretically, at 25°C this condition would hold at an applied potential of 1.23 V, whereas all the input energy would be supplied as electricity at 1.48 V.

In order to achieve realistic production rates in industry, however, high currents per unit area of electrode are used by means of over-voltage, despite the reduction in conversion efficiency. Furthermore, the overall efficiency of the production of hydrogen gas is affected adversely by the relatively low efficiency of thermal-electrical energy conversion in the generating station providing the energy for electrolysis. Large-scale production of hydrogen by electrolysis is established only in the vicinity of low-cost hydroelectric power, as in Norway, Egypt, Canada and Iceland.

Rather than follow the above thermal-mechanical-electrical energy conversion route, higher overall efficiency should be obtainable by the direct use of thermal energy, particularly if it would otherwise go to waste. However, a temperature in excess of 2500°C would be necessary for any significant extent of decomposition of water within a single step. Very many multi-step processes have been proposed within the temperature levels available from nuclear reactor coolants. Figure 12.1 shows the basic process reactions for one approach, together



(a) Schematic of Funk and Marchetti system with generalised components X and Y



(b) Schematic of de Beni MKI system

Figure 12.1 Thermochemical water splitting (derived from ref. 9) with an early concept involving closed circuits of calcium, bromine and mercury. Other proposed systems are based on iron, chlorine and oxygen, and on combinations of caesium, magnesium, chromium or copper. A hybrid thermochemical-electrochemical cycle has also been proposed using sulphur and iodine. Very few of these processes now appear to have realistic potential for industry.

The photolytic production of hydrogen is based on the decomposition of water using the energy of light. Since water is transparent, the incident light is absorbed through the electronic excitement of salts, semiconductors or dyes acting as photocatalysts. In vegetation of the blue-green algae types, the generation of biological cell material from carbon dioxide and water under the action of sunlight is accompanied by the release of hydrogen. Approaches on the above lines, including the combination of two systems, currently form the bases of several research projects.

Prior to liquefaction of gaseous hydrogen, the contaminating gases are removed by condensation, by absorption in liquid methane, or by adsorption on some solid reagent. Owing to the facts that hydrogen molecules exist in either an *ortho* or *para* form, depending on the relative direction of their nuclear spins, and that the spontaneous *ortho-para* conversion releases more than sufficient energy to vaporise an equal mass of liquid hydrogen, the *para* form is essential for long-term storage, and is effected up to about 95 per cent by the use of a catalyst such as ferric oxide. In most gases, liquefaction is achieved by isothermal compression, followed by equal-enthalpy expansion across a throttling valve, the cooled gas then being used to lower the temperature level of subsequent compression and expansion stages, until expansion occurs below the critical point. The expansion of hydrogen, however, incurs a *rise* in temperature unless the initial temperature is below the inversion value of 205 K, subsequent expansions then lowering the temperature to the boiling point of 20.2 K. Initial cooling to the inversion level is achieved by means of liquid nitrogen boiling at 77.2 K. Industrially, liquefaction of hydrogen is customarily effected by expanding the cooled gas to produce work in a centrifugal expander or, in some instances, a non-lubricated reciprocating expander.

12.1.3 Hydrocarbon Oxygenates

Of the hydrocarbon oxygenates, methanol, CH_3OH, was formerly extracted from such natural plant materials as wood by destructive distillation (hence, 'wood alcohol'), but the introduction of synthetic processes has led to large-scale production by thermal reforming of natural gas with steam to syngas, comprising hydrogen, carbon monoxide and carbon dioxide which is then synthesised to methanol over a catalyst. Alternatively, the methane may be oxidised directly to methanol.

In the medium to long term, synthesis gas may be generated by the gasification with steam of solid fuels such as coal, lignite or peat. Direct oxidation of methane may be possible by reaction with sulphur trioxide in liquid sulphuric acid. Future process routes to syngas may also include the partial oxidation of renewable sources such as wood, straw and biowaste, and also the separation of inorganic carbon dioxide from atmosphere or oceans, followed by reduction and combination with water. Synthesis of carbonate solutions by radiation or electroreduction has also been proposed.

The next member of the monohydric alcohol group, ethanol, C_2H_5OH, is produced by synthesis from oil- or coal-derived ethene, C_2H_4, with water, or of syngas, but interest is increasing in production by hydrolysis and fermentation of the carbohydrates from a variety of vegetable sources. These include the starches of artichokes, potatoes, cassava and cereal grains (hence 'grain alcohol'), the sugars from sugar cane, beet, sweet sorghum, fruit juices and molasses, the cellulosic materials from wood, tropical grasses, and straw, and the waste sulphite liquor from the production of wood pulp from paper mills.

More recently, both methanol and ethanol have been considered as feedstocks with *iso*butane for the production of methyl tert-butyl ether (MTBE), $CH_3OC_4H_9$, and also ethyl tert-butyl ether (ETBE), $C_2H_5OC_4H_9$.

Biomatter comprises all natural materials associated with living organisms, and consists largely of carbohydrates, for example, cellulose $[C_6(H_2O)_5]_n$. It therefore forms a logical source of methane, hydrogen and such hydrocarbon oxygenates as alcohols, as discussed above. On a global basis, an estimated 150 gigatonnes of vegetable biomatter is generated annually, much of it in the wild state. The total mass of vegetation existing per unit area at any instant is properly termed 'biomass', usually expressed in units of tonne per hectare (t/ha), and the total mass harvested *per annum* is 'biomass yield', in t/ha a. This ranges from the relatively small-scale collection of agricultural wastes, through the direct harvesting of naturally seeded vegetation, to energy farming by the purposeful cultivation of crops optimised for both food and energy rather than either alone. Energy crops of interest include the alcohol biosources listed above, together with giant kelp and blue-green algae. Current biomass yields extend from about 13 t/ha a for water hyacinth (Mississippi) to 120 t/ha a for napier grass (Puerto Rico), with an average dry value of about 23 t/ha a[10]. Biomatter is also generated continually in the form of municipal wastes and manure.

The oil extracted from vegetation may also serve as fuels via a more direct route. These vegetable oils comprise natural esters of the trihydric alcohol glycerol ($HOCH_2CHOHCH_2OH$), with the long straight-chain fatty acids (RCOOH), where hydrocarbon radical R varies from about $C_{15}H_{31}$ to $C_{17}H_{35}$, the approximate concentrations being 12 per cent paraffinic and 87 per cent olefinic (including 68 per cent diolefinic). They are extracted by pressing from the parent seed, flower or fruit, followed by degumming and, if confirmed by satisfactory combustion performance, may not need the complex and energy-consuming process of conventional refining.

Some species of vegetation, particularly the *Euphorbiaceae*, have been found that extend the carbon dioxide-to-cellulose process to produce hydrocarbons in the form of latex sap of relatively low molar mass, and further development may permit a useful oil yield by tapping the main stems, as in the harvesting of rubber[11]. Certain green algae may also be converted to hydrocarbons, to the extent of 75 per cent of the dry mass.

12.1.4 Hydrogen-Nitrogen Compounds

Ammonia, NH_3, is mostly manufactured by reaction of coal-derived ammonium carbonate with calcium hydroxide, but could be produced by the direct synthesis of hydrogen and nitrogen as in the Haber-Bosch catalytic method. Hydrazine, N_2H_4, is produced by oxidation of ammonia or urea with sodium hypochlorite, as in the Raschig catalytic process, but the developments by Bayer involve ammonia, chlorine and a ketone.

Currently, nitroparaffins, RNO_2, are produced by nitration of hydrocarbon feedstocks with nitric acid.

12.2 Properties of Substitute Fuels

The second major concern with substitute fuels is a comparison of their properties with those of the conventionals, since similarities will permit minor changes only in handling and performance, and also in the design and constructional materials of fuel systems and engines.

On the basis of density (table 12.3A), liquid hydrogen is seen to be outstandingly low, with liquid methane about half that of the conventionals, and hydrazine and nitromethane about 40 per cent heavier. The boiling points for liquid hydrogen, and to a lesser extent for liquid methane, are also very low, whereas those for the substitutes, with the exception of ammonia, lie within the conventional distillation ranges. The melting and/or freezing points of hydrazine and nitromethane lie above those of the conventional fuels, all the remaining values lying below. The kinematic viscosities appear either similar or, in the case of hydrazine and ammonia, significantly lower. Relatively high enthalpies of vaporisation are seen for the nitrogen hydrides and alcohols, and high specific heat capacities for hydrogen and ammonia.

The specific energies of all the fuels given in table 12.3B show a broadly direct dependence on hydrogen content, following the very high level (120 MJ/kg net) for hydrogen itself. The energy density of liquid hydrogen, on the other hand, is very low (8.5 MJ/l) owing to the low level of density (0.071 kg/l), but the energy densities of the substitutes do not reflect any clear relationship with hydrogen content. All fuels containing oxygen and/or nitrogen, of course, show lower levels of both specific energy and energy density. These points are brought out by extending the density abscissa in figure 5.4 in both the low and high directions, as in figure 12.2.

While accepting that some performance penalty may be traded against security of supply, the question arises as to the extent of power loss that may arise from the lower energy fuels, some of which may seem unworthy of further consideration at this stage. However, the fact that combustors consume mixtures of fuel and air rather than fuel alone leads to an energy analysis based on the fuel-air mixture. For convenience, a stoichiometric mixture has been assumed in each case, but comparable conclusions would be expected at any other consistent equivalence ratio.

Table 12.3A General properties of aviation fuels and substitutes

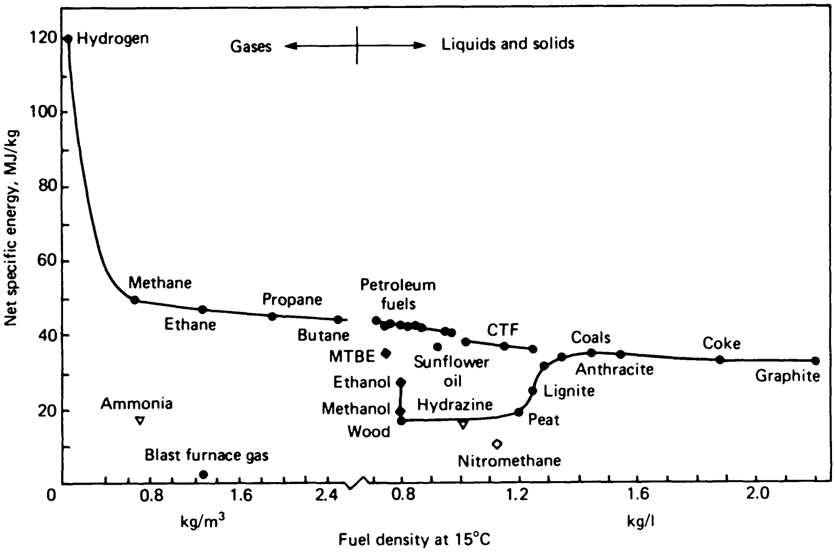
Fuel	Formula	Density at 20°C (kg/l)	Boiling pt or range (°C)	Melting pt or pour point (°C)	Viscosity at 40°C (cSt)	Vapour pressure (bar) at 20°C	Vaporisation enthalpy at 37.8°C (kJ/kg)	Specific heat capacity at mid boiling range (kJ/kg K)
Avgas	$C_{7.3}H_{15.3}$	0.72	46–145	− 65	0.50	0.245	292	2.04
Avtur	$C_{12.5}H_{24.4}$	0.80	144–252	− 48	1.10	0.001	207	1.94
Hydrogen	H_2 (l)	0.071*	− 252.7	− 259.1	0.18*	–	450	8.7*
Methane	CH_4 (l)	0.424*	− 161.5	− 182.3		–	512	3.9
Methanol	CH_3OH	0.796	64.7	− 97.8	0.55	0.128	1080	2.5
Ethanol	C_2H_5OH	0.794	78.5	− 114.9	1.10	0.059	845	2.4
Methyl tert-butyl ether	$CH_3OC_4H_9$	0.74	55	− 109		0.299	330	2.05
Ammonia	NH_3 (l)	0.615	− 33.4	− 77.7	0.20	8.6	1370	4.7
Hydrazine	N_2H_4	1.013	113.5	1.4	0.70	0.014	1254	3.1
Nitromethane	CH_3NO_2	1.123	101.1	− 28.5	0.47	0.080	564	1.8

*At boiling point.

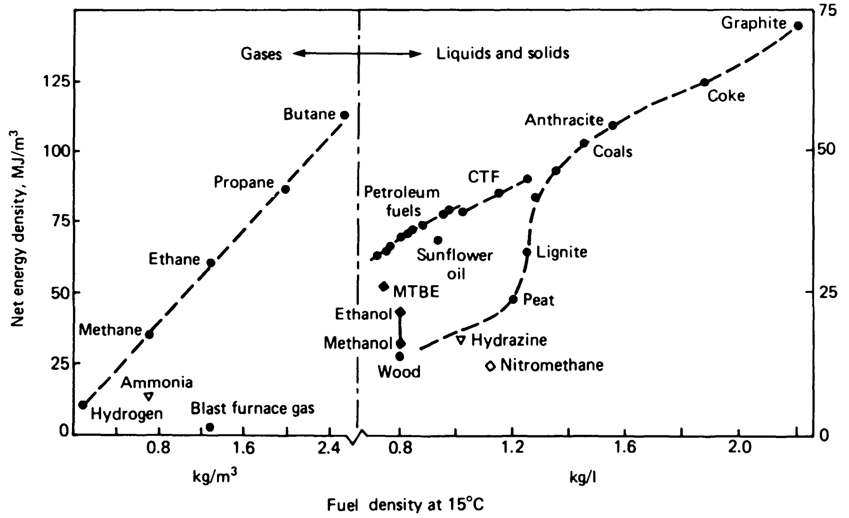
Table 12.3B Combustion properties of aviation fuels and substitutes

Fuel	Hydrogen (% mass)	Specific energy (MJ/kg)		Energy density net (MJ/l)	(A/F) mass		Flash point (°C)	Minimum ignition energy (mJ)	SIT (°C)	Research octane number
		Gross	Net		Stoic.	Flamm. range				
Avgas	14.97	47.4	44.2	31.8	14.9	26–4	–40		427	100/130* or 115/145*
Avtur	14.05	46.4	43.4	34.7	14.7	22–4	47	0.30	255	–
Hydrogen	100	142.4	120.2	8.4	34.2	345–5	–	0.019	574	
Methane	25.13	55.5	50.0	21.2	17.2	34.3–10.2	–	0.28	540	105
Methanol	12.58	22.7	19.9	15.9	6.5	12.6–1.6	15	0.19	385	114
Ethanol	13.13	30.2	27.2	21.6	9.0	18.5–2.7	14	0.65	365	111
Methyl tert-butyl ether	13.72		35.10	25.98	11.73	20.2–3.6			435	
Ammonia	17.76	22.4	18.6	11.4	6.1	8.9–4.6	–62	7.5	651	120
Hydrazine	12.58	19.4	16.7	16.9	4.3	18.3–0	52		270	110
Nitromethane	4.95	12.0	10.9	12.3	1.7				419	

*Performance number



(A) Specific energy



(B) Energy density

Figure 12.2 Variation of net specific energy and energy density with fuel density

Expressing the combustion heat with symbol Q, and the related air and fuel masses as A and F gives the following expression for heat released per unit mass of fuel–air mixture

$$\frac{Q}{(A+F)_s} = \frac{Q/F}{(A/F+1)_s}$$

where subscript s represents stoichiometric. In terms of masses, the numerator on the right-hand side, Q/F, is the specific energy of the fuel, discussed above. Any variation between fuels in the specific energy of their stoichiometric mixtures therefore depends on the relationship between specific energy of the fuel and its stoichiometric air/fuel ratio. Figure 12.3 shows this to be almost linear for a very wide range of fuels, including solid, liquid and gaseous, both conventional and substitute. It follows, therefore, that the specific energy of stoichiometric mixtures of all these fuels will vary very little from an average value, shown in figure 12.4 to be about 2.98 MJ/kg stoichiometric mixture. A similar situation

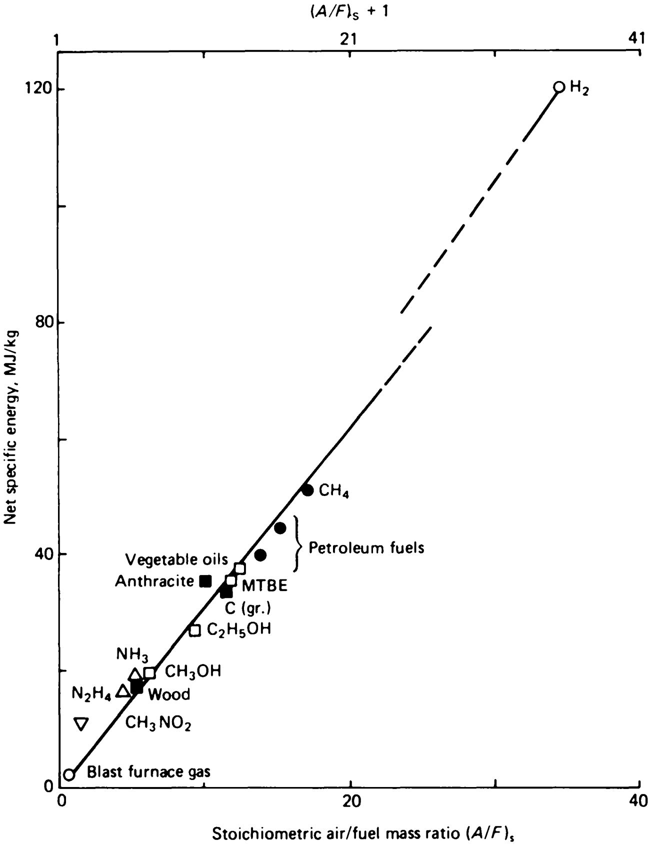


Figure 12.3 Relationship of net specific energy with stoichiometric air/fuel mass ratio

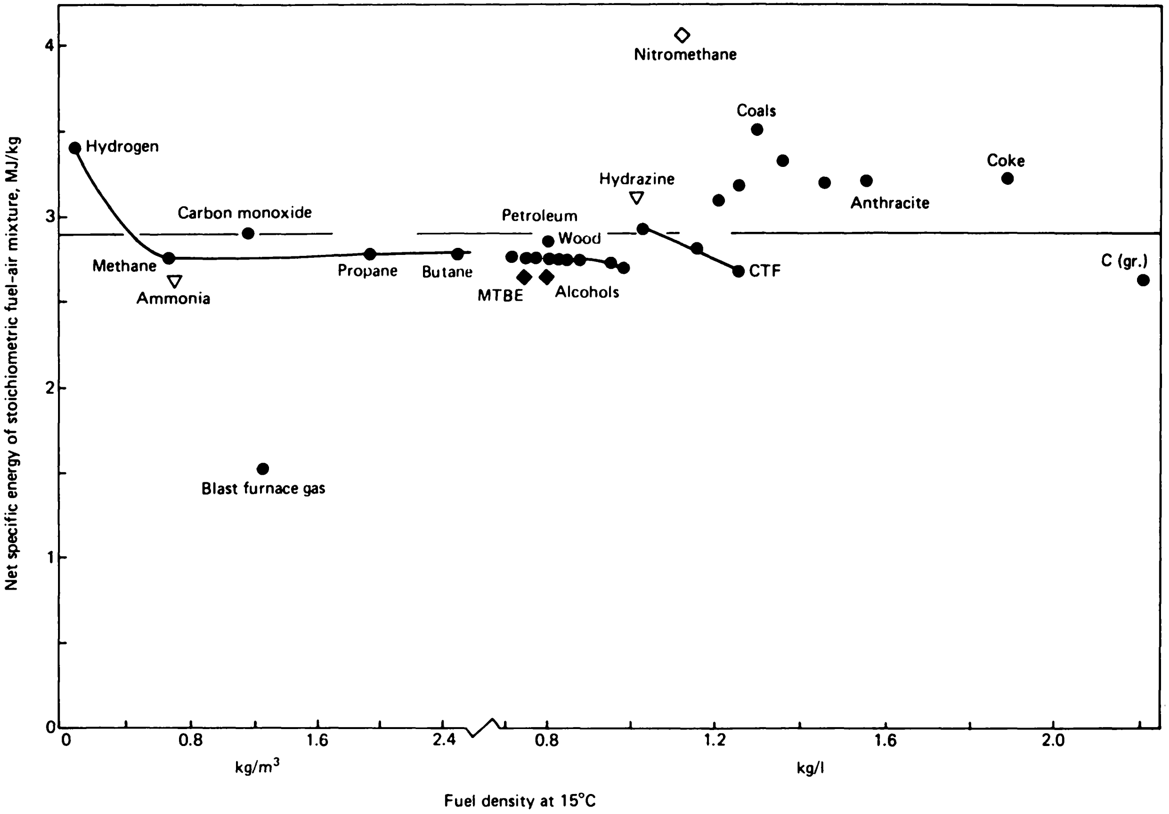


Figure 12.4 Illustration of minimal variation in specific energy of stoichiometric fuel-air mixtures

holds with energy density, the average value being about 3.1 MJ/m^3 stoichiometric mixture for fuels in the gaseous phase.

These results are particularly encouraging since it follows that, from an energy release viewpoint, combustors are virtually insensitive to fuel type, any low values of specific energy or energy density representing problems of fuel storage in aircraft systems. Of the few fuels that do not lie closely to the average value of specific energy, it is of interest to note that hydrogen has a higher value, and that nitromethane, despite its poor calorific values owing to its inert content of both nitrogen and oxygen, is particularly attractive. This feature of nitromethane, together with its high anti-knock rating, suits it to high-performance piston engines, and indicates its use for motor racing.

As shown in section 5.2.2, the flammability of a fuel may be related to volatility and expressed in terms of the fuel temperature required to promote the weak mixture limit of flammability above the liquid surface, that is, the weak temperature limit of flammability, or the flash point. Furthermore, although the weak mixture limit is common at 1 per cent volume of fuel vapour for all the petroleum liquid fuels, the level of flash point was seen to rise with fuel density owing to the fall in volatility. The flash point curve in figures 5.2 and 12.5 confirms this relationship and, in the case of wide-cut gasoline, shows clearly the marked effect of the inclusion of the volatile naphtha components. In comparison with conventional aviation turbine fuels, the flash points of the alcohols and the nitrogen hydrides are significantly lower. Fire safety in bulk handling and crash fire situations favours flash points well above ambient.

As shown in section 8.2, the ignitability of a fuel may be expressed in terms of the minimum ambient temperature required to promote spontaneous ignition of a small fuel charge. Furthermore, the level of spontaneous ignition temperature (SIT) was seen to fall with rise in fuel density because of the inability of the larger molecules to withstand thermal agitation. The SIT curve included in figure 12.5 confirms this relationship. In comparison with conventional aviation turbine fuels, the SIT levels of ammonia, hydrogen, nitromethane and the alcohols are higher, whereas hydrazine is about the same.

12.3 Liquefied Hydrocarbon Gases as Substitute Fuels

As a hydrocarbon fuel of comparatively low density, liquefied methane offers a correspondingly high specific energy and low energy density but, as indicated in the previous section, little change in either when expressed in terms of stoichiometric mixture with air. With a relatively low concentration of carbon, and existing as a gas under normal conditions, clean combustion of liquefied methane can be expected with little effect of contaminants, other than those that also exist in the gaseous phase and that were not previously removed.

For use in piston engines, methane offers the additional advantages of a wide mixture range of flammability and a high resistance to spark knock (RON = 105 approximately). Furthermore, being carburetted as a gas or a highly volatile liquid, it would be expected to promote uniform distribution throughout a

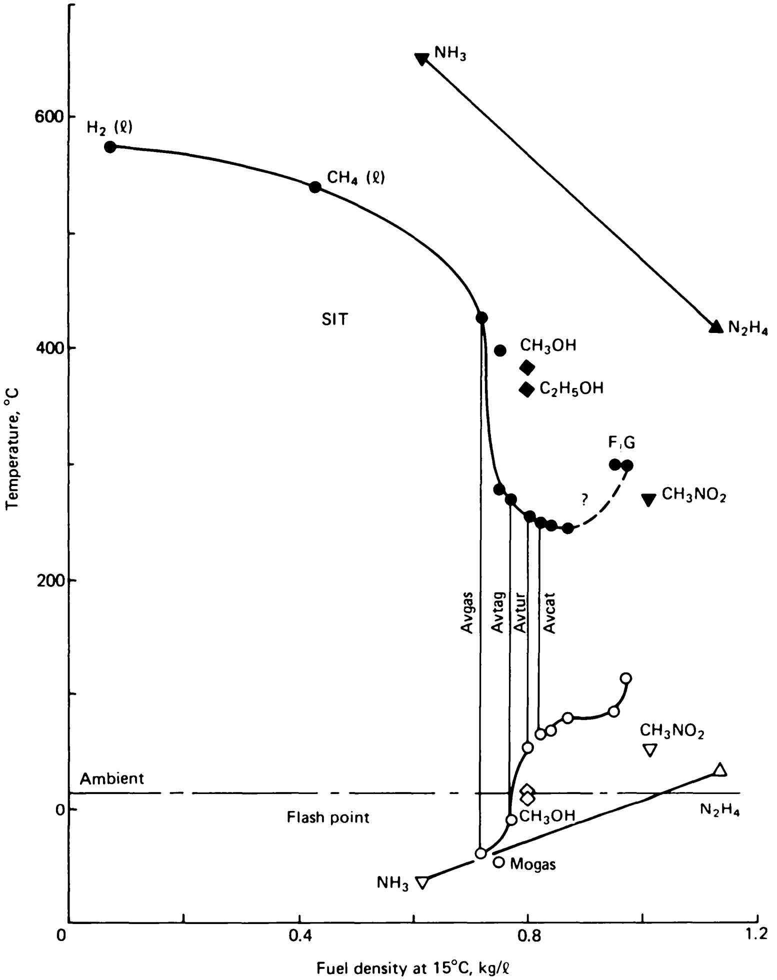


Figure 12.5 Flash points and spontaneous-ignition temperatures of conventional and substitute fuels

multi-cylinder inlet manifold. Nevertheless, a power loss of some 8 per cent is expected owing to the greater volume occupied by the gas, in comparison with unvaporised gasoline, within the manifold, and to the absence of the evaporative charge cooling effect[12]. Dynamometer and road vehicle tests confirm the reduction in combustion emissions, particularly of the smog-forming hydrocarbon type, and the possibilities of lean operation. Aircraft tests include those under way by Beech Aircraft[13] with a fixed-wing Sundowner aircraft and a TH-55A training helicopter, both using a 135 kW four-cylinder Avco Lycoming 0-360 engine. The aircraft are fitted with two vacuum-insulated cryogenic tanks of 68 or 87 l capacities, constructed of stainless steel or aluminium, together with a pressure regulator, a vaporiser unit and a modified carburettor. The operating pressure is approximately 275 kPa, and the fluid loss rate is less than 1 per cent per day. The engine ignition timing was advanced by about 10° of crank angle in view of the high anti-knock quality of methane. Tests to date confirm the anticipated power loss of about 10 per cent, which may be retrievable by supercharging, but show no change in aircraft flight characteristics. The specific fuel consumption is expected to be reduced by about 15 per cent.

For gas-turbine engines, the gaseous nature of the fuel minimises problems of mixing, combustion, temperature distribution and emissions. The increased homogeneity of the gaseous–air mixture in the primary zone is found to reduce NO_x emissions effectively, while maintaining the CO and hydrocarbons at very low levels. However, the flame stability of a continuous-flow combustor is narrowed with a gaseous fuel because this same homogeneity eliminates possible flammable regions under otherwise adverse conditions, and the equivalence ratio at the fuel-rich limit is likely to be half that with kerosine. The most satisfactory design of combustor is likely to incorporate a vaporiser type injector situated in a fuel-weak primary zone.

Results of tests on an experimental combustor fitted with multiple natural-gas burners located in an annular chamber showed combustion efficiency to be satisfactory at most normal operating conditions, but poor at low air temperatures and pressures[14]. An investigation with a cylinder type of combustion liner showed that the use of a gaseous fuel such as methane gave better control of local equivalence ratio in the primary zone, the leaner mixtures reducing the concentrations of both carbon monoxide and nitric oxide[15]. A simplified cycle analysis of a turboprop engine flying at Mach 0.8 and 10 688 m altitude showed that the use of the methane fuel to cool the bleed air for turbine blade cooling could lead to lighter, more compact engines, with increased turbine entry temperature. Combustion tests confirmed the cleaner burning, but showed that the chamber should be designed specifically for the fuel, and that altitude relight may be more difficult owing to the narrow flammability range of a gaseous fuel[16].

The major problems in handling liquid methane appear to centre on storage volume, because of the relatively low energy density (21.2 MJ/l compared with 34.7 for avtur), and the very high levels of vapour pressure at temperatures above about 150 K. With satisfactory solution of these storage problems, the relatively high specific energy (50 MJ/kg compared with 43.4 for avtur) implies a 15 per cent increase in aircraft range. Furthermore, methane is thermally stable and, as a cryogenic liquid, offers an effective heat sink capacity for cooling lubricant systems, electronics and other strategic parts of the aircraft. Both the high level of SIT, and the displacement of air from the tank by the gaseous fuel, assist fire safety in handling. Methane vapour does not present hazards to health or the environment.

The propane and butane components of LPG reflect the clean combustion characteristics of methane with significantly lower emissions. In spark-ignition piston engines, the high octane quality (RON = 94 for propane, and 111 for butane) permits knock-free compression ratios up to about 11, and the clean combustion prolongs spark-plug life with less carbon contamination of the lubricating oil[17]. Nevertheless, experience with automobile piston engines shows that the higher combustion temperatures cause nitration reactions with the lubricant, the products of which attack lead in the copper-lead bearings. Also, valves can burn, and their seats recess, owing to the absence of the lubricating action of lead additives[18].

The LPG is pre-vaporised using oil or water heating, and metered through a gas carburettor. The results derived from engine test beds, and from flight tests with a Ralleye aircraft, show improvements in power of up to about 5 per cent, and changes in fuel consumption varying ±15 per cent relative to avgas.

In comparison with kerosine, the use of liquefied butane in the combustion chamber of a Kawasaki M1A industrial gas turbine gave better ignition performance, higher combustion efficiency at weak mixtures, lower liner temperatures, and much lower concentrations of unburnt hydrocarbons and carbon monoxide. Little change was found in the outlet temperature distribution or the concentration of nitrogen oxides[19].

Since the fuel tanks need to withstand the vapour pressures of about 9 atm. (propane) and 3 atm. (butane), the tank masses are greater than with conventional fuels, but the fuel masses themselves are lighter for a given energy content.

12.4 Liquid Hydrogen as a Substitute Fuel

In addition to the elemental abundance of hydrogen, the property values shown in table 12.3 indicate a very high level of specific energy with a high flame speed, wide range of flammability, and clean burning ability. These suggest a high combustion performance in terms of good stability and temperature distribution with minimal tendencies for pollution, as shown broadly in table 12.4. Actual engine experience with hydrogen fuel has been gained by Pratt and Whitney, and by NACA. Excellent combustion performance within a J57 engine was found in 1956, with pre-vaporised fuel injected via an axial tube system. In a high-altitude Pratt and Whitney 304 engine also tested successfully, the hydrogen was vaporised by exhaust heat, the resulting expansion driving the compressor-turbine. The hydrogen was then burnt to provide thrust. The 1957 NACA flight tests further demonstrated the potential of hydrogen as an aviation fuel by using it in one of the two J65 engines in a B-57 aircraft. The liquid hydrogen was transferred from a wing-tip tank using helium under pressure, and pre-vaporised in a ram-air heat exchanger immediately prior to injection[21].

A recent study by AiResearch under contract to Lockheed California and sponsored by NASA[22] concerns liquid-hydrogen fuelling of turbofan engines for a 400 passenger subsonic airliner of 168 830 kg gross mass, and 10 190 km range. Various features of two-spool, separately exhausted engine designs were examined to exploit the particular properties of hydrogen fuel, including combustion-air cooling either prior to compression or between stages, bleed-air for high-pressure

Table 12.4 Comparison of liquid hydrogen with kerosine
(Derived from reference 20)

Feature	Advantages	Disadvantages
Combustion	Higher specific energy (x 2.8) Higher flame speed (x 7) Wider range of flammability Higher combustion temp. (+125 K) Lower flame emissivity Higher diffusion rate Improved temp. distribution	Lower energy density (x 0.25)
Pollutants	Zero CO, CO_2, UHC, sulphur, particles and odour Reduced NO_x Reduced engine noise Lower sonic boom over-pressure	Double H_2O
Engine performance	Higher specific impulse	
Aircraft dimensions	Reduced gross mass Smaller wing	Longer fuselage
Storage	Higher thermal stability High heat sink capacity Zero corrosive and erosive contaminants	Low boiling pt cryogenic Low density
Safety*	Zero oxygen in fuel system Non-radiant flame Buoyant vapour	Very low minimum ignition energy Wide flammable range
Overall energy utilisation efficiency of coal source	Higher than for coal-derived kerosine	
Costs	Lower aircraft costs Longer engine life and less maintenance	High fuel production capital costs

*Currently under investigation by NASA.

turbine cooling, and engine exhaust gas heating of fuel either alone or coupled with an expansion turbine to provide accessory power. Whereas the last two designs promoted greater engine mass, they gave greater reductions in direct operating costs (2.9 per cent). Bleed-air cooling and fuel heating designs, without expansion turbines, were selected as optimal, with turbine entry temperatures of 1755 K (takeoff) and 1652 K (cruise), cycle pressure ratio of 40, and bypass ratio of 10. No additional engine noise is anticipated over that with conventional kerosine. The concentration of nitrogen oxide emissions, which is an exponential function of combustion temperature and residence time, is expected to be lower owing to the very rapid diffusion and combustion of hydrogen, with elimination of peaks in the outlet temperature profile.

In the above study, a Tristar aircraft is envisaged, with the fuselage stretched to accommodate two large-diameter fuel tanks. Since fuel specific energy is high, a reduction of over 25 per cent in aircraft gross mass is predicted[23]. The initial proposal is for four such aircraft to be prepared as hydrogen-fuelled freighters, and to be operated jointly by the U.S.A., the U.K., the Federal Republic of Germany and Saudi Arabia over a four-point network linking Pittsburgh, Frankfurt, Riyadh and Birmingham, where facilities would exist to generate about 18 tonnes of liquid hydrogen per day from either coal or natural gas.

The three major disadvantages of liquid hydrogen concern the tankage volume required, the cryogenic nature of the liquid, and the fire hazard due partly to the wide range of flammability and high flame speed, but mainly to the very low minimum ignition energy. One contribution to fire safety is the fact that flammable mixtures cannot form within the ullage spaces of liquid hydrogen tanks since the system must be purged with hydrogen gas to eliminate blockages by slugs of frozen air. Thus hydrogen presents a fire hazard only when spilt, although diffusion from spills is rapid. Furthermore, hydrogen flames radiate little heat. The effects of fuel spills, on-board system malfunction and post-crash fires are currently under investigation by NASA. The interim conclusion is that loss of life, injury or damage resulting from an aircraft crash may well be less with liquid hydrogen than with kerosine[24], and even in the Hindenburg disaster over half the passengers escaped as the fire ball moved rapidly upwards. Nevertheless, ground safety and handling of liquid hydrogen present severe problems that still await solution. On the route proposed by Lockheed, each country would need facilities to produce and store the fuel, and some of this storage would have to be at or close by the airport. With current thinking no civil airport, certainly in Europe, would consider such a fuel for storage, handling and aircraft refuelling. In the case of hydrogen fuel, the safe handling on a civil airport probably presents a more difficult problem than handling and operating in the air.

12.5 Hydrocarbon Oxygenates as Substitute Fuels

As fuels for spark-ignition piston engines, the light alcohols appear attractive in view of their high resistance to spark knock, and much experience has now been gained in the automotive world with methanol and with ethanol, both in blend with gasoline and as unit fuels. The presence of oxygen in these fuels leads to high levels of fuel/air ratios for stoichiometric mixtures, and consequently carburettor jet sizes must be greater than those used for gasoline. The energy content of the fuel-air mixture is then comparable with that of gasoline-air, as discussed earlier. In fact, owing to the high levels of vaporisation enthalpy with alcohols, the mixture temperature tends to be lower, resulting in higher volumetric efficiency, and power *increases* of about 5-10 per cent. The specific fuel consumption, on the other hand, is likely to be doubled, although this can be offset partly by exploiting the higher knock-limited compression ratio (14 as compared with 10), together with the extended lean-mixture misfire limit. Again, in comparison with gasoline, combustion temperature is lower, and emissions generally improved, except for the concentration of aldehydes.

Over 250 flying hours have been logged with a 120 kW piston engined Piper PA-18 Super Cub aircraft using methanol[25]. Also, a Bellanca Decathlon aircraft completed a flight of nearly 2000 km powered by ethanol[26]. In both cases, the fuel flow capacity of the fuel injection system was increased, and the ignition timing advanced.

In comparison with gas turbine fuels, the low viscosity of methanol would be expected to promote smaller droplet sizes on injection and, although the vaporisation enthalpy is higher, the vapour pressure is also higher and the flammability range wider, consequently methanol should vaporise and burn well in the high-temperature region of the flame. The lower combustion temperature should reduce the levels of radiation and resulting liner temperature, together with the concentration of nitrogen oxide emissions.

Tests with methanol in the Kawasaki industrial gas turbine engine discussed earlier[19] showed spray patterns similar to those with kerosine. The tests also confirmed the weaker mixtures possible at ignition, together with the lower levels of radiation and liner temperature. However, the combustion efficiency fell at the high air/fuel ratios because of deterioration of the spray pattern, the much reduced combustion temperature, and the greater proportion of products quenched within the film-cooling air, which also led to high unburnt emissions. The nitrogen oxides, on the other hand, were considerably reduced. Broadly similar results were reported from comparative tests at the Florida Power Bayboro generating station on the full-scale FT4C-1 industrial engine, in comparison with the standard gas oil fuel[27]. The greater stability and control experienced were related to the lower specific energy of methanol, which effectively reduced the control gain by a factor of two.

In tests on a GT-225 experimental passenger-car gas-turbine engine, up to 8 per cent additional power was found with methanol in comparison with kerosine at equal turbine entry temperatures[28], no doubt owing to the larger mass flow required with a fuel of lower energy and stoichiometric air/fuel ratio. Also noted were similar effects on combustion emissions, and the absence of smoke, carbon, sulphur and metallic products. Little testing appears to have been conducted with ethanol in gas-turbine engines, but comparable results could be expected.

One of the fundamental problems in the handling of alcohols in aircraft is the unavoidable presence of oxygen in the fuel tanks which would otherwise be freely available in the atmosphere. In the case of methanol, for example, no less than half the mass of the fuel consists of oxygen which represents a loading restriction. Handling difficulties with alcohols include incompatibility with fuel system constructional materials, and lack of lubricity in fuel pumps. In the piston-engine aircraft tests described above, neoprene was substituted for the natural rubber and plastic used for hoses and gaskets. Adequate lubricity can be ensured by the addition of small quantities of lubricating oil but, in practice, problems could be expected in the control of its addition, its settlement during storage, and its unknown effects on micronic filters and filter/separators in the airfield and aircraft fuel systems.

The two problems involved with alcohol-hydrocarbon blends arise from vapour pressure and water separation. Owing to the hydrogen bonding of their polar molecules, alcohols exert a vapour pressure lower than that of gasoline, but nevertheless, the separation of the alcohol molecules when blended with gasoline, particularly with the aromatic components, leads to the formation of low-boiling azeotropes with vapour pressures higher than either component alone. Furthermore, the hydrogen bonding of alcohols with water leads to phase separation in the event of water contamination of alcohol-hydrocarbon blends, particularly if the latter components are largely non-aromatic (aliphatic). For this reason, blending of alcohols and hydrocarbon fuels in the automobile world tends to be delayed up to the point of entry to the vehicle fuel tanks, and even to the engine. In aviation, the most dangerous feature is water pick-up which will freeze at altitude and block filters, pumps and distribution systems. In present specifications for both aviation gasolines and aviation turbine fuels, alcohols are specifically excluded, and only specified additives allowed in controlled dosages. With present regulations, blending of a fuel outside the refinery is neither commercially feasible nor legally acceptable, since any subsequent addition constitutes contamination, negating the quality certificate.

As discussed above, a wide range of biomatter can serve as a source of methane, hydrogen and alcohol fuels, together with a more direct use in the case of vegetable-derived oils, as from wood, sunflowers, rapeseed, ground nuts, corn, olives, etc. Turpentine has been used in spark-ignition engined automobiles in Finland, coupled with a lower compression ratio and pre-heated fuel system, and the use of motor gasoline for starting under adverse conditions. Since these oils tend to exhibit reasonable levels of cetane number (for example, 36 for sunflower oil compared with 50 for gas oil), their application to the generation of power is currently centred on diesel engine fuelling, both as blending agents and as unit fuels. Provided that the degumming is adequate, it is likely that vegetable oils could find some limited applications to gas turbines. One instance of this is the reference to the turbine-powered Plymouth automobile which ran on peanut oil[29].

12.6 Nitrogen Compounds of Hydrogen and Hydrocarbons as Substitute Fuels

Some research has been conducted with anhydrous ammonia in spark-ignition engines[30,31] and the high enthalpy of vaporisation of the stored liquid made necessary both pre-vaporisation and controlled partial decomposition, together with a high jacket temperature. The low flame speed and high anti-knock quality tolerated a relatively advanced ignition spark, but the power output was only about 70 per cent of that with conventional motor gasoline. Although, on a stoichiometric basis, the moles of nitrogen are fewer (0.726) for ammonia than for gasoline (0.777), the equal energy quantity of this mixture for ammonia contains some 15 times more nitrogen. Relative to hydrocarbon fuels, however, the lower flame temperature of ammonia reduces the nitrogen oxide concentrations to about half on the fuel-rich side. Anhydrous ammonia has also been tested in gas-turbine engines, but, in comparison with hydrocarbon fuels, the performance of the engine and fuel system, together with the maintenance and overall costs, were not attractive[32]. Poor combustion stability and low flame temperature were also found in a single combustor rig even when the air velocity was reduced to 40 per cent of the design value with hydrocarbon fuels, and using continuous ignition[33]. In an industrial gas-turbine combustor, on the other hand, up to 20 per cent more power was obtained when hydrocarbon fuel was replaced with vaporised ammonia[34].

Hydrazine has been burnt smoothly in a CFR engine[35], but the specific fuel consumption was about three times that for gasoline. Hydrazine does not appear to have been tested significantly in gas-turbine engines, although it has served as a rocket reactant (see chapter 13).

As fuel for spark-ignition engines, the nitroparaffins have received minor attention only, although nitromethane is commonly used, in blend with methanol and a lubricant, for the miniature compression-ignition engines in model aircraft. Improvements in peak power of over 40 per cent have been reported[36] when comparing nitroethane with methanol in a CFR engine, owing largely to the high level of specific energy of the stoichiometric mixture (4.05 compared with 2.67 MJ/kg), and of products/reactants molar ratio (1.274 compared with 1.061). The peak power with nitroethane occurred at a slightly higher equivalence ratio. A blend of 80 per cent nitromethane in methanol gave a power improvement of over 50 per cent. Tendencies to pre-ignition were controlled by lowering the air and jacket temperatures. The nitroparaffins are not stable in storage, and tend to detonate if contaminated and/or if subjected to heat or shock.

12.7 Resource-to-Propulsion Energy Economy

Comparable to the treatment of energy data in table 11.6, the value of energy conversion efficiency for the production from coal of liquid hydrogen (table 12.5) is roughly similar to that for supplemental aviation turbine fuel of the kerosine type, whereas that for liquid methane is significantly higher. The corresponding figure for hydrogen produced through the electrolysis of water is very much lower, reflecting the losses involved in the generation of electricity for the purpose. The values of energy utilisation on board are less for methane, and significantly less for hydrogen, in view of the higher specific energies of these fuels, and therefore lower fuel loads which have to be carried for the given mission energy. The overall requirements for the coal resource are then seen to be roughly similar for methane and hydrogen, which are lower than that for supplemental kerosine. The resource mass for electrolytic hydrogen is for the parent water only, and does not include the mass of any fossil fuel consumed to provide the electricity required; in a nuclear-powered generating station, this fuel mass would be negligible. In summary, both liquid methane and liquid

Table 12.5 Resource-to-propulsion energy economy for substitute fuels for turbine-engined aircraft (subsonic aircraft, 400 seats, 10 190 km range)
(Derived from references 23 and 24)

	Coal			Water
	Supplemental ATF (table 11.6)	CH_4 (1)	H_2 (1)	H_2 (1)
Resource-to-fuel conversion efficiency, %	54	63	55	22
Fuel-to-propulsion energy utilisation, kJ/seat km	759	722	636	636
Resource mass required for mission, tonnes	206	165	169	195*
Fuel price $/GJ	8.04**	8.39	13.20	20.62
Mission fuel price $/seat	48**	62	78	122

*Material resource (water) only. Energy resource mass also required.
**Corresponding figures for conventional aviation turbine fuel are 5.71 $/GJ, and 34 $/seat.

hydrogen appear as feasible substitutes for conventional and supplemental aviation turbine fuels.

The prices shown are, of course, relevant only to the date of the analysis (1979), and would be expected to approach more closely to conventional-fuel levels as the price of crude oil continues to rise, and the prices of the alternative fuels continue to reduce (or to rise more slowly) as a result of large-scale production economies. The other important factors involved are the changes that would be necessary in the approach to ground handling and fuel system design for these alternative fuels to become acceptable.

12.8 References

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13 Fuels for High-Performance Flight

In aircraft propulsion, 'high performance' generally represents a particularly high engine thrust sustainable for such purposes as high rate of climb, high altitude operation, supersonic or hypersonic aircraft speed, or any other special condition where engine power takes precedence over fuel economy. The discussion in chapter 2 illustrated the logical progression in aero engine design from piston engine through turbine, ramjet and rocket engines, and this chapter therefore is concerned with the latter members of the range. The operating regimes of these aero engine types were shown in figure 2.1.

With increase in aircraft speed, the fuel loading limitation tends to move from mass to volume, consequently energy density tends to take precedence over specific energy. Nevertheless, the higher combustion temperatures permissible incur complexities of chemical dissociation and subsequent recombination within the propelling nozzle, hence some performance analyses are based more realistically on the level of thrust produced per unit mass flow rate of propelling efflux of combustion products.

13.1 Supersonic Gas Turbine Fuels

Since the earliest designs for transonic and supersonic aircraft in the 1940s, the relatively high levels of thrust have generally been based on gas turbine engines handling comparatively larger quantities of air and fuel, together with reheat, rather than fuels of superior energy quality. Engine performance analysis shows that both thrust and thermal efficiency increase with the ratio of maximum (turbine inlet) to minimum (compressor inlet) temperatures, and also with pressure ratio over a wide range, provided that the temperature ratio is in excess of 3. Consequently, although the fuel envisaged was broadly similar to conventional aviation kerosine, particular attention was directed towards those properties likely to be sensitive to the greater intensity of combustion, and the more severe environment, as discussed below.

Within the engine, one of the prime concerns is that the higher gas temperatures at turbine inlet imply correspondingly higher temperatures of combustor liner, and therefore reduced engine life. This is compounded by the fact that the transfer of heat to metallic liners, although mainly by convection, is also partly effected by radiation which increases with combustion pressure. However, this factor is already controlled by constraints upon such fuel properties as the contents of hydrogen, aromatics and naphthalenes, together with a minimum limitation on smoke point. Furthermore, as discussed in chapter 8, this problem of liner temperature rise tends to be eased above pressure levels of about 10 atm. In the specifications for aviation turbine fuels, the sulphur concentration is now limited to a maximum of 0.3 per cent mass, but the earlier limit of 0.2 is rarely exceeded in practice, at which levels freedom from sulphidation of turbine blading has been established, and is assisted by the turbine design practices of air cooling, and the use of improved blade materials.

Within the aircraft and engine fuel systems, the main problem areas relate to the effects of kinetic and/or engine-derived heating on the temperature-sensitive properties of the fuel. The theoretical stagnation temperature due to air impact and viscosity increases with the square of the relative air speed, as indicated in figure 13.1 which shows a value of about 155°C for the Concorde design cruise

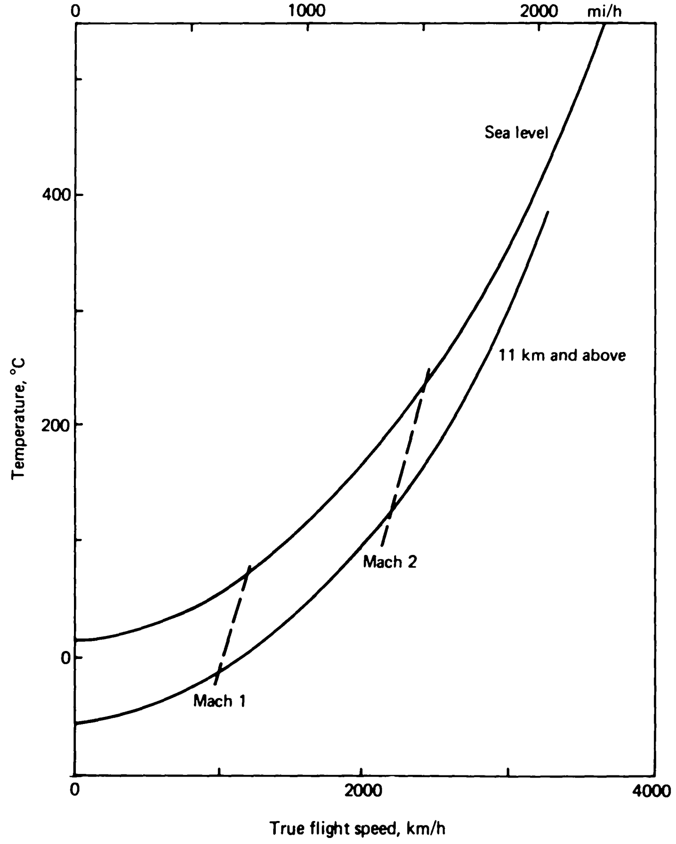


Figure 13.1 Air stagnation temperature variation with flight speed for standard atmosphere (derived from ref. 1)

speed level of 2.2 Mach number at high altitude. Hitherto, aviation kerosine has been classed as a fuel of such low volatility at the standard Reid test temperature of 37.8°C that the test itself is not included as a specification requirement since any measured result would be negligible. At a temperature of 155°C, on the other hand, even non-volatile kerosine would reach a vapour pressure of about 70 kPa, which would impose unacceptable demands on tank strength and mass (figure 13.2).

In practice, however, measurements have shown that, owing to radiation and other losses, the temperature reached at the stagnation point at the leading edge of the mainplane aerofoil section does not exceed 135°C. In Concorde, for example, the insulating effect of the epoxy resin internal coating and synthetic rubber floor of the integral wing tanks limits the fuel temperature to about 85°C. At this level, the vapour pressure of conventional aviation kerosine is no more than about 7 kPa, which is equivalent to ambient pressure at the 19 200 m (63 000 ft) cruising altitude of Concorde. Initially, the fuel tanks were designed for pressurisation to a constant 15 kPa above an altitude of 13 400 m (44 000 ft), but the tanks are now vented to atmosphere, with no resulting problems.

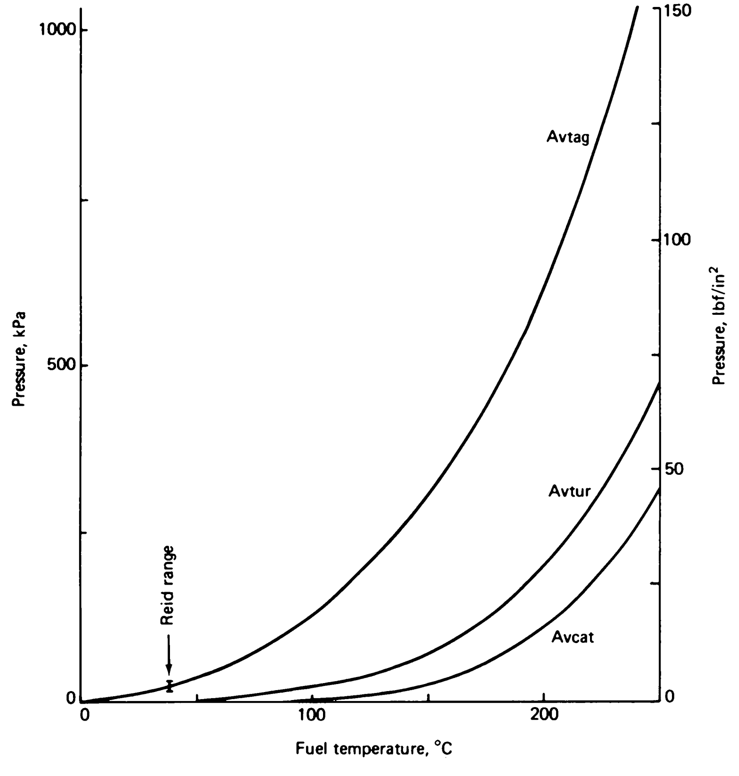
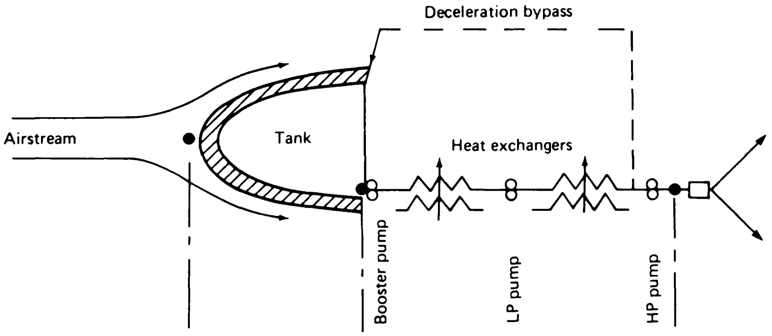


Figure 13.2 Variation of vapour pressure of gas turbine fuels with temperature (derived from ref. 2)

Since the kinetically heated atmospheric air is too hot to serve as a coolant, the fuel being transferred to the engine is used as a heat sink for cooling the cabin air, hydraulic oil, alternators and engine lubricant which, together with the energy input from the fuel pumps, increase the fuel temperature to about 160°C (figure 13.3). However, the fuel is constrained by the high pump pressure, and in any case is injected and burnt in the engine within a few seconds. Cooling capacity is reduced at high altitude owing to the marked fall in fuel consumption rate. Nevertheless, the critical condition occurs at deceleration from high speed, where the heat capacity of the fuel decreases sharply with its flow rate. This situation is eased by means of an excess of flow which is bypassed back to the main tanks.



Mach 2.2	T_{max}, °C	135	85	Thermal stability?	160
	Duration	–	3h		5 s
	Vapour pressure, kPa	–	7	Vapour loss?	
Mach 3.0	T_{max}, °C	250	110	Spontaneous ignition?	260

Figure 13.3 Representative conditions in supersonic aircraft fuel system (derived from refs 3 and 4)

Since the spontaneous-ignition temperature of aviation kerosine is above 250°C, problems of this type could arise only in the event of a fuel leak in the vicinity of the hottest parts of the engine in the absence of adequate ventilation. However, should any of the fuel components or contaminants be thermally unstable, prolonged exposure to temperatures at the 85°C level may give rise to the formation of gum or solid products through slow oxidation. This emphasises the need for the thermal stability test outlined in chapter 5, this requirement emerging initially with the first high-performance turbojet engines in view of fuel deposition in filters and injectors following heat soakage. Paraffinic components, with high heat capacities as well as high smoke points, are therefore preferred, although naphthenes form a good compromise between high density and high specific energy.

Freedom from contamination is even more important than with subsonic fuels since such materials as sulphur, nitrogen and metals (particularly copper) degrade thermal stability very markedly. Also of importance is a high energy density, normally associated with a high density, since the thin aerofoil sections of supersonic mainplanes impose a volume, rather than a mass, limitation on the quantity of fuel storable on board. However, smoke point reduces, and flame radiation increases, with increased fuel density.

The specified quality of conventional aviation kerosine is, in fact, suitable for current levels of supersonic flight speed. The fuel load represents over 50 per cent of the gross takeoff weight, and the unused reserve fuel remains as a heat-soaked 'heel' at the end of the flight. Nevertheless, no problems arise since fresh fuel is thoroughly intermixed with the heel at the next fuelling, and also during the fore-and-aft transfer of fuel for purposes of trimming the pitch of the aircraft as the centre of pressure changes with speed. Contamination with as little as 0.5 per cent of an inferior fuel, however, would place the main fuel outside the thermal stability specification. As flight speeds increase further, fuel selection will also have to be based on closer control of volatility, thermal stability and spontaneous ignitability.

13.2 Ramjet Fuels

In a turbine engine operating at constant altitude and engine speed, an increase in flight speed reduces the pressure ratio of the compressor, together with the overall pressure ratio from compressor entry to exit nozzle, and also the engine thrust. In fact, when the overall pressure ratio falls to unity, the compressor-turbine component serves merely to heat the air rather than to compress it. In high-speed subsonic flight, therefore, the level of air pressure required for efficient combustion is achieved by diffusion alone, in the absence of any rotating components, as the air decelerates to about 0.2 Mach number ready for flame stabilisation in the combustion chamber. The combustion-derived forward thrust then acts on the internal wall of the diffuser. When flight speeds become supersonic, the air velocity-to-pressure exchange is partly effected by the promotion of shock waves at entry. Shock waves may be arranged to be inclined, feeding into the lip of the entry area, by the protrusion of a tapered centre body located on the duct axis.

Ramjet propulsion is thus suited to flight at Mach numbers high enough (over 2) to give adequate rise in pressure. Consequently, although fuel specific energy is always important in air-borne vehicles, vehicle energy loading may be limited more by volume in such cases. One of the prime fuel requirements therefore centres on energy density, which controls vehicle range for a given tankage volume, but certain other characteristics are also necessary, as discussed below. In particular, with the absence of nozzle guide vanes, turbine blades and other hardware directly within the gas stream, the temperature of combustion is no longer so strictly limited, so that mixtures closer to stoichiometric are permissible, together with liquid and solid combustion products. Nevertheless, for prolonged and repeated engine operation in an aircraft, radiation from the high-temperature flames must be limited by the restriction of the content of aromatics and olefins to give non-luminous combustion, and thermal stability is essential. For one-off operation in a ramjet powered missile, on the other hand, thermal stability is secondary to a control on existent and potential gum in order to ensure long-term storage life. As shown in table 13.1, the specification requirements for the ramjet reference fuel RJ-1, for missiles, differ slightly from those for avtur in terms of higher density, narrower distillation range at higher level, higher freezing point, and much reduced contents of aromatics and olefins. Other ramjet reference fuels include RJ-4, a tetrahydromethyl cyclopentadiene dimer, and RJ-5, a Shelldyne blend.

Table 13.1 Key properties of turbine, ramjet and rocket reference fuels
(Derived from references 5 and 6)

Property	Avtur	RJ-1	RP-1
Density at 20°C, kg/l	0.775–0.830	0.842–0.863	0.800–0.815
Distillation range, °C	144–252	221–315	188–266
Specific energy, net, MJ/kg	43.4	43.0	43.5
Energy density, net, MJ/l	34.7	36.7	35.0
Aromatics, % vol. max.	22	5	2.3
Olefins, % vol. max.	5	1	0.5
Freezing point, °C	– 47	– 40	– 48

13.2.1 High-Density Hydrocarbons

For the conventional petroleum-derived fuel blends, an increase in density has been seen to accompany a reduction in hydrogen content, and thus in specific energy. Nevertheless, the rate of rise in density exceeds that of the fall in specific energy, consequently the resulting mathematical product giving energy density also rises (figure 5.3). The attainment of high energy density therefore appears to depend on high density, and this in turn depends on the packing, and thus the shape, of the individual molecules. With hydrocarbons of common carbon and hydrogen numbers, as shown in the upper part of table 13.2, the density rises as the molecular structures become cyclic, and grow in size and number of rings.

The same effect follows in these multiple rings as hydrogen is removed, resulting in unsaturation, with double carbon-carbon bonding. The energy density follows similar trends and, as shown in figure 13.4, a virtually unique line is obtained for both the simple light hydrocarbons (shown plotted up to C_{10}) and a number of complex single- and multiple-ring hydrocarbons, with energy densities above 36 MJ/l, which are under consideration as high-density candidate fuels for ramjets. These data are confirmed by the greater detail in table 13.3, where it is noteworthy that some members appear as hydrogenated

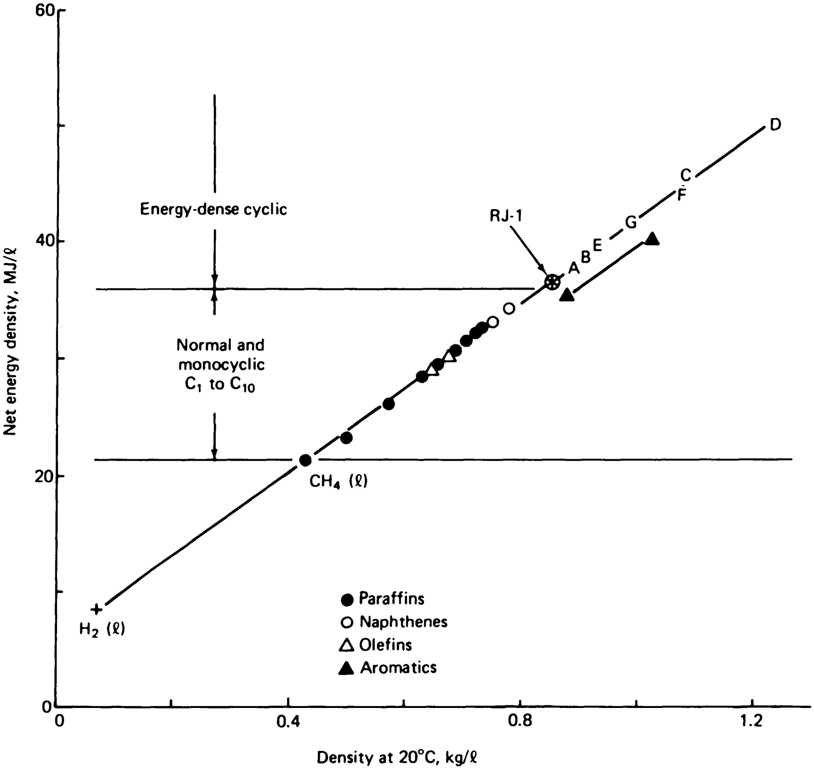
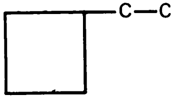
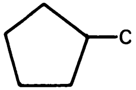
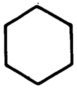
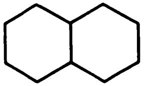
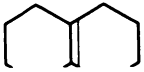
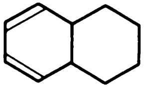
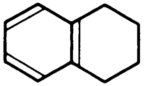
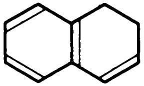
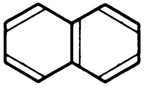


Figure 13.4 Energy density of hydrocarbons (see table 13.3)

('perhy' or 'perhydro'). As indicated above, hydrogen in fact reduces both density and energy density, but is necessary in the cases shown in order to convert either solids or very viscous liquids into liquid fuels of acceptable viscosity and freezing point, as discussed later. In the hydrocarbon range of fuels, therefore, high density would be preferred to meet the volumetric requirements of ramjet propulsion.

Table 13.2 Molecular structural effects on densities of C_6H_{12} *and* C_{10} *hydrides*
(Derived from references 5 and 6)

Formula	Name	Carbon skeletal structure	Density at 20°C, kg/l	Energy density net, MJ/l
C_6H_{12}	1-Hexene	C=C–C–C–C–C	0.673	30.15
C_6H_{12}	Ethylcyclobutane		0.728	
C_6H_{12}	Methylcyclopentane		0.749	
C_6H_{12}	Cyclohexane		0.779	34.14
$C_{10}H_{18}$	1,3-Decadiene	C=C–C=C–C–C–C–C–C–C	0.750	
$C_{10}H_{18}$	*cis*-Cyclodecene	(Single ring)	0.877	
$C_{10}H_{18}$	Decahydronaphthalene (Decalin)		0.883*	37.86*
$C_{10}H_{16}$	Octahydronaphthalene		0.905	38.18

$C_{10}H_{14}$	Hexahydronaphthalene		0.938	39.02
$C_{10}H_{12}$	1,2,3,4-Tetrahydronaphthalene (Tetralin)		0.968	39.58
$C_{10}H_{10}$	1,2-Dihydronaphthalene (Dialin)		0.993	39.94
$C_{10}H_8$	Naphthalene		1.022	40.14

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*Average of *cis* and *trans*.

Table 13.3 Calorific values of high density hydrocarbons (see figure 13.5)
(Derived from references 5, 7, 8, 9, 10, 11 and 12)

Key	Hydrocarbon	Density at 20°C (kg/l)	Energy density, net		Specific energy net (MJ/kg)
			MJ/l	% rel. RJ-1	
	RJ-1	0.853	36.70	100	43.03
A	Cyclododecane(s)	0.878	38.13	103.9	43.43
B	*cis*-Decalin	0.878	38.30	104.4	42.70
E	9-Methylperhyfluorene	0.933	39.64	108.0	42.49
G	Perhydrofluoranthene	0.983	41.46	113.0	42.18
F	Adamantine(s)	1.071	43.84	119.5	40.93
C	Tetrahydronorbornadiene dimer (Shelldyne H)	1.080	44.69	121.8	41.38
D	Hydrogenated cyclooctatetrane dimer (H-cot d)	1.230	50.58	137.8	41.42

(s) Solid at ambient temperature.

13.2.2 Elemental Reactants

The oxidation energy released by individual chemical elements is seen to undergo a cyclic variation with progressive increase in atomic number. Curves A, B and C in figure 13.5 show the net calorific values to be arranged in descending merit order as follows

Energy density (MJ/l) : B, Be, Ti, Al, Si, C, Sc, P, Mg, (RJ-1), Ca, Li, Na, H
Specific energy (MJ/kg) : H, Be, B, Li, (RJ-1), C, Si, Al, P, Mg, Sc, Ti, Ca, Na
Stoichiometric air (MJ/kg $(a)_S$): Be, Li, Mg, Al, Ca, Si, B, Sc, Ti, H, P, (RJ-1), C, Na
Specific energy

(*Note:* This third parameter is adopted since it relates to the air specific impulse, discussed later.)

Clearly, sodium can be eliminated since it appears inferior to RJ-1 on all three counts, whereas calcium and carbon are inferior on two counts each. Such materials as beryllium, lithium and scandium are not feasible for widespread adoption owing to low abundance. Furthermore, the products of beryllium are toxic, and of lithium unstable. Titanium is expensive to produce, and phosphorus very reactive in handling. Boron and possibly aluminium therefore appear attractive as fuels for high-speed volume-limited ramjet aircraft. For lower speed mass-limited ramjet aircraft, hydrogen and boron meet the requirements of vehicle storage, but magnesium and aluminium are more suited to propulsive thrust.

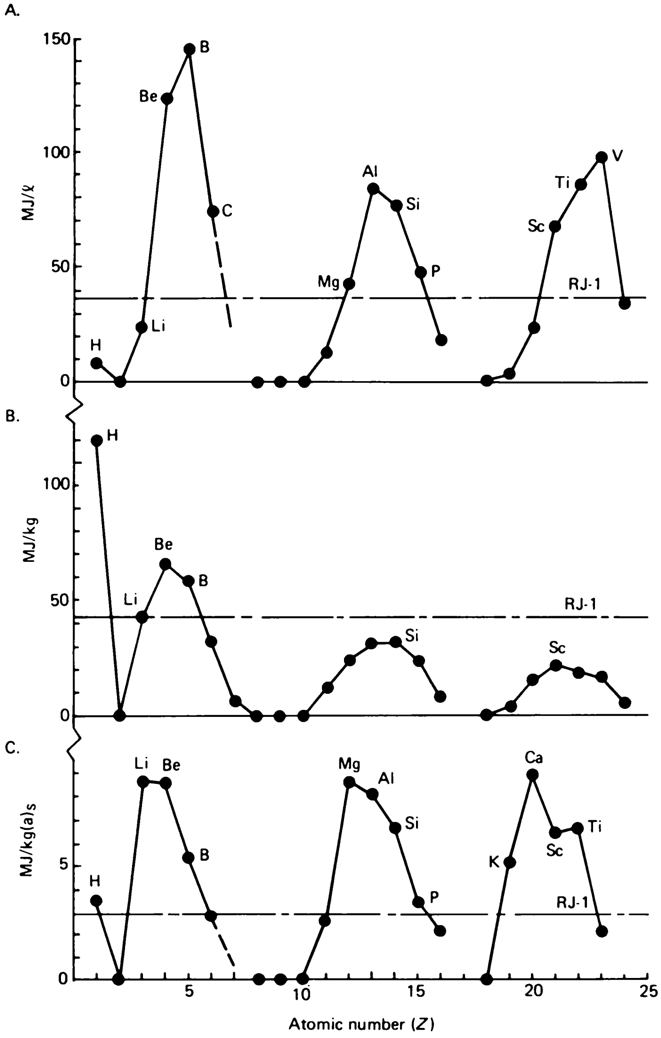


Figure 13.5 Calorific values of elements with oxygen (derived from refs 5, 6 and 7)

Apart from hydrogen, all these elements are solid at ambient temperatures, and thus present severe problems of storage and transfer within the fuel system. The two approaches to solving these problems are to pulverise and slurry the solid with some suitable liquid carrier fuel, as discussed later, or to adopt one of the elements as an alternative to carbon in a hydride compound, as examined in the following section.

13.2.3 Non-Carbon Hydrides and Metal Organics

The energy released by combustion is usually expressed in terms of enthalpy, which is appropriate to combustion reactions occurring during steady fluid flow at constant pressure. The combustion reaction enthalpy results as the difference between the total enthalpy of formation of the products and that of the reactants. These enthalpies of formation, in turn, are largely dependent on the energies of the bonds between individual atoms. The enthalpy of reaction of the fuel compound is thus not equal to the total enthalpy of reaction of a mixture of the fuel elements blended in the same ratio as in the compound ($C_{12}H_{26}$, for example, releases 44.2 MJ/kg as a paraffinic compound, but 64.8 MJ/kg as a mixture of 85 per cent (mass) elemental carbon and 15 per cent hydrogen). Nevertheless, it is likely that a hydride of higher reaction enthalpy will result if the carbon component of a hydrocarbon is replaced by an element of greater reaction enthalpy. On this basis, the hydrides of boron (boranes) would be expected to be more energetic than those of carbon (hydrocarbons).

Table 13.4 and figure 13.6, in fact, indicate the energy advantage over RJ-1 of pentaborane, decaborane, and solid boron for high-speed volume-limited ramjet aircraft. Elemental hydrogen and carbon have been included for comparison, together with the nitrogen hydrides, ammonia and hydrazine, of which only the last shows any advantage, and only on the basis of the stoichiometric air specific energy, MJ/kg $(a)_s$.

13.2.4 Slurry Fuels

In table 13.4, all the solid elements shown, with the exception of lithium, have both density and energy density higher than the comparable values for the hydrocarbon distillate RJ-1. Consequently, the introduction of these elements as particulate solids into a liquid fuel will result in slurries of higher density and energy density. This is illustrated in the upper curves on the left-hand side of figure 13.7 for slurries of boron and of magnesium in oct-1-ene. The next lower curves indicate the opposing effects of boron and magnesium on the fuel specific energy, and the lower curves show the comparable increasing effects on the air specific energy. Thus, although magnesium as a slurrying solid is acceptable with regard to engine performance, it does not appear attractive on the basis of vehicle mass loading.

Some attempts have been made to combine the values of specific energy and energy density on some graphical background such that any given fuel is represented by a single point, and two versions of this are shown in figure 13.8. In the first case, specific energy is plotted against energy density, resulting in constant density lines through the origin. In the second approach, the mathematical product of these two calorific values is expressed as a ratio of the corresponding product for a reference fuel. Hence

$$\text{Performance index of fuel} = \frac{(\text{MJ/kg})\ (\text{MJ/l})\ \text{for fuel}}{1579\ (\text{MJ})^2/\text{kg l for RJ-1}}$$

Table 13.4 Calorific values of elements, non-carbon hydrides and organometallics
(Derived from references 5, 13, 14 and 15)

Material	Symbol	Density at 20°C, kg/l	Energy density, net		Specific energy, net	
			MJ/l	% RJ-1	MJ/kg	$\mathrm{MJ/kg(a)_s}$
Kerosine	RJ-1	0.853	36.70	100	43.03	2.93
Hydrogen	H_2 (l)	0.070 (bp)	8.42	22.9	120.24	3.51
Lithium	Li (s)	0.533	23.00	62.7	43.15	8.70
Beryllium	Be (s)	1.846	122.63	334.1	66.43	8.68
Boron	B (s)	2.466	145.57	396.6	59.03	5.48
Carbon	C (gr.)	2.266	74.26	202.3	32.77	2.85
Magnesium	Mg (s)	1.738	42.98	117.1	24.73	8.71
Aluminium	Al (s)	2.698	83.77	228.3	31.05	8.10
Scandium	Sc (s)	2.992	66.12	180.2	22.10	6.47
Ammonia	NH_3 (l)	0.608	11.28	30.7	18.55	3.06
Hydrazine	N_2H_4	1.008	16.81	45.8	16.68	3.88
Diborane	B_2H_6 (l)	0.43 (bp)	31.33	85.4	72.85	4.86
Pentaborane	B_5H_9	0.63	42.73	116.4	67.83	5.17
Decaborane	$B_{10}H_{14}$ (s)	0.94	62.79	171.1	66.80	5.38
Magnesium hydride	MgH_2 (s)	1.45	42.22	115.0	29.12	5.03
Lithium borohydride	$LiBH_4$ (s)	0.666	37.52	102.2	56.34	4.03
Triethylboron (TEB)	$B(C_2H_5)_3$	0.696	32.80	89.4	47.12	2.89
Triethylaluminium (TEA)	$Al(C_2H_5)_3$	0.840	35.88	97.8	42.71	3.05
Aluminium borohydride	$Al(BH_4)_3$	0.545	29.65	80.8	54.41	4.87

(s) solid at ambient temperature. (l) liquefied. (gr.) graphite. (bp) at boiling point.

The resulting values for performance index are shown plotted against fuel density in figure 13.8B, with values of the related compounds connected by arbitrary curves. The performance index of liquid hydrogen is seen to suffer because of its very low density, whereas that for solid boron is particularly high. In practical applications, of course, the relative importances of the two energy parameters may not necessarily be equal, as is implicit in the performance index, and some different weighting may be needed for the application in hand.

13.2.5 Specific Impulse of Candidate Ramjet Fuels

In view of the higher permitted flame temperatures referred to in section 13.2, the extent of dissociation of the combustion products, and of their subsequent recombination within the propelling nozzle, may be sufficient to influence substantially the resulting thrust performance. The relationship of thrust with fuel calorific value, therefore, is not so clear cut as in piston and turbine engines

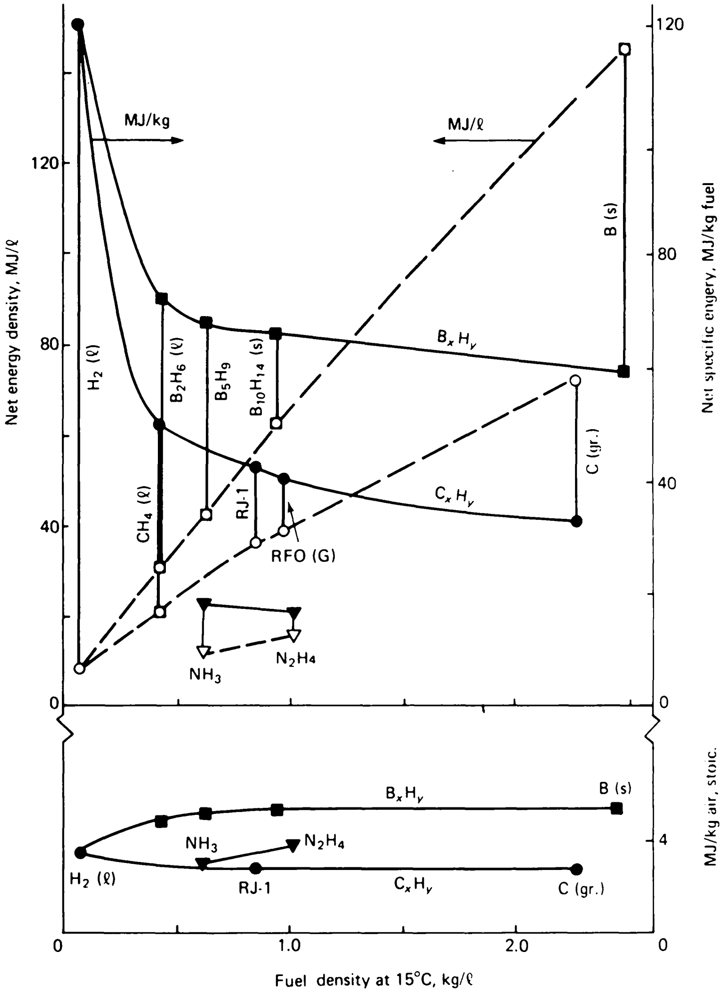


Figure 13.6 Calorific values of petroleum and other hydride fuels

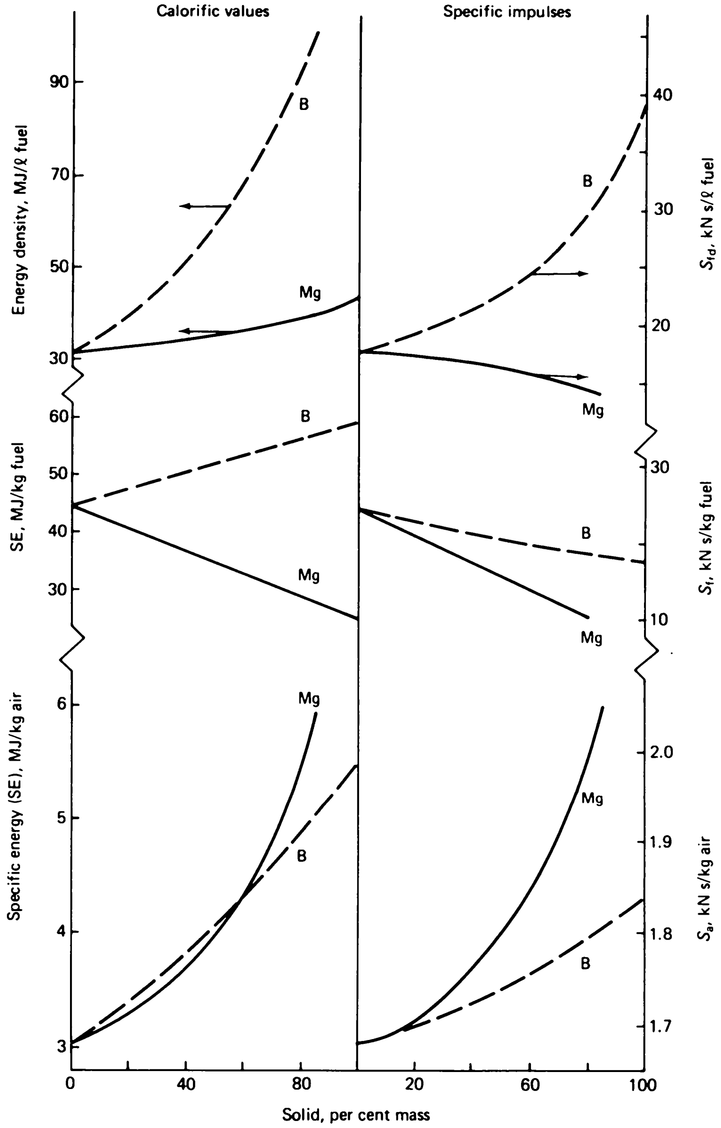


Figure 13.7 Influence of solid concentrations on performance of slurry fuels based on liquid oct-1-ene (derived from refs 7 and 16)

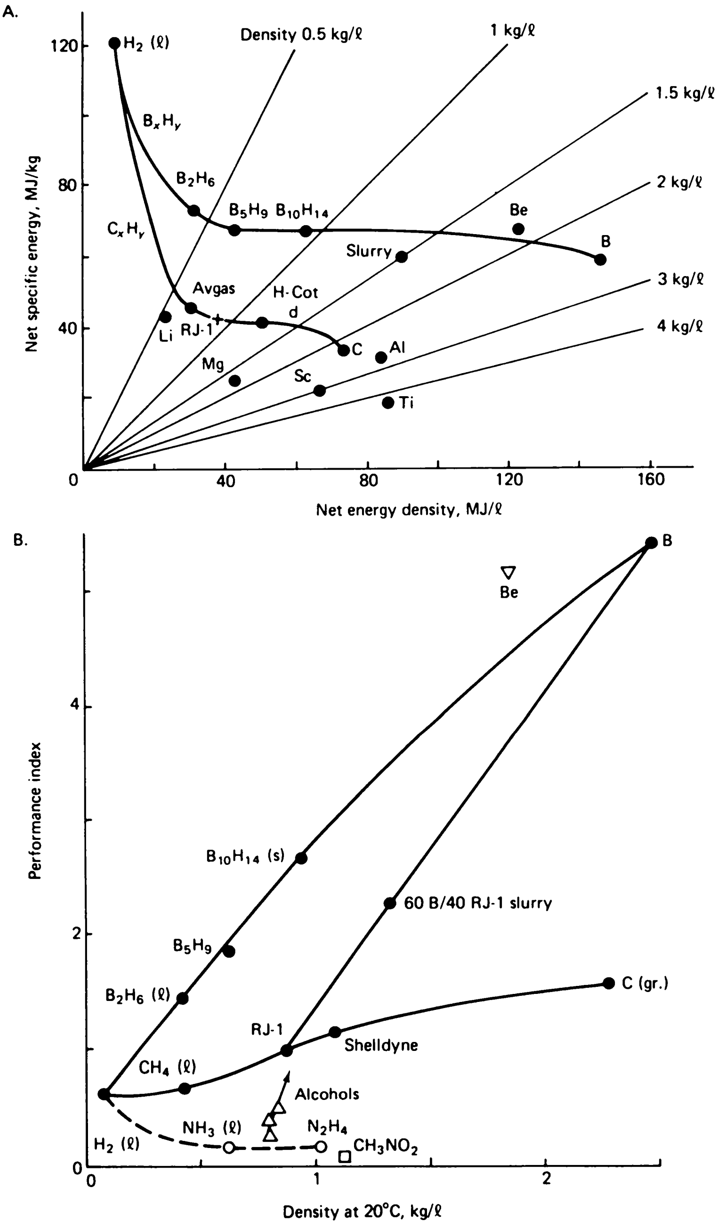


Figure 13.8 Single-point plotting of specific energy and energy density

with more modest levels of working temperature, consequently ramjet engine performance is rated in terms of the stream thrust exerted at the nozzle throat exit plane where the velocity is sonic, this parameter being termed *specific impulse* since it is based on unit flow rate of the propelling products. (The 'stream thrust' at any plane across the flow is defined by the quantity $(\dot{m}\ V + p\ A)$, as in appendix 3.) In the case of ramjet fuels, this parameter may be based on the mass flow rate of the air alone, or on either the mass or volume flow rates of the fuel alone. Thus

$$\text{Air specific impulse} = S_a = \frac{\text{Stream thrust}}{\text{Air mass flow rate}} = \frac{F}{\dot{m}_a} \quad \text{N s/kg}$$

$$\text{Fuel specific impulse} = S_f = \frac{\text{Stream thrust}}{\text{Fuel mass flow rate}} = \frac{F}{\dot{m}_f} \quad \text{N s/kg}$$

On the basis of vehicle fuel loading, this parameter may be expressed in terms of the volume flow rate of fuel, as indicated above, comparable to the energy density:

$$\text{Fuel density impulse} = S_{fd} = \frac{\text{Stream thrust}}{\text{Fuel volume flow rate}} = \frac{F}{\dot{V}_f} = S_f \rho_f \quad \text{N s/l}$$

where ρ_f = fuel density, kg/l.

For ramjet engines, the air specific impulse is frequently used since it establishes the engine size for a given level of thrust. The fuel specific impulse indicates the aircraft range for a given fuel mass, expressed as the ratio of initial to final vehicle mass, and applies at high-altitude cruise. The fuel density impulse relates to high-speed flight at lower altitudes where aircraft drag is more significant. Relative values of specific impulse for a particular set of chamber pressure and temperature conditions are given in table 13.5. A merit order comparison with related levels of calorific values in table 13.4 is given in table 13.6. This shows clearly the broad similarity between each group of ratings under the three headings, together with the differences in detailed order owing to the high-temperature thermochemical effects within the chamber and nozzle. The table also distinguishes between those fuels that are superior in performance to the hydrocarbon reference fuels, and those that are not.

It is noteworthy that, whereas the calorific values are determined under standardised conditions of test, the relative levels of specific impulse are dependent on the operating conditions. Similar effects are shown with slurry fuels in comparison with the specific impulse curves on the right-hand side of figure 13.7, and the calorific value curves on the left. Magnesium, for example, is now seen to depress the performance of the slurry on a density impulse basis, and similarly with boron on a fuel specific impulse basis. This underlines both the broad indication of ramjet fuel performance given by calorific values, and the more realistic results obtainable from the specific impulse approach. In some instances, solid fuels can be adapted for ramjet combustion.

Table 13.5 Relative stoichiometric specific impulse values of elements, non-carbon hydrides and organometallics
(Derived from reference 5)

Material	Symbol	Rel. fuel volume impulse (S_{fv})	Rel. fuel (mass) impulse (S_f)	Rel. air (mass) impulse (S_a)
Avtur	--	100 (1.08 kN s/l)	100 (25.5 kN s/kg)	100 (1.76 kN s/kg)
Hydrogen	H_2	19	254	105
Beryllium	Be	119	54	116
Boron	B	193	65	105
Magnesium	Mg	48	25	122
Aluminium	Al	96	29	122
Ammonia	NH_3	63	83	88
Hydrazine	N_2H_4	67	53	93
Diborane	B_2H_6	58	108	107
Pentaborane	B_5H_9	73	92	106
TEA	$Al(C_2H_5)_3$	69	66	108
Aluminium borohydride	$Al(BH_4)_3$	60	89	107

13.2.6 Pulsejet Fuels

As indicated in chapter 2, the pulsejet is located at the more modest end of the performance range for ramjets, with a pressure rise initiated mainly by the combustion, and only partly by the ram effect. Since the application so far is for missiles rather than aircraft, the fuel is not restricted by thermal stability, although it would require gum stability if subject to prolonged storage. The main performance requirements for the fuel appear to be a moderate level of volatility in order to permit rapid vaporisation in the combustion chamber, and not too high a level of spontaneous-ignition temperature in order to give ready self-sustaining ignition. With hydrocarbon fuels, these two requirements tend to oppose each other but, as proven by the Schmidt-Argus engine in the German V1 weapon, a low-quality (that is, relatively low spontaneous-ignition temperature) motor gasoline provides satisfactory combustion performance.

13.2.7 Scramjet Fuels

In the hypersonic regime of the ramjet, a very considerable degree of air deceleration by shock waves and diffusion would be required to bring the combustion air velocity down to the customary 0.2 Mach number. This situation can be eased by limiting the diffusion so that the air is still supersonic when it enters the combustion chamber, typically at a Mach number of about 2 for a flight Mach number of 6. In such a supersonic combustion ramjet (scramjet) flame stabilisation by the usual velocity balance between flame and mixture flow is no longer

Table 13.6 Merit order stoichiometric performance of candidate ramjet fuels (reference fuels underlined)
(Derived from references 5 and 16)

Volume limited			Mass limited			Engine thrust		
Energy density (MJ/l)	S_{fd} (N s/l)		Specific energy (MJ/kg)	S_f (N s/kg)		Specific energy (MJ/kg(a)$_s$)	S_a (N s/kg)	
	(Ref. 5)	(Ref. 16)		(Ref. 5)	(Ref. 16)		(Ref. 5)	(Ref. 16)
B	B	B	H	H	H	Mg	Mg, Al	Mg
Be	Be	Al	B_2H_6	B_2H_6	B_2H_6	Be	Be	Al
Al	Avtur	Mg	B_5H_9	Avtur	B_5H_9	Al	TEA	B
Mg	Al	B_5H_9	Be	B_5H_9	B	B	B_2H_6, $Al(BH_4)_3$	B_5H_9
B_5H_9	B_5H_9	Oct-1-ene	B	$Al(BH_4)_3$	Oct-1-ene	B_5H_9	B_5H_9	B_2H_6
RJ-1	TEA		$Al(BH_4)_3$	NH_3		$Al(BH_4)_3$	H,B	H
TEA	N_2H_4		Oct-1-ene	TEA		B_2H_6	Avtur	Oct-1-ene
Avtur	NH_3		Avtur	B		N_2H_4	N_2H_4	
Oct-1-ene	$Al(BH_4)_3$		RJ-1	Be		H	NH_3	
B_2H_6	B_2H_6		TEA	N_2H_4		NH_3		
$Al(BH_4)_3$	Mg		Al	Al		TEA		
N_2H_4	H		Mg	Mg		Oct-1-ene		
NH_3			NH_3			Avtur		
H			N_2H_4			RJ-1		

Ref.	Chamber p (atm)	Inlet air t (°C)	For S_f
5	1.52	650	I_a = 1275 N s/kg
16	2	38	S_a < 1325 N s/kg

feasible, owing to the relatively low rates of flame propagation for most fuels, consequently the incoming fuel is required to ignite spontaneously, with minimal delay, at the compression temperature and pressure of the air. Broadly, the spontaneous-ignition delay periods of hydrocarbons and many of the candidate ramjet fuels are too extended for such a simple ignition-stabilised process, consequently ignition assistance of some kind is required.

Experiments show that ignition of kerosine can be initiated by means of an inclined shock wave generated by a wedge inserted in the mixture flow[17]. Alternatively, hydrogen may be used either as the base fuel, since it is very reactive at the compression temperatures obtained, as well as having a relatively high flame speed, or as an additive to more conventional fuels such as kerosine or methane. The above experiments indicated that less than 1 per cent of hydrogen was sufficient to promote satisfactory ignition and combustion in air flowing at a Mach number of 1.98 and stagnation temperature of 1800 K when both the hydrogen and the kerosine base fuel were injected normal to the air flow. It is concluded that the scramjet could offer an attractive fuel specific impulse up to about Mach 15 with kerosine base fuel, and to over 22 with hydrogen as base fuel. Figure 13.9 shows the marked improvement offered by hydrogen, in comparison with kerosine, for both ramjets and scramjets.

13.2.8 Thermal Capacity and Stability

The kinetic heating effects on the fuel stored within the aircraft, discussed in section 13.1, are intensified when flight speeds rise above the current operating level of Mach number 2.2, particularly in the hypersonic range above Mach number 5. The key factors to the solution of this problem are the capacities of the fuel for heat soakage, and for thermal stability at prolonged high temperatures.

Initially, a fuel absorbs heat by a physical process, the resulting temperature rise depending on the specific heat capacity of the fuel liquid. The maximum temperature acceptable is limited by the onset of thermal decomposition. Broadly, as indicated in chapter 5, petroleum-based fuels remain thermally stable up to a temperature level of about 370°C. Some of the cyclic dimer hydrocarbons, of the types discussed in section 13.2.1, decompose thermally only at high levels of temperature, as shown in table 13.7, and are described as 'high-temperature' fuels. The three examples shown result from alkyl substitution (the replacement of some hydrogen atoms with paraffinic radicals as side chains) of either mono- or double-cyclic saturated (that is, single C–C bonds) structures which exhibit high thermal decomposition temperature, but are only moderately effective in absorbing sensible heat. However, improvements in this and other properties may be achieved by the substitution of further side chains up to the propyl (C_3) size.

With further increase in flight speed, the next step is to double approximately the heat sink capacity by using also the vaporisation heat of the fuel, followed by the additional sensible heat of the vapour. Three representative 'vapour' fuels are also shown in table 13.7. Again, saturated mono- or double-cyclic structures

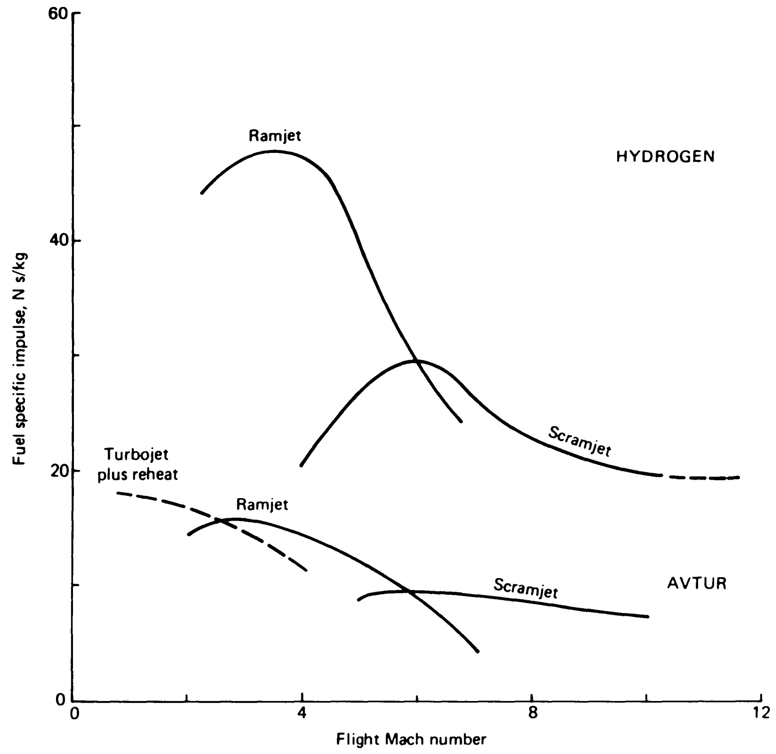


Figure 13.9 Comparative performance of hydrogen and avtur in ramjet engines (derived from refs 18 and 19)

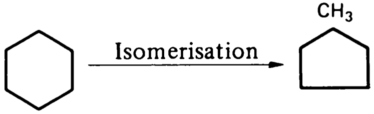
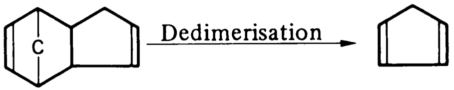
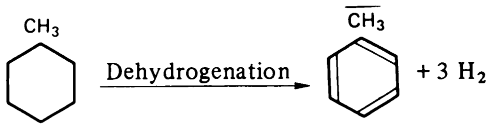
are attractive, and the substitution with paraffinic side chains may improve other properties.

Within the hypersonic regime, the additional heat sink requirements might be met by the subsequent chemical absorption of energy using 'endothermic' fuels. The representative hydrocarbon structures and their endothermic reactions shown in table 13.7 indicate a further increase in total thermal capacity. Experiments show that advanced designs of combustor are likely to operate satisfactorily with the products of these reactions, but the formation of coke must be controlled. The levels of heat absorption are shown on a specific basis in figure 13.10 against the variation of estimated heat sink requirement with Mach number for one engine fuel system.

13.2.9 Other Properties

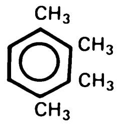
As with the conventional petroleum-based fuels, the viscosity of the high-performance hydrocarbon fuels increases with molecular size and boiling point. Freezing point follows a similar trend but, owing to the characteristics of crystalline structure, is also affected directly by molecular symmetry, as shown in the

Table 13.7 Thermal capacity and stability of high-density hydrocarbons
(Derived from references 8 and 9)

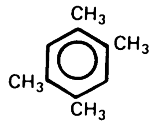
Category	Compound	Heat-absorbing reaction	Thermal decomposition temperature, T_D (°C)	Thermal capacity from 38°C to T_D (MJ/kg)
High-temperature (to Mach 4)	Ethylhexahydroindan	Sensible heating of liquid	388	0.5 approx.
	Triethylcyclohexane		389	0.5 approx.
	2,3-Dimethyl decahydronaphthalene		404	0.5 approx.
Vapour (to Mach 5)	Spiro(5,5)-undecane	Sensible heating of liquid and vapour, plus vaporisation	405	1.160
	Hydrindan		413	1.187
	cis-Decalin		420	1.226
Endothermic (to Mach 10)	Cyclohexane			1.500*
	Cyclopentadiene dimer			1.582*
	n-Octene	$C_8H_{16} \xrightarrow{\text{Cracking}} 2\,C_4H_8$		1.814*
	Methylcyclohexane			3.489*

*Heating to 427°C.

unsymmetric and symmetric configurations of the following alkyl substituted aromatic hydrocarbon



1,2,3,4-tetramethylbenzene
(Prehnitene)
Freezing point = −6.3°C



1,2,4,5-tetramethylbenzene
(Durene)
Freezing point = 79.2°C

In the polycyclic hydrocarbons shown in table 13.2, the influence of hydrogen content is not only indirect on density and energy density, but also on freezing point, with values of 80°C for naphthalene ($C_{10}H_8$) to −41°C for the decalins ($C_{10}H_{18}$). The freezing points of the elemental metals are invariably well above ambient. Pentaborane freezes at −47°C (equal to the onset of freezing of kerosine), but decaborane is a solid at ambient temperature. Lithium borohydride and magnesium hydride also are solids, but TEB is a liquid.

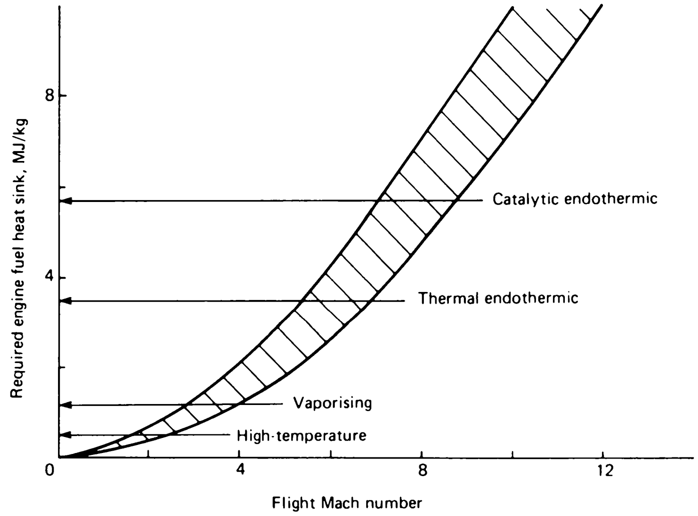


Figure 13.10 Thermal capacity of fuels, and engine requirements (derived from refs 8, 9 and 20)

As indicated in section 13.2.2, the problem of handling solid materials may be eased by the suspension of small particles in a liquid to form a slurry. The size of the particles must be very small if settling is to be avoided, and the calorific value requirements dictate solid mass concentrations in excess of 50 per cent. Settlement is also inhibited by high density and viscosity of the carrier liquid, but the overall fluidity of the resulting slurry must permit transfer and

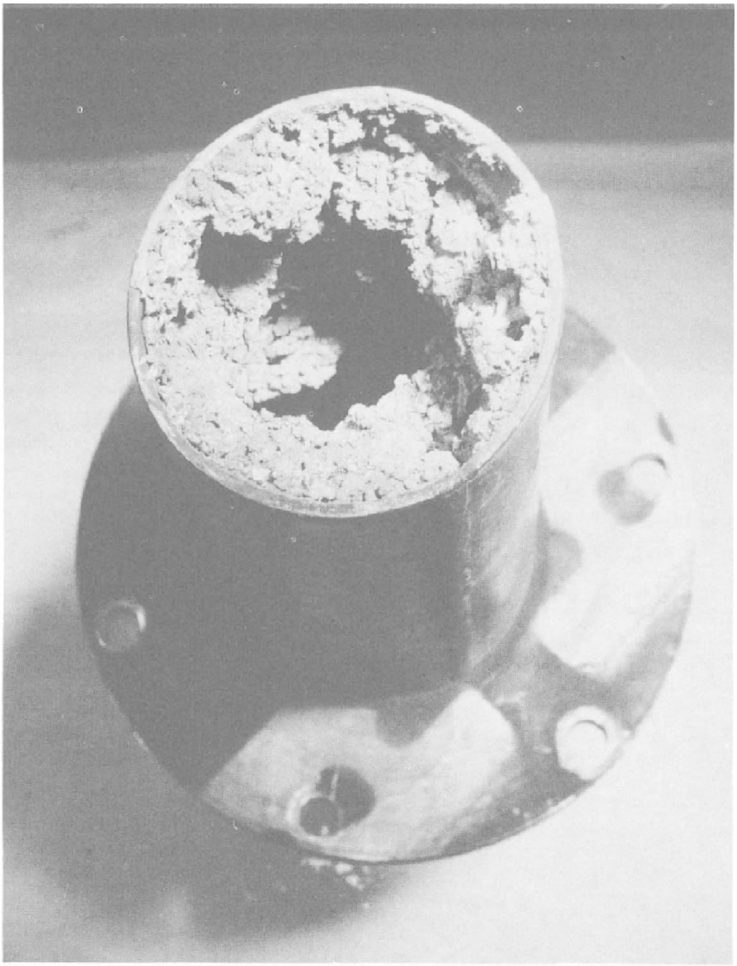


Figure 13.11 Combustion chamber deposits with aluminium–kerosine slurry fuel (courtesy of Cranfield Institute of Technology, ref. 21)

injection. Such gelling agents as fatty acids and other long-chain molecules prevent settlement by imparting high viscosity under low rates of shear, but permit fluidity under the high rates of shear in pumps and injectors. Early tests at Cranfield with a 50 per cent mass slurry of powdered aluminium, of 6 μm average particle size, in aviation kerosine realised suspension stability by the addition of 0.5 per cent mass of aluminium octoate and heating to promote a gel[21]. The further addition of a trace of polyoxyethylene sorbital mono-oleate as a surface-active agent promoted sufficient fluidity for transfer and spraying. Fuel-borne metallic particles can also give rise to abrasion of pumps and other system components.

Solidification can also be a problem with combustion products since the freezing (melting) points of some oxide products are high (for example, MgO 2800°C; CaO 2580°C; BeO 2530°C; Al_2O_3 2045°C). Reduction below these temperatures within the exhaust nozzle leads to the formation of solid molecules which, if they agglomerate, will reduce the momentum and thus the thrust, and may promote rapid build-up on the nozzle walls. These problems do not appear to be severe with magnesium-hydrocarbon slurries, but deposition is likely with boron, and very prone with aluminium, unless liquid percolates through the nozzle walls and so prevents adhesion. Figure 13.11 illustrates the extent of nozzle build-up found in a 50 mm bore solid-wall duct with a Cranfield 30/70 aluminium-kerosine slurry burnt for a period of less than 30 seconds.

The hydrides and alkyls of the light metals are characteristically pyrophoric, in that they ignite spontaneously in contact with ambient air. This property is accompanied by a high flame speed and wide range of flammability, together permitting rapid and reliable ignition with vigorous combustion performance even under the low pressures at high altitude. However, a handling fire hazard is also implied and, since these materials also have problems of toxicity and of nozzle blockage by stable combustion products, they tend to be confined to use as ignition and/or anti-screech additives in other fuels. Compatibility with fuel system components is an important factor in that the boranes, for example, cannot be stored in the presence of lead or copper, and the slow release of hydrogen causes embrittlement of any mild steel components.

13.3 Rocket Reactants

In a chemically energised rocket vehicle, all the reactants must be stored on board, and their combustion products serve as the propelling fluid. The reactants therefore have two distinct duties to perform: energy release and propulsive thrust, which may well present conflicting demands. The vehicle-based needs for energy release, as before, centre on energy density where aerodynamic drag is an important factor (high speed and low altitude), and specific energy where it is less so (lower speed, or very high altitude). The needs for propulsive thrust, on the other hand, are dependent on chemical behaviour of the products within the combustion chamber and the propelling nozzle, as in the ramjet case. The significance of this chemistry is very much greater in rocket propulsion, since the need to carry oxidant will minimise dilution with nitrogen or any other inert material, and so result in particularly high temperatures. The performance of rocket reactants, therefore, is invariably based on specific impulse.

As shown in appendix 3, the expression for specific impulse of rocket reactants contains the key terms $(T_c/\bar{M})^{1/2}$, where T_c is the combustion temperature, and $\bar{M}$ the mean molar mass of the combustion products comprising the propelling fluid. The target for high specific impulse thus centres on a maximum T_c and a minimum $\bar{M}$. The stoichiometric values plotted for the elements in figure 13.12 show a descending merit order for values of $T_c/\bar{M}_u$, where $\bar{M}_u$ is the undissociated

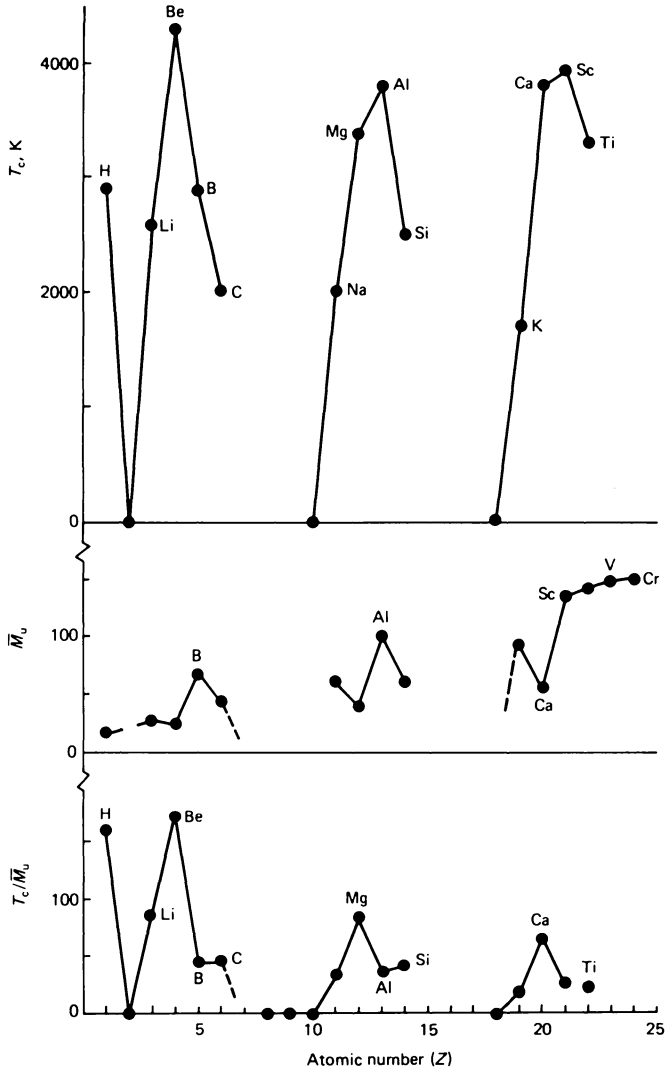


Figure 13.12 Combustion temperatures and product molar masses (undissociated) of elements with oxygen (derived from refs 7 and 22)

value of $\bar{M}$ (for example, Be is assumed to burn completely to BeO, with no dissociation), as follows

Be, H, Li, Mg, Ca, C, B and Si, Al

No consistent set of values of specific impulse appears to be available for the elements, although hydrogen is known to have attractive values, as discussed below. Furthermore, attempts have been made to use solutions in ammonia of some of the more promising elements, such as lithium, magnesium, aluminium and potassium. These solutions have the advantages of low vapour pressure, low viscosity, and high heat conductivity, but are low in density (0.50-0.65 kg/l), and tend to decompose in storage with the release of hydrogen.

For a given fuel-oxidant pair, the mixture mass ratio has marked effects on combustion temperature and molar mass of dissociated products, as indicated in figure 13.13 for the reference hydrocarbon rocket fuel RP-1 (see table 13.1) and for hydrogen burning with liquid oxygen. The peak values of specific impulse are

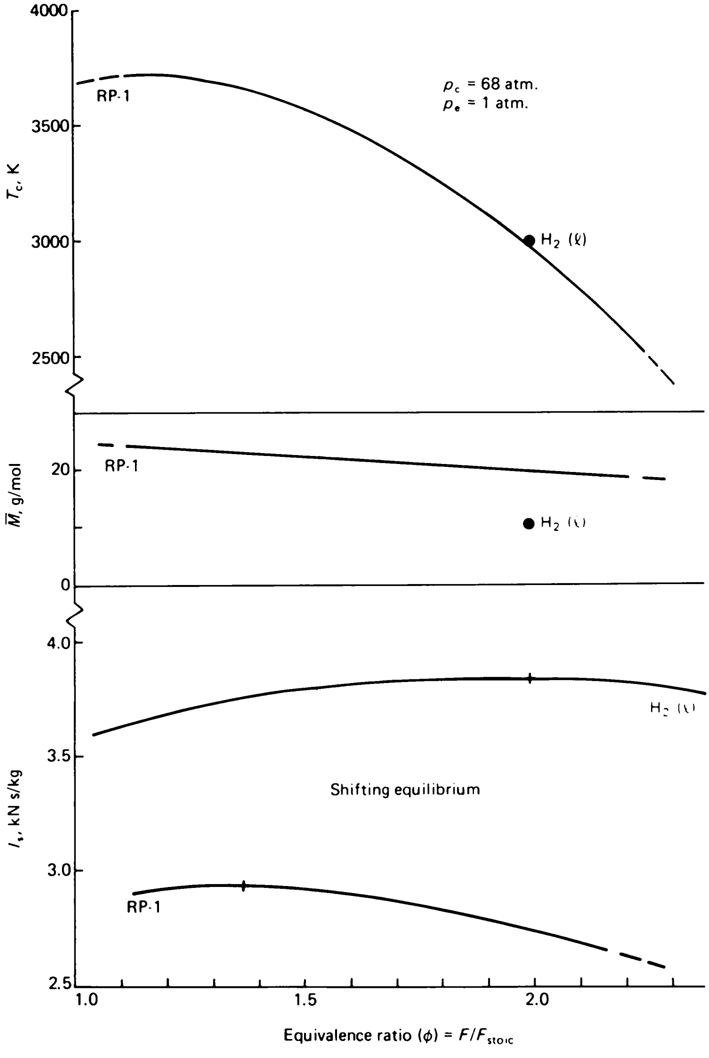


Figure 13.13 Calculated performance characteristics of RP-1 and liquid hydrogen with liquid oxygen (derived from refs 6, 23 and 24)

seen to be 2942 and 3834 N s/kg at equivalence ratios of 1.36 and 1.99 respectively. Values of specific impulse may be calculated on a basis of either 'shifting' or 'frozen' equilibrium: the former allows for the changes in product composition taking place along the propelling duct whereas the latter, for simplicity, assumes that no further chemical changes occur after combustion in the chamber, giving results that are approximately 5 per cent lower.

13.3.1 Liquid Rocket Fuels

As before, fuel performance is rated on a volume basis when aerodynamic drag of a vehicle is dominant, and on a mass basis when it is not. The rating parameters are therefore density impulse in the former case, and specific impulse in the latter, as follows

Density impulse = $I_d = I_s \rho_R$ N s/l

Specific impulse = $I_s = F/\dot{m}_P$ N s/kg

where ρ_R = density of reactant mixture at storage conditions
$\dot{m}_P$ = mass flow rate of propellants
= mass flow rate of reactant mixture in the chemical rocket.

The peak 'shifting' values of I_d and I_s are plotted in figure 13.14 against the density of the corresponding reactant mixture. In view of the broad direct relationship between peak specific impulses and calorific values of propellant mixtures, the familiar direct and inverse relationships respectively with density are observed. Because of the inclusion of density in the former impulse term, this relationship is seen to be closer. The inferiority of hydrogen on a density basis, but its superiority on a mass basis, are both clearly evident.

13.3.2 Liquid Oxidants

In chemistry, the term 'oxidation' refers to an increase in positive valency, that is, a loss of one or more electrons, and is therefore a reaction with some reagent which may not necessarily be oxygen itself. Nevertheless, the most abundant and conveniently available oxidant is oxygen, and its most appropriate form for storage is in the liquid phase. However, liquid oxygen is cryogenic, with its attendant storage complexity, consequently oxides of a more convenient physical form are considered as alternatives. The representative examples shown in table 13.8 include the oxygen compounds of hydrogen and nitrogen, together with the fluorine compounds of chlorine and oxygen. As liquids, fluorine and oxygen difluoride also require cryogenic handling in order to restrict the rate of vapour loss. High test peroxide (HTP) is stable in storage if protected from temperature rise and contamination, but will react slowly with most organic materials, and may promote spontaneous ignition. Compatible materials suited to oxidant system construction include stainless steels, aluminium, magnesium and brass for

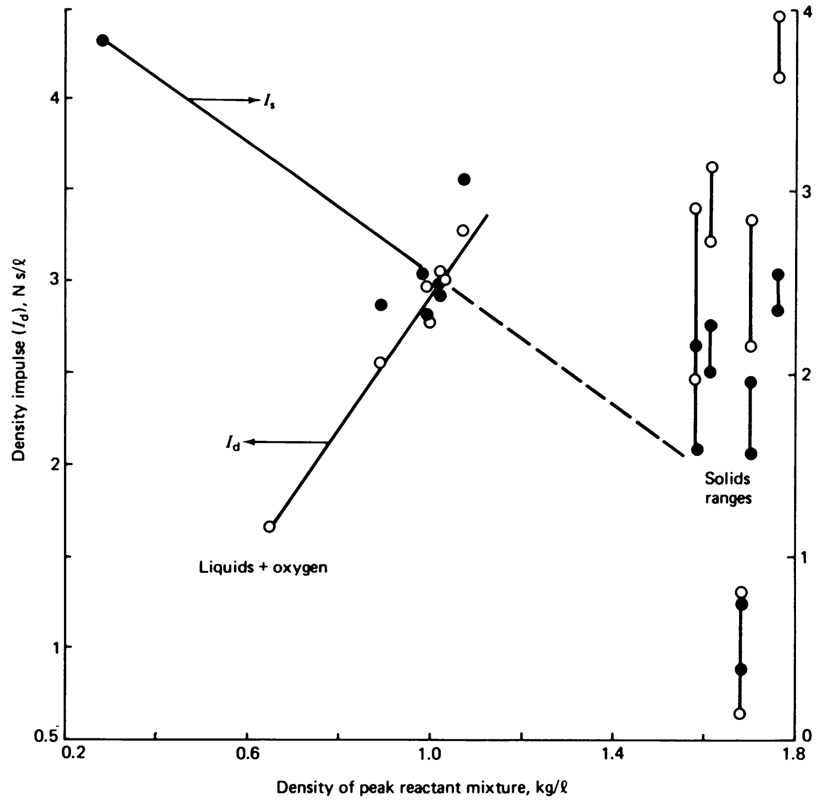


Figure 13.14 Comparative values of peak density impulse and specific impulse for liquid rocket fuels with liquid oxygen (derived from refs 13 and 23)

the cryogens, and pure aluminium and stainless steel for HTP, fuming nitric acid and nitrogen peroxide.

HTP decomposes to oxygen and steam at temperatures ranging from 450°C to 996°C (80 and 100 per cent concentrations). Decomposition is catalysed by permanganates and silver, the resulting condition being suitable for the spontaneous ignition of an added fuel such as kerosine, leading to a reliable 'thermal ignition' system for bi-reactants. Some reactant pairs are hypergolic, in that they ignite readily on contact. These include HTP and hydrazine, red fuming nitric acid and hydrazine, and fluorine and hydrogen. A minimal ignition delay is essential for satisfactory ignition, otherwise the chamber will tend to fill with reactants before the initial molecules have completed their pre-ignition reactions, resulting in a 'hard start' (comparable to 'diesel knock') or, in extreme circumstances, a destructive explosion.

In handling without adequate protection, the cryogenics give rise to 'cold' burns, whereas fluorine, chlorine trifluoride and nitric acid attack animal tissue,

Table 13.8 Oxidants

Property	Air	Oxygen	Hydrogen peroxide[a]	Nitric acid[b]	Nitrogen tetroxide	Fluorine	Chlorine trifluoride	Oxygen difluoride
Formula	–	O_2	H_2O_2	HNO_3	N_2O_4	F_2	ClF_3	OF_2
Oxidant % mass	23.2	100	94.1	76	69.6	100	100	100
% vol.	21.0	100	50	60	67.7	100	100	100
Molar mass, g/mol	28.96	31.999	34.016	63.013	92.016	37.997	92.448	53.996
Density (g), kg/m^3	1.225	1.353	1.439	2.665	3.892	1.607	3.911	1.864
Rel d at 15°C	1	1.105	1.175	2.175	3.177	1.312	3.193	1.522
Density (l), kg/l 15°C	–	1.14*	1.45	1.56	1.45	1.66*	1.84*	1.53*
bp °C	–	– 182	150	86	21.2	– 188	11.8	– 146
mp °C	–	– 219	– 0.3	– 42	– 11.6	– 220	– 83	– 223
ΔH_{vap}, kJ/kg	–	213.53	1448.6	481.48	414.03	171.66	298.10	205.15

*At boiling point.

[a] Described as High Test Peroxide (HTP) when concentration of H_2O_2 in H_2O is above 80 per cent.

[b] Nitric acid of over 97 per cent concentration (fuming) is normally ‘white’, but designated ‘red’ when containing 7 per cent or more of dissolved oxides of nitrogen.

and are toxic. HTP tends to irritate and blister the skin, but is harmless if washed away without delay.

The charts of merit order in figure 13.15 rate the combined performance of both fuels and oxidants, and show the maximum density impulse to be produced with hydrazine and fluorine, and the maximum specific impulse with hydrogen and fluorine. For fuel-oxidant selection in bi-reactant systems, therefore, the general conclusions drawn are for heavy reactants during atmospheric operation

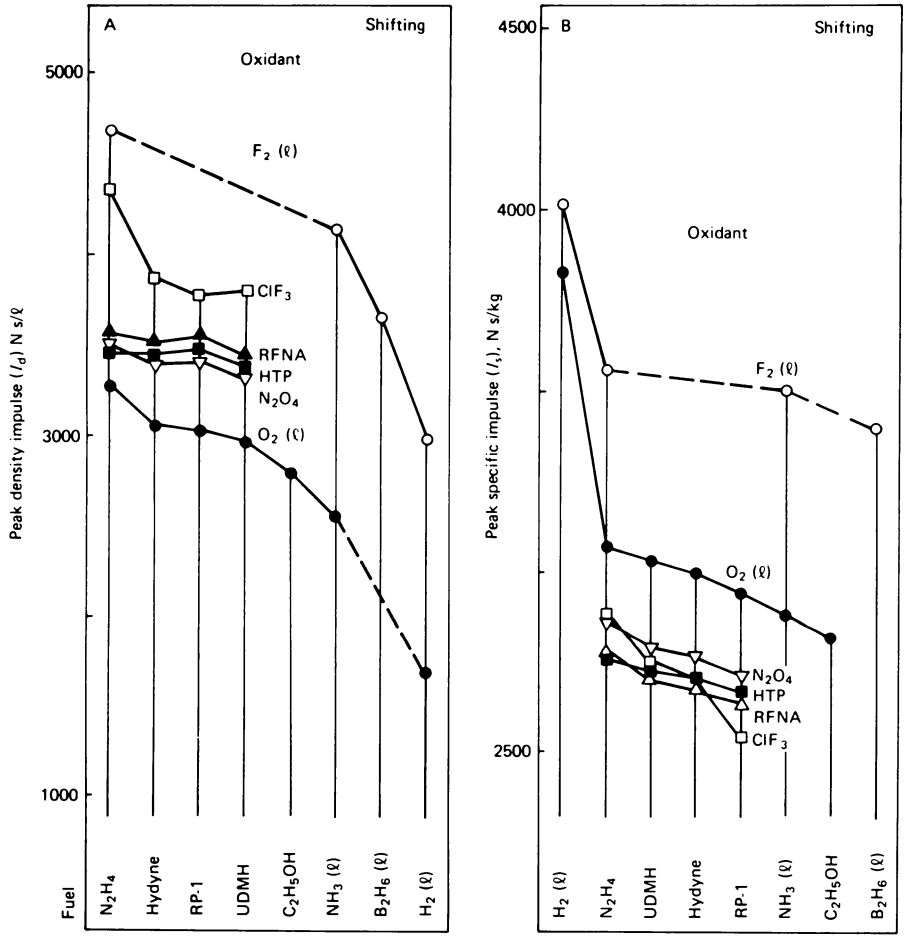


Figure 13.15 Charts for peak values of density impulse and specific impulse (derived from refs 13 and 23)

Key: HTP = high test peroxide (= conc. H_2O_2)
Hydyne = 60/40 mass mixture UDMH and diethylenetriamine
RFNA = red fuming nitric acid
RP-1 = rocket propellant 1 (= narrow-cut kerosine)
UDMH = unsymmetrical dimethyl hydrazine

where aerodynamic drag is significant, as in the early stages of an interplanetary mission, and for light reactants in space where mass performance is paramount. These conclusions are shown to apply broadly to the examples given in table 13.9, notable exceptions being the space shuttle with its high payload, which uses liquid hydrogen and liquid oxygen in the early stages, and the relatively small Scout atmospheric probe vehicle which exploits the compactness and simplicity of solid reactants (discussed later).

Table 13.9 Rocket reactant vehicle applications
(Derived from references 13 and 25)

Vehicle stage	Reactants		Representative vehicles
	Fuel	Oxidant	
1	Kerosine	HTP	Black Knight
	Aniline*	HNO_3	Aerobee
	Turpentine*	HNO_3	Veronique
	UDMH	N_2O_4	Ariane 3 and 4**; Gemini-Titan
	C_2H_5OH	O_2 (l)	Viking
	Kerosine	O_2 (l)	Thor-Agena; Atlas-Agena D; Atlas-Centaur; Delta**; N-11**; Saturn 1, 1B & V
	H_2 (l)	O_2 (l)	Space shuttle**
	Solid		Scout
2	UDMH	N_2O_4	Ariane 3 and 4; N-11
	UDMH	RFNA	Thor-Agena; Delta; Atlas-Agena D; Gemini-Titan
	H_2 (l)	O_2 (l)	Atlas-Centaur; Saturn 1, 1B and V; Space shuttle
	Solid		Scout
3	MMH	N_2O_4	Space shuttle
	H_2 (l)	O_2 (l)	Ariane 3 and 4; Saturn V
	Solid		Delta; N-11; Scout
4	Solid		Scout

*Hypergolic pairs.
**Plus strap-on boosters.
MMH Monomethyl hydrazine, $CH_3N_2H_3$.

13.3.3 Monopropellants

The simplicity, and inherent reliability, of a liquid rocket engine system can be improved, together with reduction in mass, by the adoption of a monopropellant which produces energy by means of exothermic reactions of either a decomposition or self-oxidation type, but at the expense of performance level. Monopropellants are required to be stable at ambient conditions, but to react readily when subjected to heat and pressure. Typical applications include small-scale thruster units for such duties as vehicle attitude and trajectory adjustment where they are suited to repeated operation, or for rocket turbopump drives.

The term 'monopropellant' is customarily reserved for liquids, examples of which are shown in table 13.10, although solid propellants really fit this definition also, as discussed below.

Table 13.10 Monopropellant properties and performance
(Derived from references 6, 24 and 26)

Monopropellant	Formula	Density at 20°C (kg/l)	I_d* (N s/l)	I_s* (N s/kg)	Reaction temp.* (K)
UDMH	$(CH_3)_2N_2H_2$	0.78	1530	1961	1154
Hydrazine	N_2H_4	1.008	1958	1942	905
Nitromethane	CH_3NO_2	1.12	3126	2491	2640
HTP	H_2O_2	1.44	2330	1618	1278
Tetranitromethane	$C(NO_2)_4$	1.638	2907	1775	2170

*Expanding from 68 to 1 atm.

13.3.4 Solid Rocket Reactants

The volume of rocket reactants is reduced to a minimum by storage in the solid phase. Since neither flow transfer nor mixing is then feasible, the reactants are pre-mixed and stored within the combustion chamber itself. The charge 'grain' is commonly shaped into a certain geometrical cross-sectional pattern, together with selective inhibition of some surfaces, so that the surface area exposed to combustion remains approximately constant in order to promote constant thrust. Solid reactants may combine an organic fuel such as a hydrocarbon, polymer, plastic or rubber with an inorganic oxidant such as a perchlorate or nitrate. Alternatively, they may consist of compounds that act as both fuel and oxidant (nitrocellulose, nitroglycerine). Also present may be additives (for example, lead, potassium sulphate, carbon black) to control the burning rate, the exhaust flame length, premature combustion below the surface, and many other physical and chemical characteristics. Composite reactants contain both inorganic and organic compounds, whereas some composite double-base reactants are modified with metal powders.

One of the earliest solid reactants is black powder, a mixture based on an inorganic oxidant, which has a relatively low performance (table 13.11), but has an indefinite storage life, and serves well as an igniter for large grains. Alternatively, the combined fuel–oxidant molecules may be so small as to exist in the translucent colloidal state. However, although both nitrocellulose and nitroglycerine are prone to detonation, they become relatively stable when plasticised together, and can remain so for long periods with the addition of a stabiliser. These double-base colloids can be designed for casting or extrusion. In composite reactants,

Table 13.11 Representative solid rocket reactants
(Derived from references 6 and 27)

Type	Examples	Comments	Density (kg/l)	Burning rate r (cm/s*)	T_C (K)	I_s (N s/kg) (68 to 1 atm.)
Black powder	Potassium nitrate, 62% Charcoal, 23% Sulphur, 15%	Ignition shock but low flash. Long storage life, used as igniter	1.68	0.20	1600–2300	390–785
Solid base colloidal	Nitrocellulose	Cool burning but hygroscopic and detonable				
Double-base colloidal	Nitrocellulose, 50% Nitroglycerine, 30% Plasticiser and stabiliser 20% Cast	Both nitric esters detonable but stabilise each other as colloid	1.58	0.56–0.94	1460–2240	1570–2160
	Nitrocellulose, 55% Nitroglycerine, 40% Stabiliser, 5% Extruded	Some flash and smoke. Not case bondable	1.61	1.52–2.29	2130–2910	2010–2255
Composite	Ammonium picrate, 55% Potassium nitrate, 35% C_2H_4O fuel binder, 10%	Brittle. Wide burning rate. Case bondable. Smoke	1.70	0.61–2.54	1795	1570–1960
Composite modified double base	Nitrocelluose, 25% Nitroglycerine, 25% Ammonium perchlorate, 25% Aluminium, 25%	High performance. Case bondable. Flash and smoke	1.76	0.76–2.54	4000	2350–2550

*At 68 atm and 20°C.

the organic material acts as a binder whereas the composite modified double-base reactants contain components of both nitric esters and inorganic oxidants, together with aluminium powder for additional energy. One requirement of a reactant grain is to prevent hot combustion gases from either damaging the chamber casing or initiating combustion at the local grain surface. This may be achieved by bonding the grain to the casing, or inhibiting the grain surface adjacent to the casing. In the latter case, an obturator semi-seal assists by permitting pressure equalisation but eliminating flame contact with the protected surfaces.

The storage requirement for the grain to retain its shape and consistency over extended storage periods and throughout changes in temperature and humidity imposes stringent property requirements of a physical as well as a chemical nature. In the absence of storage tanks, pumps and control valves, solid reactant systems are intrinsically simpler than liquid reactant systems, but they do not offer such flexibility of operation, and cannot easily be shut down and restarted. Furthermore, their thrust performance is lower than that of liquid reactants. Although the specific impulse parameter can be employed as a measure of propulsion performance, the 'one-shot' operation makes more appropriate the total impulse parameter expressed as

$$\text{Total impulse} = I_T = \int_0^{t_T} F\,dt = \bar{F}\,t_T$$

where t_T = total reaction time, and
$\bar{F}$ = mean value of thrust.

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14 Conclusions and Prospects

This study has reviewed the current situation with regard to aviation fuel quality arising as the dynamic resultant between the constraints of supply and the requirements of demand. It also comments briefly on both the immediate historical background to this situation, and the alternatives that offer future potential. Aviation fuel quality and availability are seen to be influenced by such technological factors as production techniques, component control, measurement precision and the various aspects of service performance. Additional factors include the supply and demand of non-aviation fuels, particularly motor gasoline and diesel fuels, and thus the relative cost values of each of these products. In turn these costs, which have become of crucial importance in airline finances, are dominated by taxes, regulations and matters of a political, and possibly military, nature. An accurate prediction of the fuel quality likely to be available from the year 2000 is needed now to give the direction for future engine, fuel system and airframe design, research and development programmes. A new design concept started now will not be ready for commercial production until after the turn of the century. This prediction could also determine the potential life of existing equipment since it will highlight those modifications that will need to be carried out to operate on these fuels.

Looking to the future, a fairly comprehensive review of the alternative fuel potential has been attempted here, mainly to show what could be available rather than to predict what will be. The technological assessment of these alternatives indicates the probable potential of these fuels but, as indicated above, economics may distort the picture drastically. The encouraging facts are that several alternatives do seem possible, and that no shortage of energy appears to exist overall. The decisions required relate to the particular forms in which the energy is to be carried and used. These decisions command some urgency since, despite the comforting realisation of some 30 to 50 years continued supply of crude oil *in the absence of any further major disruptions*, any new material is likely to require about 10 to 15 years to bring into economical quantity production. In particular, the complete fuel provisioning scene would be recast substantially if those nations with significant consumption levels decided to opt for an energy economy based broadly on methane, or methanol, or hydrogen. The ready availability and reduced price of such a standard fuel would then impact strongly on the path of aircraft design, airport fuelling layouts, and aircraft operations generally. Nevertheless, such changes could not be achieved unilaterally since civil aviation is so international in character that all major airline operators would have to change in turn. This is most unlikely in the present climate of thinking since the conversion costs of both aircraft and ground facilities would be massive.

14.1 Aero Piston Engine Fuels

The spark-ignition piston engine requires fuel of low spontaneous ignitability in order to resist spark knock, consequently light hydrocarbon blends of the gasoline type prove suitable. Being low in density, these fuels also exhibit high volatility which permits fuel metering by carburation, but adoption of the more complex timed injection would overcome the intractable problems of mixture maldistribution, and ease the difficulties of cyclic dispersion, mixture control with variation of altitude and of attitude, effects of manifold pressure, evaporative freezing, rapid acceleration, and emissions. However, aviation gasoline is manufactured in a very few refineries only, by batch production over a short period of about 5 days. This entails an expensive setting of the plant to the required quality for the avgas components, and resetting at the end of the batch. Thus, avgas is becoming a specialty product, and the high price is maintained by the expense of both batch production and the dedicated distribution to many small airfields.

In view of the price differential outlined above, and following the withdrawal of avgas 80 from the British market, pressure has been growing for approval to use four-star mogas in certain light aircraft. Problems with engine operation, and aircraft fuel systems, had already been encountered following changes from one gasoline grade to another, largely because of the different levels of lead content, indicated below:

Fuel grade	Designation	g Pb/l, max.
Aviation gasoline 80/87	Avgas 80	0.14
Motor gasoline	Mogas	0.40
Aviation gasoline 100/130 low lead	Avgas 100 LL	0.56
Aviation gasoline 100/130	Avgas 100	0.85
Aviation gasoline 115/145	Avgas 115	1.28

Each engine model is developed on a particular level of lead content, and the use of a fuel with either less or more lead can give rise to the following problems:

Lead content too high – fouling of sparking plugs
– seizure of pistons and burnt valves
Lead content too low – spark knock
– 'walk in' of valves into head owing to lack of hardening effect of lead
– cracked cylinder heads
– broken piston rings

After much discussion, the use of mogas for light aircraft has been permitted in the U.K., New Zealand and West Germany, but is restricted to named aircraft types, airfield installations, pre-takeoff tank temperatures of less than 20°C, and a pressure altitude of less than 2000 m. The situation is more complex in a large country with a wide range in climates and airfield altitudes, and a few types of aircraft only are cleared for mogas in the U.S.A., where seventeen different specifications exist, each changing seasonally four times a year. Nevertheless, despite the subsequent return of avgas 80 to the British market, user pressure to permit mogas for aircraft is likely to persist while the price differential remains significant.

Approximately 50 per cent of general aviation is served by avgas, mainly 100 LL grade, with a very small amount of 80 grade, when available, and some 115 grade which is being retained for the older, larger aircraft still in freight service. Coal can be converted directly into aromatic-rich liquid fuels of high anti-knock quality, but the cost is not likely to become competitive until it is reduced by quantity production, and offset by continued rises in crude oil prices.

In general, aero piston engines could operate satisfactorily on methane, with its high octane rating and specific energy, together with its clean burning ability which reduces emissions and also maintenance costs. The lower energy density and cryogenic nature demand larger fuel tankage of cylindrical design within the fuselage, but the loaded mass would be comparable with that of avgas-fuelled aircraft. Of all the alternatives considered, liquid methane is one fuel that is already substantially less expensive than avgas (approximately one-third of the price in the U.S.A.), nevertheless, the costs of conversion of both aircraft and ground facilities may prove unacceptable.

The high fuel economy of the compression-ignition engine has long been attractive to aviation, but the relatively high mass/power ratio has inhibited previous applications. However a recent proposal is the development of a three-cylinder two-stroke 'Merlyn' diesel engine of about 500 kW with a mass/power ratio of 0.55 kg/kW, compression ratio of 15.3, and a specific fuel consumption claimed to be 40 per cent less than an equivalent turbopropeller engine[1]. Gas oil, kerosine and wide-cut gasoline are all equally acceptable in the engine, but gas oil, of course, would be prone to freezing at altitude. Ideally, if piston engines can be developed with combustion chambers independent of fuel octane or cetane quality, the resulting multi-fuel capacity would eliminate the need for scarce and expensive avgas. There is some promise of this from the emergence of hybrid spark/compression-ignition piston engines which can already accept gasoline, gas oil, methanol, wide-cut distillate and several other types of fuel.

14.2 Aero Turbine Engine Fuels

The major engine requirement for aviation turbine fuels is cleanliness of combustion, which implies not only freedom from contaminants but also a control on carbon content in order to limit flame radiation, carbon deposition and the formation of smoke. Handling requirements impose additional limitations on flash point for fire safety, and freezing point for low-temperature operation. Thermal stability is, and will continue to be, a critical requirement for both engine and fuel systems. Maintaining future supplies of current fuel types may necessitate a reduction in the present thermal stability limit. However, the higher temperatures of the more energy-efficient engines will require thermal stability to rise, calling for compromise and/or advanced designs. The kerosines have provided the most successful compromises with regard to these property requirements, although a wide-cut blend of naphtha and kerosine was derived during the early growth of aero turbine usage in order to ensure continuity of fuel supply, and has been adopted since, together with its acknowledged crash fire hazard, for military use in certain regions.

Aviation kerosine is relatively easy to manufacture, and the yield from suitable crudes varies from about 10 to 20 per cent. Crude oil selection is expected to become more limited, and the densities to rise marginally. Since the distillation range of any petroleum cut represents the extent of yield from the parent barrel, as outlined above with wide-cut gasoline, attention has turned to broadening the actual (as distinct from the specified) distillation range in order to augment the yield. From the supply viewpoint, extension towards the lighter fractions would prove feasible if mogas production declines, whereas extension towards the heavier fractions would compete with the gas oil and diesel fuel markets. However, distillation broadening is directly limited by the changes in related properties and problems. Lowering the initial boiling point, for example, will have a corresponding effect on the flash point which, despite the absence of any deleterious effects on engine performance, represents a step towards the greater crash-fire hazard of wide-cut gasoline. Significant reductions in flash point are therefore unlikely in the near future, on the grounds of safety, but research and development may prove the feasibility of reducing flash point from 38 to 35°C and, ultimately, to 32°C. Furthermore, extending the final boiling point would incorporate heavier components which are more likely to freeze at high altitude cruise, and also lead to more flame radiation, reduced engine life and difficulties in engine relight at altitude. However, freezing point has recently been relaxed from −50°C to −47°C, and experience with civil aircraft may permit further increases to −45°C, and ultimately to −43°C.

Since only about 30 per cent of an oil field deposit is currently recoverable, enhanced oil recovery appears a logical approach to augmenting petroleum reserves, but tends to be inhibited by regulations and costs, including taxes. However, supplies of aviation kerosine may be supplemented from any of the alternative fossil sources including shale oil, tar and coal, together with the early stages of coalification represented by peat. Of these, the mainly paraffinic, low aromatic, shale oil appears to be the most suitable in terms of resource extent and quality of product. Kerosine yields reach 75 per cent of the parent shale oil, and this can be increased to above 100 per cent by including the additional hydrogen required for the more extensive hydrogenation. Nevertheless, a production rate of 2 million barrels/day of shale-derived kerosine would entail a massive shale handling task, estimated as equivalent to digging a new Panama

Canal every year! One imaginative proposal concerns the erection of a huge air-supported dome of transparent Teflon foil, 100 m high in the centre, to protect a 14 hectare mining site from intense cold in winter, and insect pests in summer[2].

The hydrogenation of coal and tar resources is expensive, but might be avoidable by the adoption of catalytic combustors that operate close to the theoretical flame temperature for the given air-fuel mixture, and therefore burn the catalytically reactive aromatic-rich fuels of low hydrogen content with exceptional stability and low emissions levels. The high fuel nitrogen contents also appear to be inhibited from forming excessive concentrations of nitrogen oxides[3].

Of the potential substitute fuels, only the cryogenics appear promising. Liquid methane could become more available and less expensive than petroleum throughout much of the world, depending on developments within the complete energy scene. As before, cylindrical tanks would be required within the fuselage, but cryogenic insulation would delay boil-off losses for several days. As a clean-burning fuel with minimal carbon content, a high flame-tube life would be expected, together with reduced emissions of carbon dioxide.

In comparison with methane, more energy is required to liquefy hydrogen, and the cryogenic handling problems are that much more acute, but a remarkably high specific energy results. Flame radiation is minimal, together with pollution. Furthermore, for those nations deprived of fossil energy feedstocks, the combination of resources of water and nuclear, hydroelectric, solar or geothermal power renders liquid hydrogen attractive as a universal aviation fuel. The 'Hindenburg syndrome' of the crash-fire hazard is yielding to logical open-minded analysis, and a balanced assessment shows the safety of liquid hydrogen to be generally comparable with that of liquid methane and kerosine, even with minor advantages in some respects (see summary in table 14.1). Innovative concepts for the future include the aerospaceplane designed to use liquid hydrogen and air on takeoff and then employ the heat-sink capability of the liquid hydrogen to liquefy the intake air at altitude, discard the liquid nitrogen, and cruise using liquid hydrogen and liquid oxygen.

In summary, the significance of aviation fuel quality, availability and price has become paramount in view of the rise in the fuel proportion of the airline total direct operating costs (from 25 to 60 per cent in 10 years), particularly since fuel prices may now rise slightly faster than inflation because of increasing resource value. This has become such a potent factor in airline profitability, and even survival, that aircraft will tend to be grounded as soon as they cease to be fuel-efficient, rather than continue in service until they suffer eventual loss of passenger appeal or of economic maintenance. In commercial aviation, however, competition controls fares to such an extent that finance is not easily available for immediate fleet replacement with the more efficient aircraft. The overall costs involved with aircraft fleets, ground storage and handling make the conversion to substitute fuels highly unlikely without some major shift in the supply pattern. The ultra-high performance required for ramjet and rocket propulsion, on the other hand, will probably involve unavoidably high costs until such time as fuel selection becomes sufficiently standardised to permit quantity production.

Table 14.1 Potential aviation fuels
(Derived from reference 4)

Fuel	Source	Comments	Piston	Turbine
Avgas	Petroleum	Conventional	✓	
Mogas	Petroleum	Four-star, conditionally	✓	
Avtag	Petroleum	Conventional military		✓
Avtur	Petroleum	Conventional civil		✓
Avcat	Petroleum	Conventional naval		✓
Supplemental				
Avgas	Coal	High aromatics and anti-knock	P	
Avtag	Shale	Low aromatics, olefins and S, but high N		P
Avtur	Tar	High aromatics, and low H, MJ/kg and smoke point		P
Avcat	Coal	Low aromatics after hydrogenation		P (?)
Substitute				
Methane (l)	NG, Hcs, SMW	High anti-knock, MJ/kg and clean burning but low MJ/l and cryogenic. Safety?	P	P
Hydrogen (l)	Hcs, coal, water	Very high MJ/kg and clean burning but very low MJ/l and cryogenic. Safety?	U	P
Oxygenates	NG, Hcs, coal, biomatter	High anti-knock and clean burning but low MJ/kg and MJ/l	U	U
Nitrogen hydrides	Coal ($N_2 + H_2$)	High anti-knock, but low MJ/kg and MJ/l, and high hazard index	U	U
Nitromethane	(Hcs + HNO_3)	High MJ/kg mixture, but low MJ/kg and MJ/l and unstable	U	U

P = Possible. U = Unlikely.
NG = Natural gas. Hcs = Hydrocarbons. SMW = Solid municipal waste.

14.3 Alternative Systems of Aircraft Propulsion

In addition to the high-temperature exothermic processes of combustion, either with flame or catalytically, energy release also occurs in biochemical processes, electrochemical reactions, nuclear reactions and dynamics. The following sections outline some possibilities of their application to aircraft propulsion.

14.3.1 Biofuels

The bio-derived hydrocarbon oxygenates have been seen to be generally unsuited to any large-scale application in aviation because of the unacceptably high mass content of oxygen. The direct use of biomatter as fuel in the form of vegetable oils is showing some promise for diesel engines, but has generated little interest to date in the gas turbine world where similar problems of oxygen content would arise, together with possible difficulties of gumming and smoke formation. One concept of popular interest, but restricted to the lightest end of the aircraft mass range, is that of human-powered flight. Successfully-flown aircraft in this category include Southampton University's 'Sumpac', Hatfield Club's 'Puffin', and the Japanese 'Linnet' series, with Dr Paul MacCready's 'Gossamer Condor' winning the 1 mile Kremer prize in 1977, and the 'Gossamer Albatross' crossing the English Channel in 1979 at about 6 m/s, piloted by Bryan Allen[5].

The human body can absorb up to 5 litres of oxygen per minute in developing pedal power steadily at about 200–300 watts for over an hour, raising this to about 400 watts for 5 minutes. For very short periods of high activity, as at takeoff, the body can go into oxygen debt, and generate a total of about 1500 watts, achieved by hydrolysis of glycogen stored within the muscles. The most suitable 'fuel' appears to be a diet rich in carbohydrates, with glucose syrup providing a rapid recovery after the exertion. It is interesting to note that the next Kremer target concerns an airspeed of 20 mi/h for 3 minutes, with the concession of storing the pilot's muscular energy for 10 minutes prior to takeoff, and that small samarium-cobalt electric motors capable of generating 750 watts at 30 000 rev/min are already in existence. These motors are about 10 cm in length and 4 cm in diameter, with a mass of 600 g, and the pre-flight electrical energy generated by the pilot is likely to be stored on board in nickel–cadmium cells.

14.3.2 Electric Propulsion

Developments in low-mass electric motors have given rise to the concept of electric propulsion for small aircraft. Under test is a Sikorsky helicopter fitted with a 270 kg pack comprising twelve 72 volt lead-acid batteries driving four electric motors and producing a total of 180 kW for about 10 minutes. Silver-zinc batteries are expected to increase flight time to 30 minutes, and a 70 kg lithium hydroxide cell system to 2 hours. The advantages claimed are low engine noise with no exhaust products, infrared signature, warm-up requirement or altitude density problem[6], but electric batteries are notoriously heavy, and a very significant break-through would be required before this application could be widely successful. The further development of fuel cells, of course, would greatly reduce the weight problem, and permit the use of light distillates, hydrogen or alcohols as fuels.

Moving closer to the lower end of the engine power range, the radiant energy from the sun could be collected by photovoltaic cells on the aircraft upper surfaces and be converted directly to electricity for propulsion. Successfully flown solar-powered aircraft include Fred To's 'Solar One' (December 1978), Larry Mauro's 'Solar Riser' (April 1979), and Dr Paul MacCready's 'Solar Challenger' which first crossed the English Channel in July 1981. These aircraft are of the ultra-light type, ranging from 57 to 104 kg empty mass, with arrays of multiple solar cells (500 to 16 000) arranged in collection areas of about 20 m^2 on mainplane surfaces, and generating up to about 4.5 kW. Flight speeds of up to 80 km/h were achieved, at altitudes of over 6 km. Typically, silicon cells of 300 micrometres thickness are connected in series and parallel, with conversion efficiencies up to 14.5 per cent, and potentials of about 66 volts.

Further activities along these lines are inhibited by the high cost of producing the large crystals of pure silicon from which the cells are sliced, but current developments centre on the manufacture of inexpensive cells by vacuum-depositing thin films of amorphous silicon, together with its appropriate circuitry, onto a plastic substrate using continuous industrial processing. Alternatively, such semi-conductor materials as gallium arsenide, cadmium zinc sulphide or copper indium selenide may be used, deposited onto a thin copper substrate[7]. Even with continuing successes in such developments, it is difficult to foresee the application of solar power to aircraft of conventional sizes, unless the radiation can somehow be concentrated by the use of orbital solar power stations, and transmitted to the aircraft by laser beams.

14.3.3 Nuclear Propulsion

The upper end of the energy spectrum involves the heavy elements capable of nuclear fission, and those proposed for aviation comprise uranium 235 and plutonium 239 in the form of enriched oxides, with water as a moderator. In the open-circuit nuclear gas-turbine engine, the reactor effectively replaces the conventional combustion chamber, giving direct heating of the air throughput, as in the General Electric HTRE (Heat Transfer Reactor Experiments) project. The heavier closed nuclear-circuit system incorporates a heat exchanger using a suitable reactor coolant, such as helium, and this overcomes both the poor heat transfer to low density air at altitude, and the danger of propellant air contamination. The fuel consumption of such a propulsion system would be negligible, and the range of the aircraft semi-global, with the possibility of a variety of special missions. A small reactor has been run to criticality, and tested in flight. All radioactive components would be enclosed in a shielding containment vessel capable of maintaining safe levels of radiation, and of withstanding a full-scale crash landing. Ground tests have already shown leak-proof impacts at Mach 1 of simulated reactor containers into a concrete wall. In view of reactor and shielding mass, payloads of some 250 tonnes are considered minimal.

In the event that nuclear fusion not only becomes practicable but can be achieved with neutron-free reactions, perhaps boron–hydrogen, the need for heavy shielding would be greatly reduced, and the concept arises of closed nuclear-circuit systems using liquid metal, helium or steam as reactor coolants in an ultra-large aircraft of some 500 tonnes payload. Apart from the costs and environmental risks involved with air-borne nuclear power plant, one serious metallurgical problem arises from the fact that the metal surfaces (of the heat exchanger) must be hotter than the propulsion air, in contrast to a conventional chamber. Likely routine operational problems include variable control of power output, absorption of 'after heat' on shut-down and, in the case of the fission reactions, expensive reprocessing of the fuel elements after given periods of use. The alternative approach, of course, is to reserve nuclear reactions for the ground-based production of chemical aviation fuels, such as liquid hydrogen.

14.3.4 Inertial Propulsion

It would be technically feasible to store sufficient energy in a system of rotating flywheel rings to power a small helicopter type aircraft for about 400 km, with electrical recharging at low rates overnight, or at high rates at a service station. More ambitious projects envisage a large fan-driven commuter aircraft based on the same principle, but significant advances would be required in the energy storage capacity of the materials constituting the flywheel rings[8].

14.4 Conspectus

It can be stated with confidence, and no undue stretching of the imagination, that aviation is not only here to stay, but is likely to develop into the realms of much greater sophistication and performance. Furthermore, the survey presented in this book leads to the conclusion that the future supply of suitable aviation fuels can be regarded with cautious optimism, but is nevertheless dependent on unremitting efforts in the winning and processing of fuel resources, the maintenance of the highest class of fuel quality in handling, and the pursuit of excellence in the design and manufacture of all the associated engineering equipment, backed by high-quality research and education. This optimism is upheld by the awareness that alternative fuels are waiting offstage to play their part when required, but offset by the implications of cost.

It is also equally clear that overall success in these endeavours can be achieved only if they are matched by comparable efforts in the field of political decision-making, incorporating wise taxation policies, fiscal incentives and sound economic management. With the successful marriage of first-class brainpower and adequate funding, as already demonstrated, the sky is no longer the limit!

14.5 References and Bibliography

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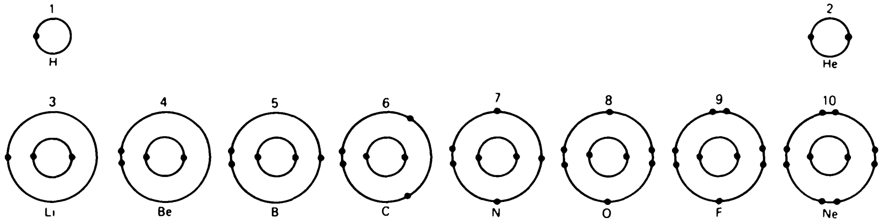
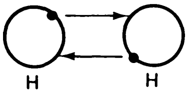
Appendix 1: Principles of Fuel Chemistry

To date, aviation fuels have invariably been derived from crude oil, and consist of blends of many different hydrocarbons, that is, compounds of hydrogen and carbon. The locations of both these elements within the Periodic System are shown below, together with the numbers of electrons (the *atomic number*) orbiting in their electron shells



Not shown are the central nuclei which comprise progressively increasing numbers of protons and neutrons.

An element is seen to be inert when its outermost shell becomes saturated with electrons, that is, with 2 in the case of the first shell (He), and 8 in the next outer shell (Ne). Each of the four subshells comprising the outer shell is saturated when it contains two electrons. Elements therefore react with each other, and their fellow members, until electron saturation occurs. Hydrogen, for example, combines with a like atom by means of the sharing of two electrons, as shown below, to give a single *covalent* bond, consequently the *valency* of hydrogen is unity.

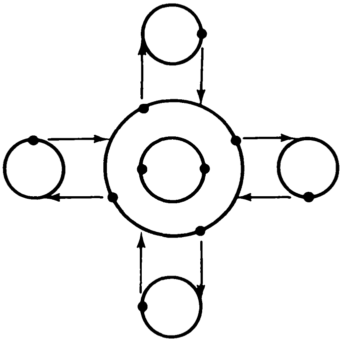


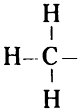
written as H–H, or H_2

The above configuration thus indicates that elemental molecular hydrogen gas normally exists in the stable diatomic state as H_2. Consequently, while these two atoms exist so bonded, their electron shells behave as saturated shells of helium which are inert and therefore react no further. Note that the nuclei remain those of hydrogen and not helium.

A1.1 Hydrocarbons

Similar covalent bonding occurs between hydrogen and carbon, with the lending and borrowing of electrons so that each hydrogen electron shell simulates that of helium, and each carbon outer electron shell simulates neon, giving overall stability provided that the atoms remain bonded to each other. In the simplest case, therefore, the molecule of methane appears as

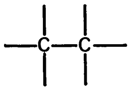
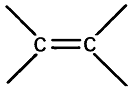


written as  $H-\overset{H}{\underset{H}{C}}-H$, or CH_4

(Extended formula) (Condensed formula)

Since the approximate molar masses of hydrogen and carbon are 1 and 12 g/mol. respectively, inspection of this structure shows its molar mass to equal $(1 \times 12) + (4 \times 1) = 16$ g/mol. Methane is thus seen to be lighter than air which, as a mixture of N_2 (28 g/mol.) and oxygen (32 g/mol.), has a mean molar mass of 28.96 g/mol.

As well as combining with hydrogen, carbon has the ability to combine with itself by covalent bonding which may comprise one, two or three separate bonds, appearing as follows

			$-C\equiv C-$
Carbon bond types	σ	1σ and 1π	1σ and 2π
Carbon-carbon bond length, pm	154	134	120

Since carbon is tetravalent, these structures leave six, four and two links respectively available for bonding with hydrogen or any other monovalent element. It should be noted that one of the bonds in each case is of the strong, sigma, type whereas the others are formed by electrons located in subshells which form a weaker, pi, type of bond. Consequently, although a double bond appears to be stronger overall than a single bond, as supported by the reduced inter-carbon spacing, the π bonds are vulnerable to disruption by any additional energy that becomes available. Single bonding between carbon atoms is classed as 'saturated', and multiple bonding as 'unsaturated'.

It is clear from the above that hydrocarbon molecules may be segregated into various groups depending on their carbon bonding and, in fact, on the overall molecular shape of either open or closed chains. These main groups, known as *series*, are as shown in table A1.1, with their different names used in fuel technology and in organic chemistry, together with their general formula where x, the number of carbon atoms in the molecule, is known as the ***carbon number***. The individual members increase in molar mass, and in density, with carbon number, and pass through the phases of gas to liquid to solid. Figure A1.1 shows how boiling points vary with carbon number in relation to distillation ranges.

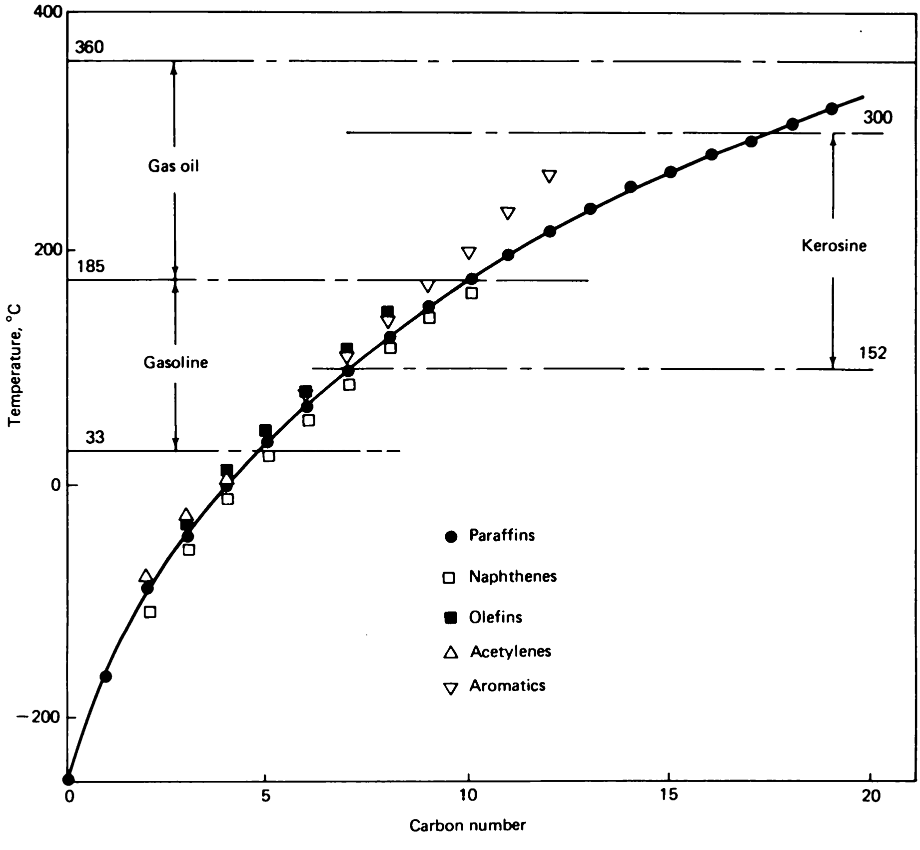
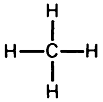
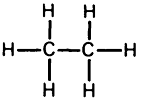
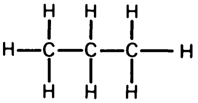
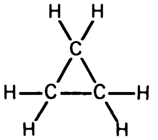
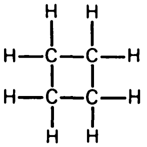
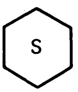
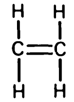
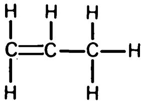
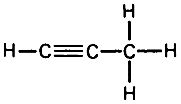
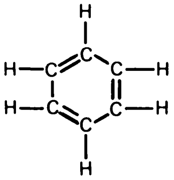
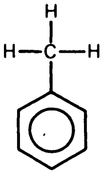
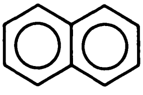
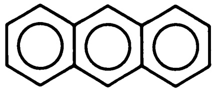


Figure A1.1 Variation of boiling points with carbon number in relation to distillation ranges

From the above discussion, the double bonding of the olefins represents instability in storage because of the addition of molecules to each other as the vulnerable π bonds disrupt. Thus

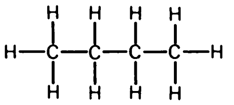
$$4\,C_4H_8 \longrightarrow 2\,C_8H_{16} \longrightarrow C_{16}H_{32}$$

Table A1.1 Structure of lighter members of the major hydrocarbon series

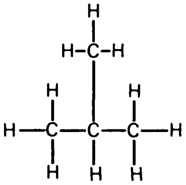
Paraffins (Alkanes) C_xH_{2x+2}	 CH_4, methane	 C_2H_6, ethane	 → C_3H_8, propane
Naphthenes (Cyclanes) $(CH_2)_x$	 C_3H_6 cyclopropane	 → C_4H_8, cyclobutane	 → C_6H_{12}, cyclohexane
Olefins (Alkenes) C_xH_{2x}	 C_2H_4, ethene	 C_3H_6, propene	→
Acetylenes (Alkynes) C_xH_{2x-2}	$H—C\equiv C—H$ C_2H_2, acetylene	 C_3H_4, methylacetylene	→
Aromatics	(Monocyclics) C_xH_{2x-6}	 C_6H_6, benzene	 → C_7H_8, toluene
	(Polycyclics) C_xH_{2x-12} C_xH_{2x-18} etc.	 $C_{10}H_8$, naphthalene	 → $C_{14}H_{10}$, anthracene

for example, and olefins gradually *polymerise* in storage to form gums ('Olefin' = oil forming). For this reason, their concentration in aviation fuels must be strictly limited. In fact, bonding by an *addition* process is typical of an unsaturated hydrocarbon compound, whereas a saturated compound tends to bond by the *substitution* of hydrogen atoms by groups of hydrogen and carbon atoms representing incomplete molecules known as *radicals*. A methyl radical thus constitutes CH_3–, and ethyl radical C_2H_5–, and so on, the hyphen indicating the free valence available for bonding. The symbol R is commonly used to indicate any hydrocarbon radical.

The structure of the hydrocarbon molecule determines its properties and behaviour, consequently there are significant differences between, say, cyclopropane and propene, as shown in table A1.2, despite the common formula of C_3H_6. This point is underlined very strongly in the case of *isomerism*. Molecules of the basic structures shown are described as *normal*, but an *isomer* of one such molecule represents a rearranged structure with exactly the same number of hydrogen and carbon atoms. The lightest of the paraffin molecules to exhibit isomerism is butane, which appears as

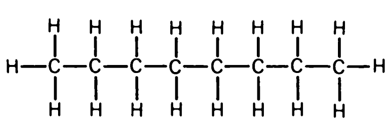


normal butane, n-C_4H_{10}

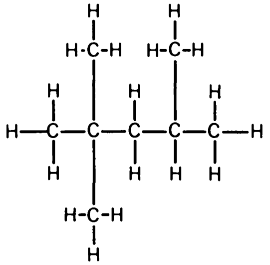


*iso*butane, i-C_4H_{10}

Again, significant differences occur between the properties of these two structures. Clearly, as the carbon number increases, the number of possible isomers rises very rapidly, as demonstrated by the total of 17 isomer octane (C_8H_{18}) structures, and 366 318 isomer eicosane ($C_{20}H_{42}$) structures. The effects of isomerism on hydrocarbon properties can be dramatic, as shown by the increase in spontaneous-ignition temperature from 230°C to 467°C from normal octane, n-C_8H_{18}, to the particular *iso*octane, i-C_8H_{18}, known as 2,2,4-trimethylpentane because of its basic pentane structure with three methyl (CH_3–) radicals located at carbon atoms 2, 2 and 4 numbered from the left-hand side, as shown



normal octane, n-C_8H_{18}



*iso*octane, i-C_8H_{18}
(2,2,4-trimethylpentane)

Table A1.2 *Physical and chemical properties of representative hydrocarbons*

Name	Formula	Molar mass (g/mol)	Density at 20°C (kg/l)	b.p. (°C)	f.p. (°C)	Specific energy* (MJ/kg)	(Fuel/air) stoic. ratio mass	Dissociated combustion temp. (K)
n-Paraffins (Alkanes)								
Methane	CH_4	16.042	0.415^b	-161.5	-184	50.05	0.0582	2247
Ethane	C_2H_6	30.068	0.561^b	-88.3	-172	47.52	0.0623	2282
Propane	C_3H_8	44.094	0.585^b	-44.5	-190	46.39	0.0640	2289
Butane	C_4H_{10}	58.120	0.600^b	0.6	-135	45.77	0.0649	2293
Pentane	C_5H_{12}	72.146	0.626	36.2	-131.5	45.38	0.0654	2295
Hexane	C_6H_{14}	86.172	0.660	69.0	-94.3	45.13	0.0658	2296
Heptane	C_7H_{16}	100.198	0.684	98.4	-90.0	44.95	0.0661	
Octane	C_8H_{18}	114.224	0.707	124.6	-56.5	44.82	0.0663	2299
Nonane	C_9H_{20}	128.250	0.718	150.6	-51.0	44.71	0.0664	
Isomers								
2,2,3-Trimethylbutane (Triptane)	C_7H_{16}	100.198	0.690	81.0	-26.0		0.0661	
2,2,4-Trimethylpentane	C_8H_{18}	114.224	0.691	99.5	-108	44.73	0.0663	
Naphthenes (Cyclanes)								
Cyclopropane	C_3H_6	42.078	0.720	-34.4	-126.6		0.0678	
Cyclobutane	C_4H_8	56.104	0.703	13	-80		0.0678	
Cyclopentane	C_5H_{10}	70.130	0.751	49.5	6.5	44.23	0.0678	2310
Cyclohexane	C_6H_{12}	84.156	0.778	81	-8	43.86	0.0678	2305
Cycloheptane	C_7H_{14}	98.182	0.811	119			0.0678	
Isomer								
Methylcyclopentane	C_6H_{12}	84.156	0.794	72	-141		0.0678	

n-Olefins (Alkenes)								
Ethene (ethylene)	C_2H_4	28.052		− 103.8	− 169.4	47.19	0.0678	2420
Propene	C_3H_6	42.078	0.610[b]	− 47.0	− 185.2	45.81	0.0678	2362
But-1-ene	C_4H_8	56.104	0.668	− 2.0		45.35	0.0678	2348
Pent-1-ene	C_5H_{10}	70.130	0.641	34	− 139	45.03	0.0678	2339
Hex-1-ene	C_6H_{12}	84.156	0.673			44.83	0.0678	2333
Hept-1-ene	C_7H_{14}	98.182	0.697			44.69	0.0678	2329
Oct-1-ene	C_8H_{16}	112.208	0.716	99		44.59	0.0678	2326
Isomers								
2-Methylprop-1-ene	C_4H_8	56.104		− 6.5	− 147		0.0678	
2,3,3-Trimethylbut-1-ene (Triptene)	C_7H_{14}	98.182	0.705	79	− 112		0.0678	
Acetylenes (Alkynes)								
Ethyne	C_2H_2	26.036	0.621[b]	− 83.8	− 81.5	48.26	0.0755	2583
Propyne	C_3H_4	40.062	0.679[b]	− 27.5	− 104.7	46.20	0.0726	2476
Aromatics								
Benzene	C_6H_6	78.108	0.878	80	5.5	40.61	0.0755	2366
Toluene	C_7H_8	92.134	0.866	110.5	− 95	40.97	0.0743	2348
ortho-Xylene	C_8H_{10}	106.160	0.879	144.0	− 27.1		0.0733	
meta-Xylene	C_8H_{10}	106.160	0.865	139.0	− 53.6	41.25 avge.	0.0733	2342 avge.
para-Xylene	C_8H_{10}	106.160	0.861	137.7	13.2		0.0733	
Isomers								
Ethylbenzene	C_8H_{10}	106.160	0.868	136.5	− 95	41.53	0.0733	
*Iso*propylbenzene (Cumene)	C_9H_{12}	120.186	0.863	153	− 97		0.0726	
Parent elements								
Hydrogen	H_2	2.016	0.070[b]	− 252.7	− 259	120.24	0.0292	2431
Carbon (graphite)	C (gr.)	12.011	2.21	3667 (sublimes)		32.76	0.0871	2313

---

*Net values, with fuel in gaseous phase at 25°C (except graphite).

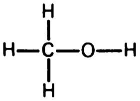
[b] At boiling point.

This influence on properties underlines the value of isomer paraffins in gasolines for the suppression of the spontaneous-ignition processes constituting spark knock. The aromatics also show high levels of spontaneous-ignition temperature, and are similarly attractive in gasolines. They are, however, low in hydrogen and thus high in carbon (particularly the polycyclic variants), which reduces their specific energies and raises their tendencies to produce smoke, as discussed in the text.

A1.2 Hydrocarbon Oxygenates

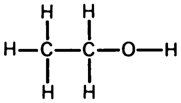
A hydrocarbon oxygenate molecule such as an alcohol consists of a hydrocarbon in which one atom of hydrogen has been substituted by the hydroxyl group, thus represented by the formula ROH, where R is the remaining radical. If the original hydrocarbon is a paraffin, the resultant alcohol appears with the general formula $C_xH_{2x-1}OH$. More generally, the radical may be any open or cyclic chain, and may contain a double carbon-carbon bond, an aromatic ring, or a halogen atom (chlorine, bromine, iodine, fluorine).

The simplest paraffinic-based alcohols thus appear as



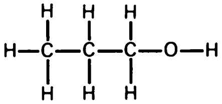
CH_3OH

methanol



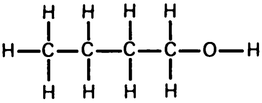
C_2H_5OH

ethanol



C_3H_7OH

propanol

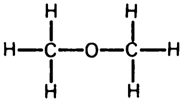


C_4H_9OH

butanol

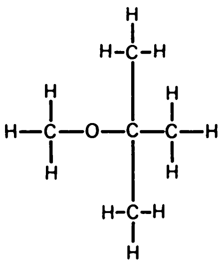
Isomeric structures are possible above carbon number 2, with the hydroxyl group located on the side, instead of the end, of the molecule.

The ethers also contain an oxygen atom with the hydrocarbon groups, but the oxygen is contained within the carbon chain, thus R–O–R, or R–O–R′ where R and R′ are different, as shown below

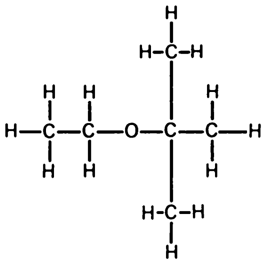


methyl ether, $(CH_3)_2O$

Similarly with methyl ethyl ether, $CH_3OC_2H_5$, and di-ethyl ether, $(C_2H_5)_2O$. The ethers of interest in connection with gasoline blending are the methyl and ethyl tertiary-butyl variants



methyl tert-butyl ether, $CH_3OC_4H_9$



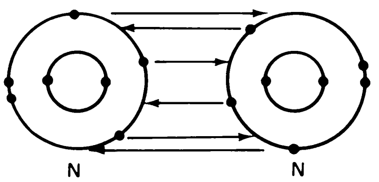
ethyl tert-butyl ether, $C_2H_5OC_4H_9$

The term 'tertiary' indicates that the oxygen atom is located next to a carbon atom which is itself connected to three other carbon atoms.

Many of the naturally occurring materials within vegetation consist of carbohydrates, with the general formula $(C_6H_{10}O_5)_n$.

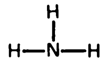
A1.3 Hydrogen-Nitrogen Compounds

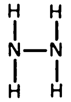
As with the combination of 2H to H_2, atoms of elemental nitrogen also combine with each other by covalent bonding to produce a diatomic molecule, in this case N_2. However, three covalent bonds are required in order to saturate the outer electron shells of both atoms, thus



written as N≡N, or N_2

Thus, the valency of nitrogen is 3 (sometimes 8 − 3 = 5), and the corresponding hydrides obtained by combining with univalent hydrogen appear as

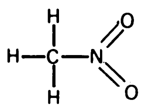




etc.

ammonia, NH_3 hydrazine, N_2H_4

The following compound is an example of a combination of a hydrocarbon radical with both nitrogen and oxygen



nitromethane, CH_3NO_2

Appendix 2: Relationship between Aromatics and Hydrogen Contents

In petroleum-derived hydrocarbon fuels there is, of course, no unique relationship between the contents of aromatics and hydrogen since the former represents a variety of compounds of different molecular structures, sizes and, consequently, hydrogen contents. This is illustrated in the following examples of two blends of C_8H_{18} (octane) each with 20 per cent volume of aromatics

Fuel	Aromatics type	Hydrogen per cent mass
A	C_6H_6 (benzene)	14.6
B	$C_{10}H_8$ (naphthalene)	13.7

Nevertheless, broad relationships exist in commercial hydrocarbon blends between these component concentrations, several of which have been published, together covering a large number of fuel samples. The results shown in figure A2.1 are representative, and have been used to determine an overall mean relationship which appears as follows

$$\text{Hydrogen per cent mass} = 14.90 - 0.0638\ (\text{Aromatics per cent volume})$$

Figure A2.2 shows this relationship of hydrogen content with aromatics content, together with that for the H/C atomic ratio.

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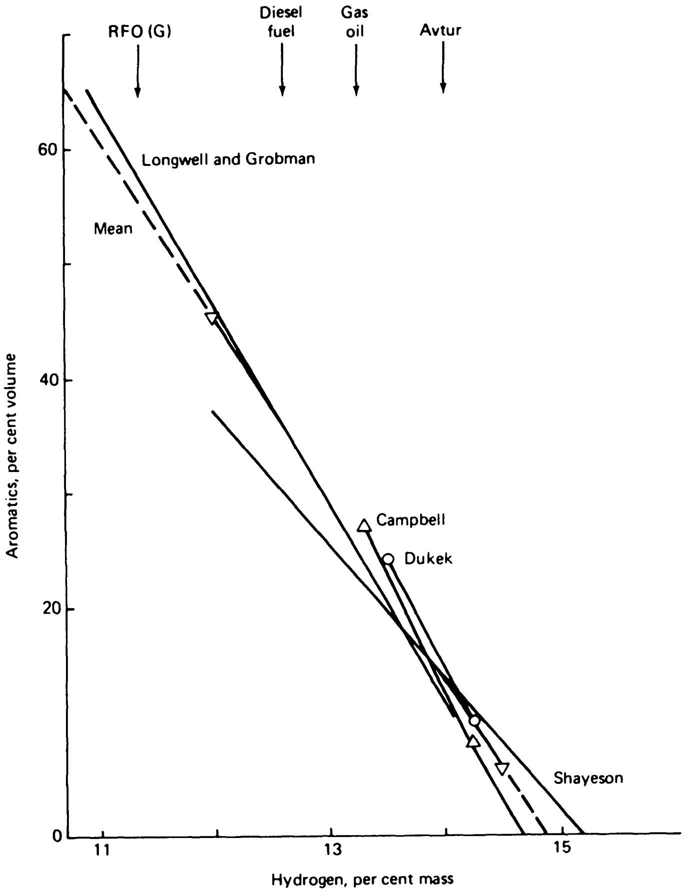


Figure A2.1 Relationships between fuel aromatics and hydrogen contents

Appendix 3: The Derivation of Specific Impulse

As indicated in chapter 2, the basic design of an air-breathing jet-propulsion duct-type engine comprises an entry diffuser to raise the pressure of the entry air at the expense of its velocity, a heat release chamber to raise the temperature and thus the velocity of the air at constant pressure, and a nozzle to accelerate the air further at the expense of its pressure, as outlined in figure A3.1, where the fluid axial velocities are defined as relative to the duct.

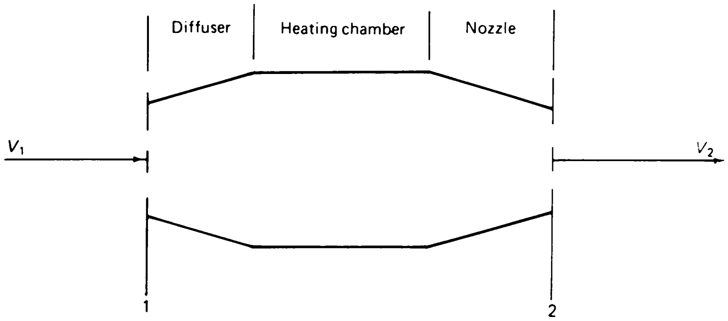


Figure A3.1 Schematic of air-breathing jet-propulsion duct

The first stage in analysis is to establish the sign convention that all forces are considered positive in the direction of flight, and all air velocities positive in the reverse direction. Furthermore, fluid friction is ignored together with, initially, the effects of atmospheric pressure on the external walls of the duct.

The total effect of the internal pressure on the duct wall promotes an internal forward thrust given by

$$F_{\mathrm{INT}} = \int (p\,\mathrm{d}A)_{\mathrm{INT}}$$

The total force on the stream tube fluid flowing through the duct is given by

$$F_{\mathrm{f}} = -\int (p\,\mathrm{d}A)_{\mathrm{INT}} + p_2 A_2 - p_1 A_1$$

since the first term represents the reaction of the duct on the fluid, and the second term is positive by acting on the fluid in the direction of flight. This total force on the fluid promotes an acceleration, and can therefore be expressed by Newton's second law, which equates force with the time rate of change of linear momentum. Thus

$$F_f = -\dot{m}(V_2 - V_1)$$

which is negative since it opposes the flight direction.

Hence

$$\begin{aligned} F_{\text{INT}} = \int (p\,\mathrm{d}A)_{\text{INT}} &= \dot{m}(V_2 - V_1) + p_2 A_2 - p_1 A_1 \\ &= (\dot{m} V_2 + p_2 A_2) - (\dot{m} V_1 + p_1 A_1) \qquad \text{(A3.1)} \\ &= \text{change in stream thrust between planes 1 and 2} \end{aligned}$$

Considering now the effect of the atmospheric pressure p_a existing outside the air-breathing duct, an external thrust also applies, envisaged in figure A3.2 as acting over the net area of a converging duct, giving a net external thrust for the complete duct as

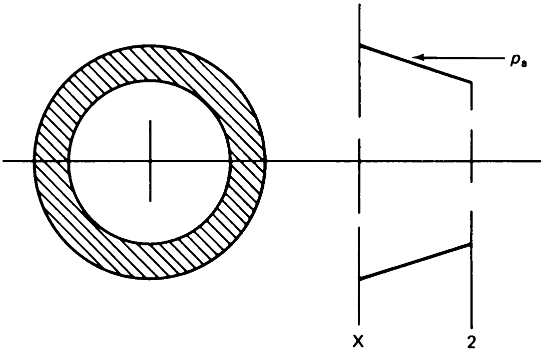
$$F_{\text{EXT}} = p_a (A_1 - A_2) \qquad \text{(A3.2)}$$

The total thrust acting on the duct is thus given by

$$\begin{aligned} \text{Total thrust} = \Sigma F &= F_{\text{INT}} + F_{\text{EXT}} \\ &= (\dot{m} V_2 + p_2 A_2) - (\dot{m} V_1 + p_1 A_1) + p_a (A_1 - A_2) \end{aligned} \qquad \text{(A3.3)}$$

When the flight speed is subsonic, p_1 is nominally equal to p_a, and the above expression reduces to

$$\begin{aligned} \Sigma F_{\text{SUB}} &= \dot{m}(V_2 - V_1) \quad + (p_2 - p_a) A_2 \\ &= \text{momentum thrust} + \text{pressure thrust} \end{aligned} \qquad \text{(A3.4)}$$



Force = p_a (Net area) = p_a $(A_x - A_2)$

Figure A3.2 External force exerted on duct by atmospheric pressure

Furthermore, when the expansion in the propelling nozzle is sufficient to bring the fluid pressure down to the atmospheric level so that $p_2 = p_a$, the pressure thrust term vanishes, and the thrust is derived entirely by momentum change. However, when the flight speed of the duct becomes supersonic, as is customary in ramjet practice, the usual subsonic effects of the entry diffuser and exit nozzle are augmented by discontinuities at the entry and exit planes. At entry, for example, the creation of a shock wave will also raise the pressure of the air at the expense of its velocity, and a similar discontinuity will occur at the nozzle exit throat, where the velocity becomes sonic. In such cases, the air pressures acting at the entry and exit planes no longer equal atmospheric, and the complete expression shown in equation (A3.3) applies.

In the laboratory, calorific values are determined under closely prescribed conditions, whereas the levels of thrust developed depend on both the fuel/air mixture ratio, and the expansion ratio from combustion chamber to exhaust plane. Nevertheless, because of the complexities incurred by dissociation at the high temperature of combustion, and by subsequent recombination in the nozzle, the performance of fuels used in a propulsive duct of the ramjet type shown in figure A3.1 is based more realistically on the thrust produced at the nozzle throat for optimal mixture ratio and a stated expansion ratio. The parameter adopted, therefore, is the specific impulse, defined as the thrust produced per unit flow rate of the material providing the thrust, thus

$$\text{Specific impulse} = \frac{\text{thrust}}{\text{flow rate of propelling material}}$$

The precise form of this parameter, together with its value and units, depends on the selection of the particular expression for thrust, of the plane at which the thrust applies, and of the propelling material and its units. In ramjet analysis, it is customary to employ the stream thrust corresponding to the nozzle throat (at which the fluid velocity reaches the sonic level), which comprises the exit plane in the subsonic ramjet, and also to express the denominator separately in terms of air mass, fuel mass, and fuel volume. This gives rise to the following expressions:

$$\text{Air specific impulse} = S_a = \frac{(\dot{m}\ V + p\ A)^*}{\dot{m}_a}\ \text{N s/kg} \tag{A3.5}$$

$$\text{Fuel specific impulse} = S_f = \frac{(\dot{m}\ V + p\ A)^*}{\dot{m}_f}\ \text{N s/kg} \tag{A3.6}$$

$$\text{Fuel density impulse} = S_{fd} = S_f\, d_f\ \ \text{N s/l} \tag{A3.7}$$

where $\dot{m}$ = mass flow rate of propelling products = $\dot{m}_a + \dot{m}_f$

$\dot{m}_a$ = mass flow rate of air

$\dot{m}_f$ = mass flow rate of fuel

V = velocity of propelling products

p = pressure of propelling products

A = cross-sectional area of duct

d_f = density of fuel under conditions of storage

$*$ = plane of nozzle throat where V = sonic.

In some instances, the total thrust, rather than the exit stream thrust, is used, with corresponding symbols I_a, I_f and I_{fd}.

If the duct is closed at the upstream plane, with the propelling fluid generated from within the heating chamber, as in the chemical rocket (figure A3.3), the initial velocity and entry area both become zero, hence equation (A3.4) reduces to

$$\text{Total rocket thrust} = \Sigma F_R = \dot{m}\,V_2 + (p_2 - p_a)A_2 \tag{A3.8}$$

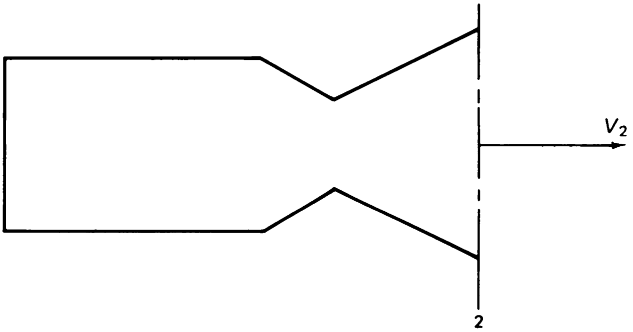


Figure A3.3 Rocket duct with supersonic nozzle

In the case of the rocket, the propelling nozzle is invariably of the convergent-divergent type, with acceleration to supersonic speed of the propellant after reaching the sonic level at the throat, and plane 2 applies to the exit of the divergent section. With reduction in p_a at altitude, the pressure thrust increases to a maximum of $(p_2\,A_2)$ within a vacuum environment but, for the general case where p_2 is finite and does not equal p_a, a theoretical value of exit velocity may be imagined to give the same level of total thrust, ΣF_R, with no pressure component. This theoretical velocity is known as the *effective exit velocity,* V_e, hence

$$\Sigma F_R = \dot{m}\,V_e$$

and

$$\text{effective exit velocity} = V_e = \frac{\Sigma F_R}{\dot{m}}$$

$$= \frac{\text{total rocket thrust}}{\text{mass flow rate of propellant}}$$

However, specific impulse (I_s) is also defined as the thrust per unit mass flow rate of propellant, and hence

$$I_s = \frac{\Sigma F_R}{\dot{m}} \quad \text{N s/kg}$$
$$= V_e \quad \text{m/s}$$

(In many cases, specific impulse is still expressed in mixed British units, that is, lbf s/lb (mass) which is numerically equal to lbf s/lb (weight) and thus reduces to seconds (s), but lb (weight) is not appropriate to space applications where gravity forces vary widely from that at the Earth's surface. The conversion from mixed British to SI units is as follows

1 lbf s/lb = 9.8066 N s/kg)

The effective exit velocity, and thus the specific impulse, may be derived in more fundamental terms from the principle of conservation of energy for an adiabatic flow process by applying the Bernoulli expression to the inlet (c) and exit (e) planes of the nozzle, as follows

$$\text{Total energy of propellant flow} = \text{kinetic energy} + \text{enthalpy}$$
$$= \tfrac{1}{2} m\, V_c^2 + m\, h_c, \text{ at inlet}$$
$$= \tfrac{1}{2} m\, V_e^2 + m\, h_e, \text{ at exit}$$

assuming no losses in the nozzle, where h is the specific enthalpy. Since V_c is nominally zero, rearrangement of the expression gives

$$V_e = \sqrt{\{2\,(h_c - h_e)\}}$$

On the assumption of frozen equilibrium, that is, that the chemical equilibrium established within the reaction chamber does not have time to change during flow through the nozzle, and taking a mean value of c_p (the specific heat capacity at constant pressure) over the range of operating temperature, this becomes

$$V_e = \sqrt{\left\{2\, c_p\, T_c \left(1 - \frac{T_e}{T_c}\right)\right\}}$$

From the following thermodynamic relationships

$$\frac{T_e}{T_c} = \left(\frac{p_e}{p_c}\right)^{(\gamma-1)/\gamma}$$

$c_p - c_v = R$, the gas constant for the propellant

$c_p/c_v = \gamma$, the specific heat ratio for the propellant

and $c_p = R\gamma/(\gamma - 1) = R_0\gamma/\overline{M}\,(\gamma - 1)$

where R_0 = universal gas constant = 8.314 kJ/kmol K for all ideal gases
and $\overline{M}$ = mean molar mass of propelling products within the nozzle,
the expression for specific impulse becomes

$$I_s = V_e = \sqrt{\left\{\frac{2\,R_0\gamma\,T_c}{\overline{M}\,(\gamma - 1)}\left[1 - \left(\frac{p_e}{p_c}\right)^{(\gamma-1)/\gamma}\right]\right\}}$$

Examination of this expression shows a need for reactants giving a high combustion temperature T_c (and thus pressure p_c), and producing propelling products of low molar mass and, preferably, low γ. It is difficult to meet all these requirements with a single pair of reactants, and the situation is eased appreciably when the reactant and propellant materials are entirely independent, as in the nuclear heat-transfer rocket. Low molar-mass hydrogen is therefore an attractive propellant as well as a fuel and, in fact, recent work on chemical 'tri-propellant' rockets is based on the addition of hydrogen to a reactant pair in order to reduce the molar mass of the propellant products rather than supply additional reaction energy. The use of a Be-O_2-H_2 mixture, for example, provides an improvement in specific impulse of about 12 per cent over a conventional liquid hydrogen-liquid fluorine mixture.

Appendix 4: Units

In any system of units, a number of quantities are defined as basic to the system, and all the remaining quantities derived from them. If the system is coherent, the products and quotients of any two or more unit quantities themselves become the units of the derived quantities, in the absence of any conversion factors or proportionality constants. The rationalised system of metric units known as SI (Système International d'Unités) is coherent in this way, and applies to all branches of science and engineering.

The quantities and units of interest in this study consist of the following.

	Quantity	*Unit*	*Symbol*
(Basic)	length	metre	m
	mass	kilogram	kg
	time	second	s
	electric current	ampere	A
	thermodynamic temperature	kelvin	K
	amount of substance	mole	mol
(Derived)	force	newton	N (= kg m/s^2)
	pressure	pascal	Pa (= N/m^2)
	energy	joule	J (= N m)
	power	watt	W (= J/s)

No change is made to any symbol to indicate the plural, and quantities are expressed in units that result in numerical values between 0.1 and 1000, with preferred single multiples and submultiples that differ in stages of 10 raised to a power which is a multiple of ±3, ranging normally from 10^{18}, exa, to 10^{-18}, atto. Those used most commonly are as follows.

Factor	*Prefix*	*Symbol*
10^{18}	exa	E
10^9	giga	G
10^6	mega	M
10^3	kilo	k
10^{-3}	milli	m
10^{-6}	micro	μ

SI has been adopted by various industries (for example, *Recommended SI units*, Institute of Petroleum, London, 1970), some of which also use earlier metric units (litre, bar, centipoise, centistokes) together with a non-metric unit (atmosphere) which are considered acceptable. Since the adoption of SI is not yet worldwide, the following conversion factors and other metric relationships are given.

Length	1 in. = **25.4 mm** 1 ft = **0.304 8 m** 1 mile = 1.609 km
Volume	1 ft^3 = 0.028 32 m^3 1 U.K. gal = 1.201 U.S. gal = 4.546 l 1 U.S. gal = 0.832 7 U.K. gal = 3.785 l 1 U.S. barrel = 34.97 U.K. gal = **42 U.S. gal** = 158.9 l
Mass	1 lb = 0.453 6 kg 1 (long) ton = **2240 lb** = 1016 kg 1 short ton = **2000 lb** = 907.6 kg 1 tonne = 0.984 2 (long) ton = **1000 kg = 1 Mg**
Density	1 lb/ft^3 = 16.02 kg/m^3
Force	1 lbf = 4.448 N
Pressure	1 lbf/in.^{2} = 6.895 kPa 1 mm Hg = 133.3 Pa 1 atm. = **1.013 25 bar = 101.325 kPa** 1 bar = **100 kPa = 10^5 Pa**
Energy	1 Btu = 1.055 kJ 1 Chu = 1.899 kJ 1 kcal (International table) = **4.186 8 kJ** 1 kcal (Thermochemical) = 4.184 kJ 1 kWh = **3.6 MJ** 1 hp h = 2.685 MJ 1 therm = **10^5 Btu** = 105.5 MJ
Specific energy	1 Btu/lb = **2.326 kJ/kg** 1 Chu/lb = **4.186 8 kJ/kg**
Specific energy capacity	1 Btu/lb °R = **1 Chu/lb K = 4.186 8 kJ/kg K**
Energy density	1 Btu/ft^3 = 0.037 26 kJ/l (or MJ/m^3) 1 Chu/ft^3 = 0.067 07 kJ/l (or MJ/m^3) 1 Btu/U.K. gal = 0.232 kJ/l (or MJ/m^3)
Power	1 hp = 745.7 W

(Figures in **bold type** are exact.)

Approximate fuel energy equivalents (derived from British Petroleum Company, plc)

	b.o.e.	t.o.e.	t.c.e.	c.m.n.g.e.
1 barrel crude oil equivalent (b.o.e.)	1	0.136	0.204	151.1
1 tonne crude oil equivalent (t.o.e.)	7.33	1	1.50	1111
1 tonne coal (t.c.e.)	4.90	0.667	1	740.7
1 cubic metre natural gas equivalent (c.m.n.g.e.)	0.0066	0.0009	0.0014	1

Note: 100 ppm = 0.01 per cent.

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