

CONVENTIONAL AND ALTERNATIVE AVIATION FUELS: AN OVERVIEW ON COMPOSITION, PROPERTIES AND AIRCRAFT ENGINE TEST

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***Abstract.** The present paper provides an overview of alternative aviation fuels in comparison with their conventional counterpart in terms of feedstock, production, relationship between chemical composition and properties, fuel performance and emissions as well as data obtained in flight demonstrations and engine test programmes. The current level of scientific understanding is such that the use of synthetic fuels is allowed by international aviation standards within a 50% limit by volume since these alternative jet fuels have negligible naphthenic and aromatic fractions, whose role in engine operation and fuel properties include critical features like low temperature fluidity and material compatibility.*

***Keywords:** Alternative fuels, Aviation fuels, Combustion, Fuel properties, Fuel surrogates*

1. INTRODUCTION

Since the early 2000's the scientific and engineering community have been investing a lot of effort in the identification of 'green fuels' that assure energy security and continued availability as well as to reduce the carbon footprint of transport and its impact on climate change (Chevron, 2006). Petroleum products have always been the preferred transportation fuels since they offer an optimal combination of availability, ease of handling, energy content, performance and, most of all, price. For aviation the search for alternative fuels is more complex due to several restrictions: (a) any alternative fuel must be compatible with conventional fuel so it can be transported and stored within the existing infrastructure; (b) airlines keep their aircrafts in service for around forty years (Blakey *et al.*, 2011) so the alternative fuel must provide safe and reliable operation of engines and airframes with minimal increase in maintenance.

The present paper provides an overview of alternative aviation fuels in comparison with their conventional counterpart therefore discussing feedstocks for alternative fuel production, correlations between chemical com-

position and fuel properties, fuel performance and emissions as well as some data obtained in flight demonstrations and engine test programmes.

2. CONVENTIONAL AVIATION FUELS

As gasoline (petrol) and diesel, jet fuel, also known as kerosene, is produced by fractional distillation of crude oil. This separation process, also referred to as rectification, is carried out since the thousands of different hydrocarbons present in the crude oil have boiling points just slightly different from one another. In general terms, small hydrocarbons are more volatile, less viscous and more flammable than heavier ones.

Hydrocarbons up to four carbon atoms are gaseous at ambient temperature while pure hydrocarbons with five to eighteen carbon atoms are usually liquid at this conditions. The three liquid transportation fuels, gasoline, kerosene and diesel are roughly defined by the size of their typical linear alkane chains: gasoline from C₅ to C₈, kerosene from C₉ to C₁₄ and diesel from C₁₅ to C₂₀.

The specifications for aviation turbine fuels were developed considering the great variability in crude oil quality e.g. different proportions of cyclic alkanes and aromatics. Therefore the fuel properties are ‘operational’ requirements related to the intended application and not a formulation with strictly defined species. Table 1 presents the main properties established for commercial jet fuels while Table 2 presents average compositions of Jet A-1 (World Survey) and Jet A (Colket *et al.*, 2007).

Table 1. Selected specification properties of jet fuels

Fuel	Jet A	Jet A-1
Specification	ASTM D 1655	DEF STAN 91-91
Distillation, °C, 10% recovered, max	205	205
Distillation, °C, end point	300	300
Flash point, °C, min	38	38
Density, 15°C, kg/m ³	775–840	775–840
Freezing point, °C, max	–40	–47
Viscosity, –20°C, mm ² /s, max	8.0	8.0
Net heat of combustion, MJ/kg, min	42.8	42.8
Aromatics, % vol max	25	25
Naphthalenes, % vol, max	3.0	3.0

Source: Chevron - Aviation Fuels Technical Review (2006)

Table 2. Average jet fuel compositions, % vol

Compound	World Survey	Composite Jet A
paraffins, n- + i-	58.78	55.2
monocycloparaffins	10.89	17.2
dicycloparaffins	9.25	7.8
tricycloparaffins	1.08	0.6
alkyl benzenes	13.36	12.7
indanes + tetralins	4.9	4.9
naphthalene	0.13	<0.2
substituted naphthalenes	1.55	1.3

Source: Colket *et al.* - 45th AIAA Aerospace Science Meeting and Exhibition (2007)

The main difference between Jet A, the fuel specified for U.S. domestic market, and the international Jet A-1 is the lower freezing point of the latter, –47°C, compared to –40°C of the former. Even though this difference

seems minor it greatly affects the definition of the distillation end point hence the refinery yield of kerosene for a given crude oil.

Such limitation is caused by the different properties of each hydrocarbon class that are determined by H/C ratio and molecular shape. Linear alkanes and unsubstituted aromatics crystallize at much higher temperatures than branched and cyclic alkanes with the same carbon number since their geometry allows them to easily pack together into a crystalline structure. Table 3 summarizes how the contribution of each hydrocarbon class affects overall fuel properties in terms of beneficial effect (denoted by '+'), neutral or minor contribution (denoted by 'o') or a detrimental effect (denoted by '-').

Table 3. Potential contribution of each hydrocarbon class to selected jet fuel properties

Property	n-paraffin	i-paraffin	naphthene	aromatic
Gravimetric energy content	+	+	o	-
Volumetric energy content	-	-	o	+
Combustion quality	+	+	+	-
Low-temperature fluidity	--	o/+	+	o/-

Source: Chevron - Aviation Fuels Technical Review (2006)

As can be inferred from the table, if a crude oil has low naphthenic fraction, for example below 15%, it is important to control the distillation end point and also evaluate the need for hydrotreatment in order to promote the isomerization of some linear paraffins to branched ones. The table also shows that i-paraffins present intermediate properties between aromatics and n-paraffins thus being interesting as a main component of the fuel mixture.

It is important to stress the role of aromatic hydrocarbons in the jet fuel composition. While the aliphatic fractions of the fuel present largely dispersive intermolecular forces, some aromatic compounds shows polar and hydrogen-bonding character thus increasing the water solubility in the fuel and also causing some types of elastomers used in fuel system to swell, which the industry considers as a safeguard against fuel leaks. This swelling occurs in seals made of nitrile rubber, a copolymer composed of poly(butadiene) and poly(acrylonitrile), the latter presenting a highly polar cyano group ($-C\equiv N$) on adjacent polymer chains. The net negative charge in the cyano group interact with the electropositive aromatic hydrogens, therefore breaking the polymer-polymer and penetrant-penetrant intermolecular bonds and forming polymer-penetrant intermolecular bonds thus producing the swelling (Graham *et al.*, 2006).

Besides this seal swell issue aromatics also affect fuel's density and energy content but since this hydrocarbon class, specially the naphthalenic compounds, are precursors of soot formation, their fraction is limited to a maximum of 3% in volume for naphthalenes and 25% for total aromatics. Given this brief overview of jet fuel's composition and properties, the ensuing section discusses alternative and renewable aviation fuels.

3. ALTERNATIVE FUELS

Alternative fuels, primarily the so-called first generation biofuels, are already employed in land transportation like ethanol obtained from fermentation of starch and sugar and fatty acids esters (FAE), known as biodiesel, produced from edible and inedible oils and fats by transesterification. Second generation biofuels comprise the hydroprocessed esters and fatty acids (HEFA), produced with feedstocks similar to biodiesel that undergo hydrogenation and hydroisomerization to yield synthetic hydrocarbons without functional groups.

Another production pathway for alternative fuel is the Fischer-Tropsch (FT) synthesis, where a carbon

source like methane, coal or biomass is partially oxidized to form a gaseous mixture of carbon monoxide and hydrogen known as ‘syngas’, that is converted to hydrocarbons through heterogeneous catalysis (Dry, 2002).

Since the primary function of aviation turbine fuel is to power the aircraft, an analysis of alternative fuel’s energy content is of crucial importance. Another important fuel property is density as aircraft range and performance depend on maximum takeoff weight. Table 4 presents a comparison of density and energy content of conventional and alternative fuels (Chevron, 2006; Corporan *et al.*, 2011).

Table 4. Density and energy Content of conventional and alternative fuels.

Fuel	Density at 15°C, kg/l	Gravimetric Energy, MJ/kg	Volumetric Energy, MJ/l
Jet A/A-1	0.808	43.2	34.9
Methanol	0.796	19.9	15.9
Ethanol	0.794	27.2	21.6
Biodiesel	0.870	38.9	33.9
Fischer-Tropsch Synfuel	0.759	44.2	33.6
Camelina HEFA	0.751	44.1	33.1
Beef tallow HEFA	0.758	44.1	33.4

It can be seen from the Tab. 4 that first generation biofuels are inadequate for aviation since alcohols have a gravimetric energy content well below 40 MJ/kg while biodiesel has an adequate heating value but its density is higher than the specification maximum of 0.840 kg/l. On the other hand Fischer-Tropsch synthetic fuel and HEFAs present satisfactory energy content but with density slightly below the specification minimum of 0.775 kg/l. Since liquid fuels are typically bought and sold by volume and commercial aircraft range is dictated by a balance of fuel and passenger/cargo weight, a more dense, high volumetric energy content jet fuel is preferred.

Density and heat content requirements are only a small part of the fuel specification, which includes distillation curve, lubricity, freezing point and others properties that depend on trace or bulk amounts of certain compounds. Some important fuel properties associated with different hydrocarbon classes include: seal swelling (Graham *et al.*, 2006), freezing point, viscosity, hence lubricity, associated with naphthenes and trace amounts of heterocompounds; soot propensity, which increases with total aromatic and total naphthalenic (polycyclic aromatic hydrocarbon - PAH) content.

Regarding oxygenates, it is remarkable that their use as alternative aviation fuel was restricted to a single flight test by Virgin Atlantic. In February 2008, during a 45-minute flight between London and Amsterdam, one of the four GE CF6-80C engines of a Boeing 747-400 was fueled with a blend of 80% Jet A-1 and 20% fatty acid methyl ester from coconut and babassu palm oil. Regardless the successful demonstration, Boeing issued a disclaimer stating that the FAME used was the only suitable, ‘fit-for-purpose’ oxygenate fuel available at the time and that it did not consider FAEs a viable option for aviation. In fact, an analysis of the composition of several vegetable oils and animal fats (Budin *et al.*, 1995; Huber *et al.*, 2006; Achten *et al.*, 2008; Hong *et al.*, 2013) shows that babassu, coconut and palm oil are the only biodiesel feedstocks with significant amounts of fatty acids with alkyl chains up to 14 carbons thus similar to the hydrocarbons in conventional Jet A/A-1.

However oxygenates are not viable gas turbine fuels for several reasons related to their functional groups like vapor pressure, viscosity and low energy content by mass. Fatty acid esters present further issues since

there is a carry through of contaminants, like zinc, nickel and vanadium from the raw oil into the FAE and these contaminants could cause severe damage to the hot end materials in the turbine. Another problem to be addressed is related to multi-product pipeline transport of conventional jet fuel and biodiesel blends since the subsequent flow of different fuels may contaminate the latter with residues of the former (DSTAN, 2012). While FAEs are considered contaminants in jet fuel, within a 5 mg/kg limit, the sulfur content of typical Jet A/A-1 is around 500-1000 parts per million (ppm) thus well above the 10 ppm limit for diesel.

Another type of biofuel is upgraded oil by hidrotreatment. The triglycerides present in oils and fats can be hydrotreated in a way similar to the latter stages of conventional refinery and Fischer-Tropsch processes thus promoting deoxygenation, saturation, hydrocracking and isomerization of the alkyl chains. Many different sources of triglycerides could be harnessed this way, like algae, animal fats, brown and yellow grease.

Experimental work (Corporan *et al.*, 2011) revealed that alternative paraffinic fuels produced via hydroprocessing or FT present inferior lubricity, lesser seal swelling and lower density. The following subsections describe the on-aircraft engine testing procedures of two alternative fuels.

3.1 Fischer-Tropsch aviation fuel

South African company Sasol pioneered the development of a synthetic, coal-to-liquid (CtL) FT jet fuel, with its iso-paraffinic kerosene (IPK) being included in the DEF STAN 91-91 Issue 3 in 1999 as a 50% vol. component for Jet A-1. In 2008 the Issue 6 of this standard was published with the certification of a fully synthetic jet fuel also developed by Sasol and until 2009 Sasol's IPK remained the only alternative to Jet A-1 in commercial use. Since then FT kerosene fuels were developed by Shell, Syntroleum and Rentech using gas-to-liquid (GtL) processes, a pathway adopted by Sasol in its Oryx plant in Qatar. These synthetic fuels are mainly composed by branched paraffins and do not have aromatics, with Sasol fuel being the only also presenting naphthenic (cycloalkane) fraction (Edwards *et al.*, 2010).

A test programme called Aircraft Alternative Fuel Emissions eXperiment (AAFEX) (Anderson *et al.*, 2011) was conducted by NASA in 2009 to evaluate gaseous and particulate emissions of CFM56-2C1 engines fueled with standard JP-8, Shell GtL, Sasol CtL and 50/50 blends of each FT fuel with JP-8. In the study was observed that burning FT fuel did not affect engine performance hence not offering advantage or penalty in terms of fuel economy. However alternative fuels exhibited higher combustion efficiencies at low power settings thus indicating a general trend of being less polluting. The use of 50/50 blends resulted in negligible reductions in certification gas emissions, pointing out a clearly relationship between aromatic content and emissions.

Other tests of engine performance were conducted by the US Air Force to study Syntroleum and Shell GtL fuels and their blend with JP-8 in several transport and fighter platforms (Blakey *et al.*, 2011) with only beneficial impacts being reported. Therefore, since July 2011 the ASTM D7566 allows the use of FT synthetic hydrocarbons as 'drop-in' components, in amounts up to 50%, in blends with Jet A/A-1 thus assuring minimum density and aromatic content that prevents fuel leaking (ASTM, 2011).

3.2 Aviation biofuel

Regarding biofuels for aviation, HEFAs are the primary option since these fuels are similar to FT synthetic products thus comprising linear and branched alkanes. While FT fuels are catalytically 'assembled' from syngas, HEFAs are produced by hydrogenation and hydroisomerization of triglycerides which promotes branching and cleavage of long alkyl chains. Many different sources of triglycerides could be harnessed this way, spe-

cially babassu, coconut, palm and olive oils that provide significant amounts of fatty acids with carbon chains similar to kerosene, i.e. up to 15 carbons.

Several test programmes and flight demonstrations (Rahmes *et al.*, 2009; Blakey *et al.*, 2011) occurred during the 2007-2010 span and it is possible to draw a parallel between airline efforts and military/manufacturer works. Test flights conducted by Air New Zealand, Japan Airlines and KLM/Air France favored the use of HEFAs made from algae, camelina and jatropha oils. Algae HEFA is considered a third generation biofuel and was used in amounts below 10% but is expected to play a major role in future biofuel scenarios, while jatropha is able to grow under drought conditions and in sandy soils that are otherwise unused for farming thus presenting strong sustainability and social responsibility appeal. These HEFAs were blended, in amounts up to 50%, with Jet A/A-1 to fuel one engine of the aircraft, thus allowing the study of engine relight and overall performance. Results of such tests were mostly qualitative, with Air NZ claiming a potential fuel saving of 1.2% with its jatropha HEFA.

On the other hand US Air Force and US Navy, accompanied by manufacturers like Boeing and Pratt & Whitney, elected HEFAs made from camelina and animal fats for engine testing, that included engine performance, gaseous and particulate emissions. These feedstocks are widely available in the United States since camelina is well established in states like Montana, Idaho and North Dakota for its use in biodiesel production. When used in pure form, HEFA fuels produced less particle matter which is expected due to the absence of aromatic compounds. In fuel blends an increase in aromatic content and molecular weight resulted in a decrease in combustion efficiency hence increasing carbon monoxide and unburned hydrocarbon emissions. The CO₂ and H₂O emissions are mostly related to the H/C ratio hence heating value of the fuel, with HEFAs presenting hydrogen to carbon ratio close or above 2.0 while for conventional jet fuel this value is usually 1.9 or below. Since July 2011 the ASTM standard D7566 allows the use of HEFA synthetic hydrocarbons, in amounts up to 50%, in blends with Jet A/A-1 thus assuring minimum density and aromatic content.

4. CONCLUSIONS

An aviation fuel is complex mixture of aliphatic and aromatic hydrocarbons obtained from crude oil by fractional distillation. Its properties, combustion performance and emissions result from the complex interaction of hundreds, if not thousands, of different compounds. It is important to note that some characteristics of this fuel, like the smooth boiling curve, are directly related to its mosaic composition with dozens of isomers of each chemical species. The specifications of jet fuel include implicit assumptions that are met by petroleum-derived products, thus making the search for alternative fuels an intricate task.

Since the pioneer efforts of Sasol during the 1990's several alternative aviation fuels have been developed, using feedstocks like coal, natural gas, vegetable and animal triglycerides. Jet fuels produced through Fischer-Tropsch synthesis or triglyceride hydrotreatment are mainly comprised of linear and branched paraffins thus presenting density and energy content similar to JP-8 and Jet A/A-1. However, these pure synthetic fuels lack significant naphthenic and aromatic fractions, which contribute to important properties like freezing point, viscosity and material compatibility. Therefore, commercial use of these synthetic hydrocarbons is still limited to 50% blends with conventional fuels.

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