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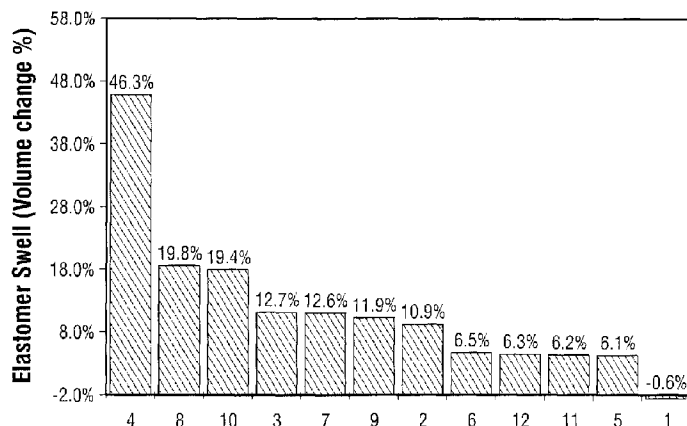
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(54) **Titre : PROCÉDE POUR PRÉPARER DES CARBURANTS AVIATION ET SES PRODUITS**

(54) **Title: PROCESS TO PREPARE JET FUELS AND ITS PRODUCTS**



(57) **Abrégé/Abstract:**

A jet fuel containing a major amount of a synthetic paraffinic kerosene fuel component is provided by:

- a) providing a synthetic paraffinic kerosene fuel component in the jet boiling range having at least 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by ASTM D2425;
- b) providing a petroleum-based jet fuel component in the jet boiling range;
- c) providing pinane; and
- d) blending component a), b) and c), wherein component c) is present in an amount of to 40 weight percent, based on the blend, and component a) and b) are in a ratio of greater than 1 to 1 thereby providing a jet fuel blend having a density of from 775 to 840 kg/m³.

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- b) providing a petroleum-based jet fuel component in the jet boiling range;
- 10 c) providing pinane; and
- d) blending component a), b) and c), wherein component c) is present in an amount of 5 to 40 weight percent, based on the blend, and component a) and b) are in a ratio of greater than 1 to 1 thereby providing a jet fuel blend having a density of from 775 to 840 kg/m³.

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PROCESS TO PREPARE JET FUELS AND ITS PRODUCTS

Field of the Invention

This invention relates to a process to prepare a jet fuel and its products.

Background of the Invention

5 Typical Jet fuels are prepared in a refinery from a crude mineral oil source. Typically the crude mineral oil is separated by means of distillation into a distillate kerosene fraction boiling in the aviation fuel range. If required, these fractions are subjected to hydroprocessing to reduce sulfur and nitrogen levels.

10 Increasing demand for jet fuel and the environmental impact of aviation related emissions places the aviation industry at the forefront of today's global energy challenge. Perhaps more tangible than the global impact of green house gases is the impact of local emissions from aircraft. Emissions near and around airports have a direct impact on the composition air and therefore have been linked with poor local air quality, that can be further linked to impacts on human health. Particulates and oxides of sulphur and nitrogen are considered to be the main contributors to poor local air quality.

15 Thus, local air quality is seen as an integral element in the pursuit of environmentally friendly fuels. This has led to increased focus on the development of cleaner burning fuels such as Fischer-Tropsch fuels that do not contain sulphur or aromatic components, often seen as precursors to the formation of particulates and undesirable oxides. It is also important that novel fuels meet the jet fuel specification without having a detrimental impact on safety or performance of aircraft. However, because of the nature of Shell's Fischer-Tropsch fuels (i.e. purely paraffinic and absent of both aromatics and sulphur) these components do not exhibit all of the desired properties expected from a jet fuel. For example, due to the lower density of the gas to liquids Fischer-Tropsch-derived fuel it is not considered as an on-spec fuel in its pure state. Hence, the current semi synthetic specification for jet fuel (ASTM D7566-11a),
20 limits the Fischer-Tropsch component to a maximum of 50% by volume.

25 Further to this, certain elastomers do not perform at a level considered to be fit-for-purpose when a pure Fischer-Tropsch fuel is used in aviation turbine/jet fuel (i.e. nitrile elastomers do not swell in pure Fischer -Tropsch fuels). Elastomers, when in contact with fuel, tend to swell to a small degree and this swelling helps to prevent leakages while allowing certain parts to move relatively freely. Nitrile elastomers are used extensively in aviation
30 applications and are commonly found in many legacy aircraft. Although the use of these

elastomers is diminishing (or even diminished) there are many operational aircraft that still contain this type of elastomer. Swelling in nitrile elastomers is known to be approximately proportional to aromatic content of a fuel. Hence, paraffinic fuels are limited in their application due to the absence of aromatic species. Again, for this reason paraffinic fuels are blended up to
5 50% by volume of the base fuel for aviation turbine fuel.

Summary of the Invention

Accordingly, one embodiment of the invention, a method for increasing the amount of a synthetic paraffinic kerosene fuel component in a jet fuel comprising:

- 10 a) providing a synthetic paraffinic kerosene fuel component in the jet boiling range having at least 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by ASTM D2425;
- b) providing a petroleum-based jet fuel component in the jet boiling range;
- c) providing pinane; and
- 15 d) blending component a), b) and c), wherein component c) is present in an amount of 5 to 40 weight percent, based on the blend, and component a) and b) are in a ratio of greater than 1 to 1 thereby providing a jet fuel blend having a density of from 775 to 840 kg/m³.

In another embodiment of the invention, a jet fuel composition is provided having a
20 density of from 775 to 840 kg/m³ comprising:

- a) a petroleum-based jet fuel component other than b) boiling for more than 90 vol% at from 130 to 300°C;
- b) greater than 50 weight percent, based on combined components a) and b), of a synthetic paraffinic kerosene fuel component in the jet boiling range having at least
25 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by ASTM D2425; and
- c) 5 to 40 weight percent, based on the jet fuel composition, of pinane.

In accordance with another aspect there is provided a method for increasing the amount of a synthetic paraffinic kerosene fuel component in a jet fuel comprising: a) providing a synthetic paraffinic kerosene fuel component in the jet boiling range having at least 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by ASTM D2425; b) providing a petroleum-based jet fuel component boiling for more than 90 vol% at from 130 to 300°C; c) providing pinane; and d) blending component a), b) and c), wherein component c) is present in an amount of 5 to 40 weight percent, based on the blend, and component a) and b) are in a ratio of greater than 1 to 1 thereby providing a jet fuel blend having a density of from 775 to 840 kg/m³ at 15°C.

In accordance with yet another aspect there is provided a jet fuel composition having a density of from 775 to 840 kg/m³ at 15°C comprising: a) greater than 50 weight percent, based on combined components a) and b), of a synthetic paraffinic kerosene fuel component in the jet boiling range having at least 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by ASTM D2425; b) a petroleum-based jet fuel component other than a) boiling for more than 90 vol% at from 130 to 300°C; and c) 5 to 40 weight percent, based on the jet fuel composition, of pinane.

Brief Description of the Drawing

Fig. 1 represents the elastomer swell of neat fuels and fuel blends of the invention from the Examples.

Fig. 2 represents the density of neat fuels and fuel blends of the invention from the Examples.

Fig. 3 represents the aromatic content of neat fuels and fuel blends of the invention from the Examples.

5 Detailed Description of the Invention

It has been found that pinane facilitates the blending of Petroleum-based jet fuel component and synthetic paraffinic kerosene fuel component to allow the blend with increased concentration of the synthetic paraffinic kerosene fuel component. The jet fuel composition of the invention provides jet fuel within the specification range and have acceptable elastomer swelling of the elastomer sealants used in jet engines along with acceptable density range.

The petroleum based jet fuel component is blended with pinane and Fischer-Tropsch derived kerosene fuel component in an amount of a ratio of Fischer-Tropsch derived kerosene fuel component to petroleum based jet fuel component of greater than 1 to 1 thereby providing a jet fuel blend having a density of from 775 to 840 kg/m³ at 15°C.

The amount of a synthetic paraffinic kerosene fuel component in a jet fuel may be increased above 50 vol% by providing a synthetic paraffinic kerosene fuel component in the jet boiling range, a petroleum-based jet fuel component in the jet boiling range, and pinane in an amount of 5 to 40 weight percent, 5 to 35 weight percent, 10 to 35 weight percent, 5 to 30 weight percent, 10 to 30 weight percent, 5 to 25 weight percent, even 10 to 25 weight percent, based on the blend, of pinane.

It has further been found that the method provides fit for purpose fuel meeting density specification and elastomer swelling values while having aromatic content of less than 10vol.% or even less than 8 vol.%. Pinane, (2,6,6-trimethylbicyclo[3.1.1]heptanes), has an empirical formula C₁₀H₁₈ and available commercially from sources such as Sigma Aldrich Co. LLC, Alfa Aesar, Fisher Scientific International Inc.

In an embodiments, the petroleum-based fuel is any jet fuel known to skilled artisans can be used herein. The American Society for Testing and Materials (“ASTM”) and the United Kingdom Ministry of Defense (“MOD”) have taken the lead roles in setting and maintaining specification for civilian aviation turbine fuel or jet fuel. The respective specifications issued by these two organizations are very similar but not identical. Many other countries issue their own national specifications for jet fuel but are very nearly or

completely identical to either the ASTM or MOD specification. ASTM D1655 is the Standard Specification for Aviation Turbine Fuels and includes specifications for Jet A, Jet A-1 and Jet B fuels. Defense Standard 91-91 is the MOD specification for Jet A-1.

Jet A-1 is the most common jet fuel and is produced to an internationally standardized set of specifications. In the United States only, a version of Jet A-1 known as Jet A is also used. Another jet fuel that is commonly used in civilian aviation is called Jet B. Jet B is a lighter fuel in the naphtha-kerosene region that is used for its enhanced cold-weather performance. Jet A, Jet A-1 and Jet B are specified in ASTM Specification D1655.

Alternatively, jet fuels are classified by militaries around the world with a different system of JP numbers. Some are almost identical to their civilian counterparts and differ only by the amounts of a few additives. For example, Jet A-1 is similar to JP-8 and Jet B is similar to JP-4.

Optionally, the fuel compositions disclosed herein may comprise one or more aromatic compounds. In some embodiments, the total amount of aromatic compounds in the fuel compositions is from 1% to 50% by weight or volume, based on the total weight or volume of the fuel composition. In other embodiments, the total amount of aromatic compounds in the fuel compositions is from 15% to 35% by weight or volume, based on the total weight or volume of the fuel compositions. In further embodiments, the total amount of aromatic compounds in the fuel compositions is from 15% to 25% by weight or volume, based on the total weight or volume of the fuel compositions. In other embodiments, the total amount of aromatic compounds in the fuel compositions is from 5% to 10% by weight or volume, based on the total weight or volume of the fuel composition. In still further embodiments, the total amount of aromatic compounds in the fuel compositions is less than 25% by weight or volume, based on the total weight or volume of the fuel compositions.

Jet fuel is a product boiling for more than 90 vol% at from 130 to 300°C, having a density from 775 to 840 kg/m³, preferably from 780 to 830 kg/m³, at 15°C (e.g. ASTM D4502), an initial boiling point in the range 130 to 160°C and a final boiling point in the range 220 to 300°C, a kinematic viscosity at -20°C (ASTM D445) suitably from 1.2 to 8.0 mm²/s and a freeze point of below -40°C, preferably below -47°C.

Jet fuel will typically meet one of the following standards. Jet A-1 requirements in DEF STAN 91-91 (British Ministry of Defence Standard DEF STAN 91-91/Issue 5 of 8 Feb. 2005 for Turbine Fuel, Aviation “Kerosene Type,” Jet A-1, NATO code F-35, Joint Service

Designation AVTUR, or versions current at the time of testing) or “Check List” (Aviation Fuel Quality Requirements for Jointly Operated Systems (AFQRJOS) are based on the most stringent requirements of ASTM D1655 for Jet A-1 and DEF STAN 91-91 and some airport handling requirements of the IATA Guidance Material for Aviation Turbine Fuels Specifications. Jet fuel that meets the AFQRJOS is usually referred to as “Jet A-1 to Check List” or “Check List Jet A-1”). Examples of mineral derived kerosenes meeting Jet A-1 requirements and a kerosene stream used in Jet A-1 production are listed in Table 1.

Table 1

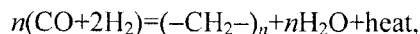
<p>Jet fuel produced by Merox® process. Hydroprocessed jet fuel, with 19 mg/L of antioxidant Ionox 75 (RDE/A/609). Jet fuel produced by caustic washing of straight run kerosene. Straight run kerosene stream.</p>
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The low boiling fraction as separated from the mineral gas oil may be used as such or in combination with a mineral derived kerosene, suitably made at the same production location. As the low boiling fraction may already comply with the jet fuel specifications it is evident that the blending ratio between said component and the mineral kerosene may be freely chosen. The mineral derived kerosene will typically boil for more than 90 vol% within the usual kerosene range of 130 to 300°C, depending on grade and use. It will typically have a density from 775 to 840 kg/m³, preferably from 780 to 830 kg/m³, at 15°C (e.g., ASTM D4502 or IP 365). It will typically have an initial boiling point in the range 130 to 160°C and a final boiling point in the range 220 to 300°C. Its kinematic viscosity at -20°C (ASTM D445) might suitably be from 1.2 to 8.0 mm²/s.

The mineral kerosene fraction may be a straight run kerosene fraction as isolated by distillation from said crude mineral oil source or a kerosene fraction isolated from the effluent of typical refinery conversion processes, preferably hydrocracking. The kerosene fraction may also be the blend of straight run kerosene and kerosene as obtained in a hydrocracking process. Suitably the properties of the mineral derived kerosene are those of the desired jet fuel as defined above.

The synthetic paraffinic kerosene fuel component may be a Fischer-Tropsch derived fuel component or Bio-derived fuel component or derived from other feedstocks such as coal and petroleum. By “Fischer-Tropsch derived” is meant that a fuel is, or derives from, a

synthesis product of a Fischer-Tropsch condensation process. The term “non-Fischer-Tropsch derived” may be interpreted accordingly. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into long chain, usually paraffinic, hydrocarbons:



5 in the presence of an appropriate catalyst and typically at elevated temperatures, for example 125 to 300°C, preferably 175 to 250°C, and/or pressures, for example 5 to 100 bar, preferably 12 to 50 bar. Hydrogen:carbon monoxide ratios other than 2:1 may be employed if desired.

The carbon monoxide and hydrogen may themselves be derived from organic or inorganic, natural or synthetic sources, typically from coal, biomass, for example wood chips, residual fuel fractions or more preferably natural gas or from organically derived methane. A Fischer-Tropsch derived fuel is sometimes referred to as a GTL (Gas-to-Liquids) fuel because the most commonly published source of carbon monoxide and hydrogen is natural gas. When in the context of the present invention reference is made to a GTL fuel, also coal or biomass derived fuels are meant.

15 Fischer-Tropsch derived kerosene or gas oil fraction may be obtained directly from the Fischer-Tropsch reaction, or indirectly, for instance by fractionation of Fischer-Tropsch synthesis products or from hydrotreated Fischer-Tropsch synthesis products. Hydrotreatment can involve hydrocracking to adjust the boiling range as for example described in GB-B-2077289 and EP-A-0147873, and/or hydroisomerization which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0583836 describes a two step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerization of hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and isomerization occur to yield a substantially paraffinic hydrocarbon fuel. The desired kerosene fraction(s) or gas oil fraction may subsequently be isolated for instance by distillation.

Typical catalysts for the Fischer-Tropsch synthesis of paraffinic hydrocarbons comprise, as the catalytically active component, a metal from Group VIII or the periodic table, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP-A-0583836. The Fischer-Tropsch reactor may be for example a multi-tubular reactor or a slurry reactor.

An example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis Process) described in "The Shell Middle Distillate Synthesis Process," van der Burgt et al. The process (also sometimes referred to as the Shell "Gas-To-Liquids" or "GTL" technology) produces middle distillate range products by conversion of a natural gas (primarily methane) derived synthesis gas into a heavy long chain hydrocarbon (paraffin) wax, which can then be hydroconverted and fractionated to produce liquid transport fuels such as the kerosene fractions used in the present invention. A version of the SMDS process, utilizing a fixed bed reactor for the catalytic conversion step, is currently in use in Bintulu, Malaysia. Kerosene and gas oil fractions prepared by the SMDS process are commercially available for instance from Shell companies.

By virtue of the Fischer-Tropsch process, a Fischer-Tropsch derived kerosene or gas oil fraction has essentially no, or undetectable levels of, sulfur and nitrogen. Compounds containing these heteroatoms tend to act as poisons for Fischer-Tropsch catalysts and are therefore removed from the synthesis gas feed. This can yield additional benefits, in terms of effect on catalyst performance, in fuel compositions in accordance with the present invention.

Further, the Fischer-Tropsch process as usually operated produces no or virtually no aromatic components. The aromatics content of a Fischer-Tropsch derived fuel, suitably determined by ASTM D2425, will typically be below 1% w/w, preferably below 0.5% w/w and more preferably below 0.1% w/w.

Generally speaking, Fischer-Tropsch derived kerosene and gas oil fractions have relatively low levels of polar components, in particular polar surfactants, for instance compared to petroleum derived fuels. It is believed that this can contribute to improved antifoaming and dehazing performance in the final automotive gas oil fuel. Such polar components may include for example oxygenates, and sulfur and nitrogen containing compounds. A low level of sulfur in a Fischer-Tropsch derived fuel is generally indicative of low levels of both oxygenates and nitrogen containing compounds, since all are removed by the same treatment processes.

The synthetic paraffinic kerosene fuel component may also be bio-derived from sources such as algae and other plants. Fatty acids from such bio-derived oil source may be hydrotreated to produce the synthetic paraffinic kerosene fuel component. Sources and jet usage of bio-derived synthetic paraffinic kerosenes for example were tested and discussed in

an industry report "Evaluation of Bio-Derived Synthetic Paraffinic Kerosene (Bio-SPK)" published June 2009, by The Boeing Company.

5 The synthetic paraffinic kerosene fuel component in the jet boiling range typically contains at least 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by as measured by ASTM D2425. Preferably the distillation of jet range is nominally 150-300°C measured by ASTM D86. The paraffinic kerosene fuel component has a carbon and hydrogen content of greater than 99.5wt% measured by ASTM D5291 and preferably contains normal, iso, and mono-cyclic paraffics of greater than 98.5wt% as measured by GCGC and less than 10 1wt% bicyclic aromatic and/or paraffinic material measured by GCGC.

A Synthetic paraffinic kerosene fuel preferably has the properties as described in Tables A1.1 and A1.2 of ASTM D7566 (Standard Specification for Aviation Turbine Fuel containing Synthesised Hydrocarbons) namely a density of from 0.730 to 0.770 g/cm³ and a sulfur content of 15 ppmw (parts per million by weight) or less.

15 Optionally, the fuel composition may further comprise a fuel additive known to a person of ordinary skill in the art. In certain embodiments, the fuel additive is from 0.1% to 50% by weight or volume, based on the total weight or volume of the fuel composition. The fuel additive can be any fuel additive known to those of skill in the art. In further embodiments, the fuel additive is selected from the group consisting of oxygenates, antioxidants, thermal stability improvers, stabilizers, cold flow improvers, combustion improvers, anti-foams, anti-haze additives, corrosion inhibitors, lubricity improvers, icing inhibitors, injector cleanliness 20 additives, smoke suppressants, drag reducing additives, metal deactivators, dispersants, detergents, de-emulsifiers, dyes, markers, static dissipaters, biocides and combinations thereof.

25 The amount of a fuel additive in the fuel composition disclosed herein may be from a 0.1% to less than 50%, from 0.2% to 40%, from 0.3% to 30%, from 0.4% to 20%, from 0.5% to 15% or from 0.5% to 10%, based on the total amount of the fuel composition. In certain embodiments, the amount of a fuel additive is less than 50%, less than 45%, less than 40%, less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 10%, less 30 than 5%, less than 4%, less than 3%, less than 2%, less than 1% or less than 0.5%, based on the total amount of the fuel composition. In some embodiments, the amount is in wt.% based

on the total weight of the fuel composition. In other embodiments, the amount is in vol.% based on the total volume of the fuel composition.

Illustrative examples of fuel additives are described in greater detail below. Lubricity improvers are one example. In certain additives, the concentration of the lubricity improver in the fuel falls in the range from 1 ppm to 50,000 ppm, preferably from 10 ppm to 20,000 ppm, and more preferably from 25 ppm to 10,000 ppm. Some non-limiting examples of lubricity improver include esters of fatty acids.

Stabilizers improve the storage stability of the fuel composition. Some non-limiting examples of stabilizers include tertiary alkyl primary amines. The stabilizer may be present in the fuel composition at a concentration from 0.001 wt% to 2 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

Combustion improvers increase the mass burning rate of the fuel composition. Some non-limiting examples of combustion improvers include ferrocene (dicyclopentadienyl iron, iron-based combustion improvers (e.g., TURBOTECT™ ER-18 from Turbotect (USA) Inc., Tomball, Tex.), barium-based combustion improvers, cerium-based combustion improvers, and iron and magnesium-based combustion improvers (e.g., TURBOTECT™ 703 from Turbotect (USA) Inc., Tomball, Tex.). The combustion improver may be present in the fuel composition at a concentration from 0.001 wt% to 1 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

Antioxidants prevent the formation of gum depositions on fuel system components caused by oxidation of fuels in storage and/or inhibit the formation of peroxide compounds in certain fuel compositions can be used herein. The antioxidant may be present in the fuel composition at a concentration from 0.001 wt% to 5 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

Static dissipaters reduce the effects of static electricity generated by movement of fuel through high flow-rate fuel transfer systems. The static dissipater may be present in the fuel composition at a concentration from 0.001 wt% to 5 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

Corrosion inhibitors protect ferrous metals in fuel handling systems such as pipelines, and fuel storage tanks, from corrosion. In circumstances where additional lubricity is desired, corrosion inhibitors that also improve the lubricating properties of the composition can be used. The corrosion inhibitor may be present in the fuel composition at a concentration from

0.001 wt% to 5 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

Fuel system icing inhibitors (also referred to as anti-icing additive) reduce the freezing point of water precipitated from jet fuels due to cooling at high altitudes and prevent the formation of ice crystals which restrict the flow of fuel to the engine. Certain fuel system icing inhibitors can also act as a biocide. The fuel system icing inhibitor may be present in the fuel composition at a concentration from 0.001 wt% to 5 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

Biocides are used to combat microbial growth in the fuel composition. The biocide may be present in the fuel composition at a concentration from 0.001 wt% to 5 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

Metal deactivators suppress the catalytic effect of some metals, particularly copper, have on fuel oxidation. The metal deactivator may be present in the fuel composition at a concentration from 0.001 wt% to 5 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

Thermal stability improvers are used to inhibit deposit formation in the high temperature areas of the aircraft fuel system. The thermal stability improver may be present in the fuel composition at a concentration from 0.001 wt% to 5 wt%, based on the total weight of the fuel composition, and in one embodiment from 0.01 wt% to 1 wt%.

In some embodiments, the fuel composition has a flash point greater than 32°C, greater than 33°C, greater than 34°C, greater than 35°C, greater than 36°C, greater than 37°C, greater than 38°C, greater than 39°C, greater than 40°C, greater than 41°C, greater than 42°C, greater than 43°C, or greater than 44°C. In other embodiments, the fuel composition has a flash point greater than 38°C. In certain embodiments, the flash point of the fuel composition disclosed herein is measured according to ASTM Standard D 56. In other embodiments, the flash point of the fuel composition disclosed herein is measured according to ASTM Standard D 93. In further embodiments, the flash point of the fuel composition disclosed herein is measured according to ASTM Standard D 3828-98. In still further embodiments, the flash point of the fuel composition disclosed herein is measured according to any conventional method known to a skilled artisan for measuring flash point of fuels.

In some embodiments, the fuel composition has a density at 15°C from 775 kg/m³ to 840 kg/m³. In certain embodiments, the density of the fuel composition disclosed herein is

measured according to ASTM Standard D 4052. In further embodiments, the density of the fuel composition disclosed herein is measured according to any conventional method known to a skilled artisan for measuring density of fuels.

5 In some embodiments, the fuel composition has a freezing point that is lower than -30°C, lower than -40°C, lower than -50°C, lower than -60°C, lower than -70°C, or lower than -80°C. In other embodiments, the fuel composition has a freezing point from -80°C to -30°C, from -75°C to -35°C, from -70°C to -40°C, or from -65°C to -45°C. In certain embodiments, the freezing point of the fuel composition disclosed herein is measured according to ASTM Standard D 2386. In further embodiments, the freezing point of the fuel
10 composition disclosed herein is measured according to any conventional method known to a skilled artisan for measuring freezing point of fuels.

In some embodiments, the fuel composition has an initial boiling point that is from 140°C to 170°C. In other embodiments, the fuel composition has a final boiling point that is from 180°C to 300°C. In still other embodiments, the fuel composition has an initial boiling
15 point that is from 140°C to 170°C, and a final boiling point that is from 180°C to 300°C. In certain embodiments, the fuel composition meets the distillation specification of ASTM D 86.

In some embodiments, the fuel composition has a Jet Fuel Thermal Oxidation Tester (JFTOT) temperature that is equal to or greater than 245°C. In other embodiments, the fuel composition has a JFTOT temperature that is equal to or greater than 250°C, equal to or
20 greater than 255°C, equal to or greater than 260°C, or equal to or greater than 265°C.

In some embodiments, the fuel composition has a viscosity at -20°C that is less than 6 mm²/sec, less than 7 mm²/sec, less than 8 mm²/sec, less than 9 mm²/sec, or less than 10 mm²/sec. In certain embodiments, the viscosity of the fuel composition disclosed herein is measured according to ASTM standard D 445.

25 In some embodiments, the fuel composition meets the ASTM D 1655 specification for Jet A-1. In other embodiments, the fuel composition meets the ASTM D 1655 specification for Jet A. In still other embodiments, the fuel composition meets the ASTM D 1655 specification for Jet B.

In another aspect, the invention provides a jet fuel composition having a density of from
30 775 to 840 kg/m³ comprising:

- a) a petroleum-based jet fuel component other than b) boiling for more than 90 vol% at from 130 to 300°C;

b) greater than 50 weight percent, based on combined components a) and b), of a synthetic paraffinic kerosene fuel component in the jet boiling range having at least 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by ASTM D2425; and

c) 5 to 40 weight percent, based on the jet fuel composition, of pinane.

In other embodiments, the pinane is present in an amount that is between 5% and 40% by weight, based on the total volume of the fuel composition. In still other embodiments, the pinane is present in an amount that is between 5% and 35% weight, based on the total weight of the fuel composition. In still other embodiments, the pinane is present in an amount that is between 10% and 35% weight, based on the total weight of the fuel composition. In still other embodiments, the pinane is present in an amount that is between 5% and 30% weight, based on the total weight of the fuel composition. In still other embodiments, the pinane is present in an amount that is between 10% and 30% weight, based on the total weight of the fuel composition. In still other embodiments, the pinane is present in an amount that is between 5% and 25% weight, based on the total weight of the fuel composition. In still other embodiments, the pinane is present in an amount that is between 10% and 25% weight, based on the total weight of the fuel composition.

In other embodiments, the synthetic paraffinic kerosene fuel component is present in amount greater than 50 weight percent, preferably greater than 55 weight percent, greater than 60 weight percent, greater than 65 weight percent, greater than 70 weight percent, or even greater than 75 weight percent, based on combined components a) and b).

In certain other embodiments, the jet fuel composition has a density at 15°C of between 770 and 840 kg/m³, has a aromatic content of less than 10 vol. %, preferably less than 8 vol. % (as measured according to ASTM D7566) – specifically ASTM D1319, flash point that is equal to or greater than 38°C; and freezing point that is lower than -40°C. In still other embodiments, the petroleum-based fuel is Jet A and the fuel composition meets the ASTM D 1655 specification for Jet A. In still other embodiments, the petroleum-based fuel is Jet A-1 and the fuel composition meets the ASTM D 1655 specification for Jet A-1. In still other embodiments, the petroleum-based fuel is Jet B and the fuel composition meets the ASTM D 1655 specification for Jet B.

In another aspect, a fuel system is provided comprising a fuel tank containing the fuel composition disclosed herein. Optionally, the fuel system may further comprise an engine cooling system having a recirculating engine coolant, a fuel line connecting the fuel tank with the internal combustion engine, and/or a fuel filter arranged on the fuel line. Some non-limiting examples of internal combustion engines include reciprocating engines (e.g., gasoline engines and diesel engines), Wankel engines, jet engines, some rocket engines, and gas turbine engines.

In some embodiments, the fuel tank is arranged with said cooling system so as to allow heat transfer from the recirculating engine coolant to the fuel composition contained in the fuel tank. In other embodiments, the fuel system further comprises a second fuel tank containing a second fuel for a jet engine and a second fuel line connecting the second fuel tank with the engine. Optionally, the first and second fuel lines can be provided with electromagnetically operated valves that can be opened or closed independently of each other or simultaneously. In further embodiments, the second fuel is a Jet A.

In another aspect, an engine arrangement is provided comprising an internal combustion engine, a fuel tank containing the fuel composition disclosed herein, a fuel line connecting the fuel tank with the internal combustion engine. Optionally, the engine arrangement may further comprise a fuel filter and/or an engine cooling system comprising a recirculating engine coolant. In some embodiments, the internal combustion engine is a jet engine.

When using a fuel composition disclosed herein, it is desirable to remove particulate matter originating from the fuel composition before injecting it into the engine. Therefore, it is desirable to select a suitable fuel filter for use in a fuel system disclosed herein. Water in fuels used in an internal combustion engine, even in small amounts, can be very harmful to the engine. Therefore, it is desirable that any water present in fuel composition be removed prior to injection into the engine. In some embodiments, water and particulate matter can be removed by the use of a fuel filter utilizing a turbine centrifuge, in which water and particulate matter are separated from the fuel composition to an extent allowing injection of the filtrated fuel composition to the engine, without risk of damage to the engine. Other types of fuel filters that can remove water and/or particulate matter also may be used.

In another aspect, a vehicle is provided comprising an internal combustion engine, a fuel tank containing the fuel composition disclosed herein, and a fuel line connecting the fuel

tank with the internal combustion engine. Optionally, the vehicle may further comprise a fuel filter and/or an engine cooling system comprising a recirculating engine coolant

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of examples herein described in detail. It should be understood, that the detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims. The present invention will be illustrated by the following illustrative embodiment, which is provided for illustration only and is not to be construed as limiting the claimed invention in any way.

Illustrative Examples

Test methods

Elastomer swelling test:

Immersion of a nitrile o-rings in a range of fuels (in triplicate) was performed over a single 24 hour period. The volume change of the nitrile o-ring was calculated by measuring the mass of displaced water.

The fuel blends were prepared with the composition listed in the following Table 2.

Materials

Table 2: Fuels.

Fuel	Description
1	GTL
2	Jet A-1 (a)
3	Jet A-1 (b)
4	Pinane
5	50% GTL and 50% Jet A-1 (a)
6	50% GTL and 50% Jet A-1 (b)
7	50% GTL, 35% Jet A-1 (a), 15% Pinane
8	50% GTL, 15% Jet A-1 (a), 35% Pinane
9	50% GTL, 35% Jet A-1 (b), 15% Pinane
10	50% GTL, 15% Jet A-1 (b), 35% Pinane
11	70% GTL and 30% Jet A-1 (a)
12	70% GTL and 30% Jet A-1 (b)

5

Table 3: Table jet specification results for Fuels 1-3.

Test	Unit	Fuel 1	Fuel 2	Fuel 3
Appearance		Satisfactory	Satisfactory	Satisfactory
Specific energy, net	MJ/Kg	44.25	43.246	42.988
Smoke point	mm	>50.0	23	14
Freezing point	°C	-55.5	-53.7	-65.6
Density @ 15C	Kg/m ³	736.7	801.6	821.1
Flash point	°C	40.5	41.0	42.5
IBP	°C	157.1	149.4	153.9
10% recovered	°C	163.2	168.8	168.6
50% recovered	°C	164.5	195.7	200.4
90% recovered	°C	184.6	234.6	238.9
FBP	°C	205.0	252.2	258.0
Residue	%V/V	0.2	1.0	1.6
Loss	%V/V	0.0	0.9	0.2
Mercaptan sulphur	%m/m	0.0	0.0011	<0.0003
Total sulphur	%m/m	0.0	0.0385	<0.0003
FIA Aromatics	%vol	0.0	16.5	20.3
Total acidity	mg KOH/g	<0.002	0.009	<0.001

Pinane was obtained from SENYUAN IND. & TRADE CO.,LTD, China.

Examples

Elastomer swell

Table 4: Elastomer swell results for all fuels.

Fuel	Description	Volume change %
1	GTL	-0.6
2	Jet A-1 (a)	10.9
3	Jet A-1 (b)	12.7
4	Pinane	46.3
5	50% GTL and 50% Jet A-1 (a)	6.1
6	50% GTL and 50% Jet A-1 (b)	6.5
7	50% GTL, 35% Jet A-1 (a), 15% Pinane	12.6
8	50% GTL, 15% Jet A-1 (a), 35% Pinane	19.8
9	50% GTL, 35% Jet A-1 (b), 15% Pinane	11.9
10	50% GTL, 15% Jet A-1 (b), 35% Pinane	19.4
11	70% GTL and 30% Jet A-1 (a)	6.2
12	70% GTL and 30% Jet A-1 (b)	6.3

5

Fig. 1 shows the elastomer swell results for all fuels. Fuel 1 (FT GTL) does not cause swelling in nitrile elastomers. The results indicate a slight shrinkage in the elastomer. However, this small degree of shrinkage could be considered to be within experimental error. Hence, it is assumed that the elastomer volume is unaffected by Fuel 1. For this reason Fuel 1 would be considered unfit-for-purpose as a jet fuel – according to ASTM D4054 the effect of jet fuels on a range of nitrile elastomeric should fall between a range of swelling characteristics.

Fuel 4 (pinane) elicits the greatest amount of elastomer swelling observed amongst the fuels examined here. However, this level of swelling would render this material unfit-for-purpose, this time due to the higher than required levels.

Fuels 2 and 3 (Jet A-1 (a) and (b)) swell the elastomers to a similar degree (Fuel 2: 10.9% and Fuel 3: 12.7%). Fuel 3 contains a larger volume of aromatic components and this difference in elastomer swelling is expected (swell of nitrile elastomers is proportional to aromatic content). The swell observed due to immersion in Fuels 2 and 3 is within an acceptable level and these fuels are considered to be fit-for-purpose.

Fuels 8 and 10 (tri-component blends containing 35% pinane) cause the elastomer material to swell by 19.8% and 19.4% respectively. This level of swelling is considerably higher than crude derived jet fuels (Fuels 2 and 3) but may be considered fit-for-purpose.

Fuels 7 and 9 (tri-component blends containing 15% pinane) cause the elastomer material to swell by 12.6% and 11.9% respectively. This degree of swelling is similar to that observed in crude derived jet fuels (Fuels 2 and 3) and would be considered fit-for-purpose.

Table 5 demonstrates that the ratio of GTL: Jet A-1 for the tri-component blends is above the current 1:1 constraint, as described in ASTM D7566-11a. This constraint is due to impaired/reduced swelling of nitrile elastomers as a result of the highly paraffinic GTL fuel – elastomer swelling is proportional to aromatic content.

However, when pinane is present, blends containing >1:1 GTL: Jet A-1 ratio (i.e. >50% GTL) elicit swelling characteristics that would be considered fit-for-purpose – see Table 5 below.

Table 5: Tri-component fuels.

Fuel	Elastomer swell (% vol)	Ratio of GTL: Jet A-1
7	12.6	1.4
8	19.8	3.3
9	11.9	1.4
10	19.4	3.3

Hence, the addition of pinane allows a greater proportion of FT-GTL fuel to be used in combination with jet fuel and remain on spec with respect to elastomer swell.

Density

Table 6: Density results for all fuels.

Fuel	Description	Density (kg/m ³ @ 15°C)	Pass/Fail
1	GTL	736.7	Fail by: -38.3
2	Jet A-1 (a)	801.6	Pass by: 26.6
3	Jet A-1 (b)	821.1	Pass by: 46.1
4	Pinane	861.4	Pass by: 86.4
5	50% GTL and 50% Jet A-1 (a)	769.2	Fail by: -5.8
6	50% GTL and 50% Jet A-1 (b)	778.9	Pass by: 3.9
7	50% GTL, 35% Jet A-1 (a), 15% Pinane	778.1	Pass by: 3.1
8	50% GTL, 15% Jet A-1 (a), 35% Pinane	790.1	Pass by: 15.1
9	50% GTL, 35% Jet A-1 (b), 15% Pinane	784.9	Pass by: 9.9
10	50% GTL, 15% Jet A-1 (b), 35% Pinane	793.0	Pass by: 18.0
11	70% GTL and 30% Jet A-1 (a)	756.2	Fail by: -18.8
12	70% GTL and 30% Jet A-1 (b)	762.0	Fail by: -13.0

Fig. 2 shows the density results at 15 °C for all fuels. As Table 6 shows, Fuel 1 (FT GTL) has a density that considerably lower than the spec requirement for jet fuel. When Fuel 1 is blended with Fuel 2 (Jet A-1 (a)) in a 1:1 ratio the resulting fuel (Fuel 5) has a density that is below the jet spec (i.e. 769.2 kg/m³). Hence, a more dense Jet A-1 fuel is required to blend with Fuel 1 in order to furnish an on-spec jet fuel. A blend of Fuel 1 with Fuel 3 (i.e. GTL and Jet A-1 (b)) furnishes Fuel 6. This fuel is on-spec with respect to density according to the jet fuel spec. This illustrates the need for careful selection of jet fuel (with sufficiently high density) when blending a GTL and jet fuel to form a semi-synthetic fuel according to ASTM D7566-11a.

Pure pinane has a density of 861.4 kg/m³, which is higher than any of the pure components tested here and above the jet spec limit.

The ratio GTL to Jet A-1 within Fuels 7-10 (the tri-component blends) is higher than 1:1 i.e. greater than 50% GTL. However, because of the presence of pinane the density of the final fuel is on-spec or fit-for-purpose – see Tables 6 and 7.

Table 7: Density results for tri-component fuels.

Fuel	Density ((Kg/m ³ @ 15°C)	Ratio of GTL: Jet A-1	Pass/Fail
7	778.1	1.4	Pass
8	790.1	3.3	Pass
9	784.9	1.4	Pass
10	793.0	3.3	Pass

Table 8: Density results for bi-component fuels.

Fuel	Density ((Kg/m ³ @ 15°C)	Ratio of GTL: Jet A-1	Pass/Fail
5	769.2	1.0	Fail
6	778.9	1.0	Pass
11	756.2	2.3	Fail
12	762.0	2.3	Fail

Hence, the addition of pinane allows a greater proportion of GTL fuel to be used in combination with jet fuel and remain on spec with respect to density.

Table 9: Aromatic content for all fuels.

Fuel	Description	% Volume aromatics
1	GTL	0.0
2	Jet A-1 (a)	16.5
3	Jet A-1 (b)	20.3
4	Pinane	0.0
5	50% GTL and 50% Jet A-1 (a)	8.3
6	50% GTL and 50% Jet A-1 (b)	10.2
7	50% GTL, 35% Jet A-1 (a), 15% Pinane	5.8
8	50% GTL, 15% Jet A-1 (a), 35% Pinane	2.5
9	50% GTL, 35% Jet A-1 (b), 15% Pinane	7.1
10	50% GTL, 15% Jet A-1 (b), 35% Pinane	3.0
11	70% GTL and 30% Jet A-1 (a)	5.0
12	70% GTL and 30% Jet A-1 (b)	6.1

Fig. 3 shows the aromatic content for all fuels in % volume. The semi-synthetic jet fuel spec (ASTM 7566-11a) states that the aromatic content of a semi-synthetic jet fuel should be no less than 8%. However, this level of aromatics is required to satisfy elastomer swell properties and to ensure that the jet fuel has a density that is sufficiently high. The jet fuel spec (ASTM D7566) actually considers aromatics to be “undesired” and only limits an upper limit of 25%. Hence, although Fuels 7-10 are off-spec according to the current semi-synthetic specification for aromatics, these fuels are in fact fit-for-purpose with respect to the properties of density and elastomer swell.

CLAIMS

1. A method for increasing the amount of a synthetic paraffinic kerosene fuel component in a jet fuel comprising:
 - a) providing a synthetic paraffinic kerosene fuel component in the jet boiling range having at least 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by ASTM D2425;
 - b) providing a petroleum-based jet fuel component boiling for more than 90 vol% at from 130 to 300°C;
 - c) providing pinane; and
 - d) blending component a), b) and c), wherein component c) is present in an amount of 5 to 40 weight percent, based on the blend, and component a) and b) are in a ratio of greater than 1 to 1 thereby providing a jet fuel blend having a density of from 775 to 840 kg/m³ at 15°C.
2. The method according to claim 1, wherein component c) is present in an amount of 5 to 35 weight percent, based on the blend.
3. The method according to claim 1 or claim 2, wherein component c) is present in an amount of 10 to 35 weight percent, based on the blend.
4. The method according to any one of claims 1 to 3, wherein component c) is present in an amount of 10 to 30 weight percent, based on the blend.
5. The method according to any one of claims 1 to 4, wherein the jet fuel blend has an aromatic content of less than 10 vol.% based on the jet fuel blend.
6. The method according to any one of claims 1 to 5, wherein the jet fuel blend has an aromatic content of less than 8 vol% based on the jet fuel blend.
7. A jet fuel composition having a density of from 775 to 840 kg/m³ at 15°C comprising:

- a) greater than 50 weight percent, based on combined components a) and b), of a synthetic paraffinic kerosene fuel component in the jet boiling range having at least 99.5wt% hydrocarbon, said hydrocarbon being at least 98.5wt% paraffins, less than 1wt% bicyclic compounds, and less than 0.5wt% total aromatics as measured by ASTM D2425;
 - b) a petroleum-based jet fuel component other than a) boiling for more than 90 vol% at from 130 to 300°C; and
 - c) 5 to 40 weight percent, based on the jet fuel composition, of pinane.
8. The jet fuel composition according to claim 7, wherein pinane is present in an amount of 5 to 35 weight percent, based on the blend.
9. The jet fuel composition according to claim 7 or claim 8, wherein greater than 55 weight percent, based on combined components a) and b), of the synthetic paraffinic kerosene fuel component is present.
10. The jet fuel composition according to any of claims 7 to 9, wherein greater than 60 weight percent, based on combined components a) and b), of the synthetic paraffinic kerosene fuel component is present.
11. The jet fuel composition according to any of claims 7 to 10, wherein pinane is present in an amount of 10 to 35 weight percent, based on the blend.
12. The jet fuel composition according to any of claims 7 to 11, wherein pinane is present in an amount of 10 to 25 weight percent, based on the blend.
13. The jet fuel composition according to any of claims 7 to 12, wherein greater than 70 weight percent, based on combined components a) and b), of the synthetic paraffinic kerosene fuel component is present.

1/2

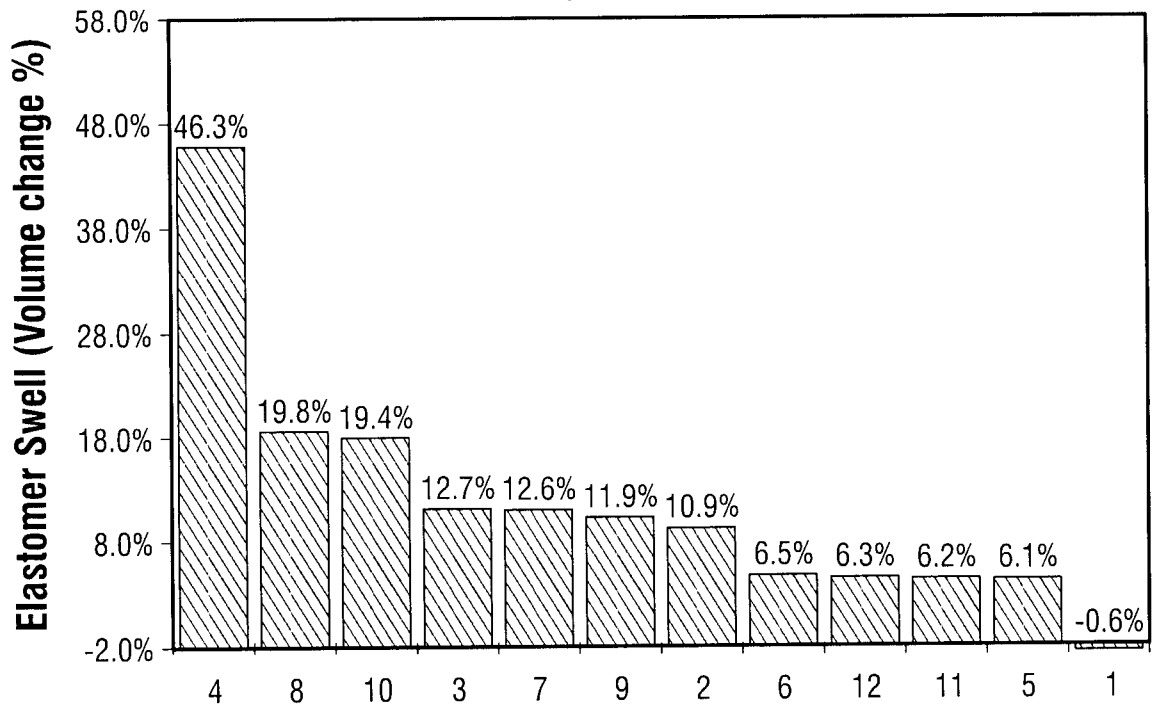


FIG. 1

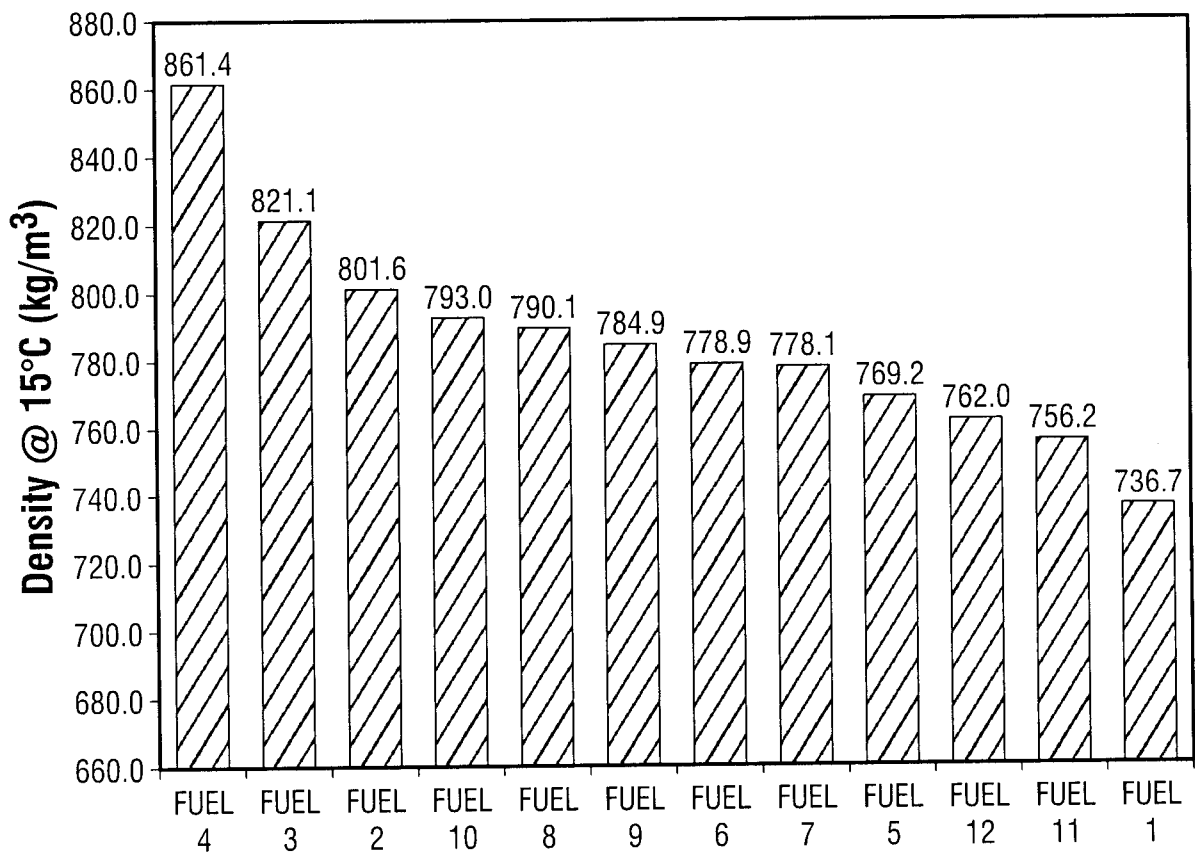


FIG. 2

2/2

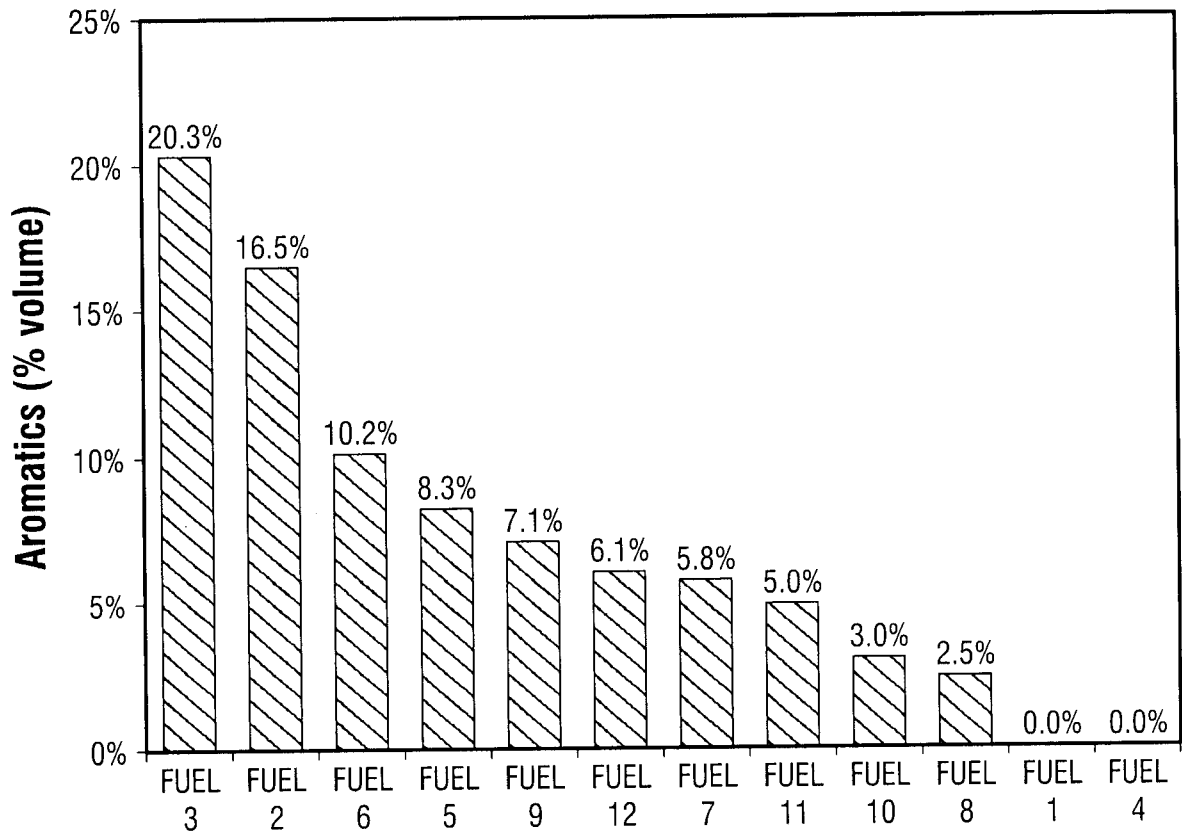


FIG. 3

