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Aulich et al.(10) **Pub. No.: US 2011/0061290 A1**(43) **Pub. Date: Mar. 17, 2011**(54) **AVIATION-GRADE KEROSENE FROM
INDEPENDENTLY PRODUCED
BLENDSTOCKS**(60) Provisional application No. 60/947,126, filed on Jun.
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(US)(52) **U.S. Cl. 44/308; 44/307; 44/403; 44/385;
585/14**(21) Appl. No.: **12/950,795**(57) **ABSTRACT**(22) Filed: **Nov. 19, 2010****Related U.S. Application Data**(62) Division of application No. 12/147,783, filed on Jun.
27, 2008.Aviation-grade kerosene comprising a first blendstock
derived from non-petroleum feedstock and comprising pri-
marily hydrocarbons selected from the group consisting of
isoparaffins and normal paraffins, and a second blendstock
comprising primarily hydrocarbons selected from the group
consisting of cycloalkanes and aromatics.

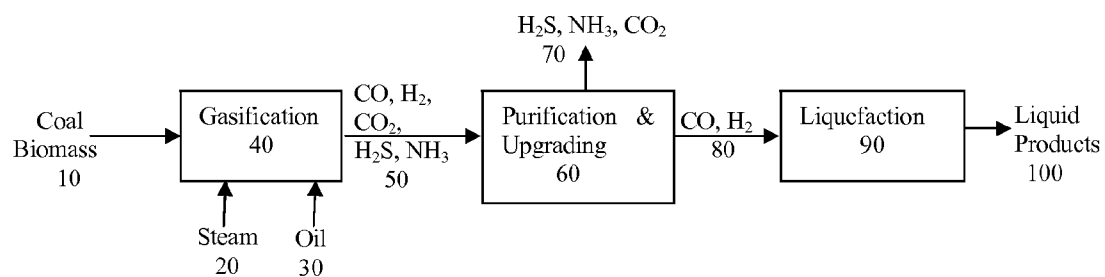


Fig. 1

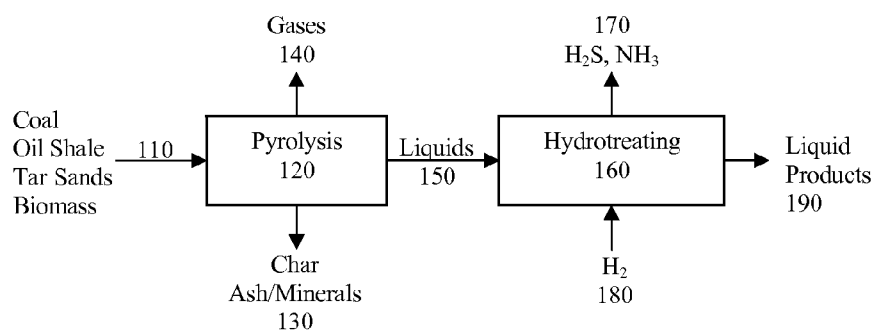


Fig. 2

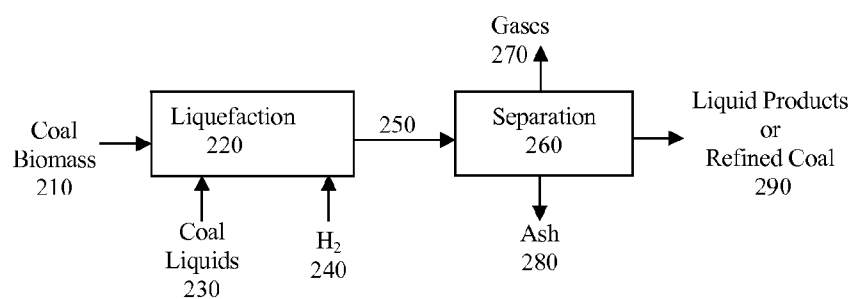


Fig. 3

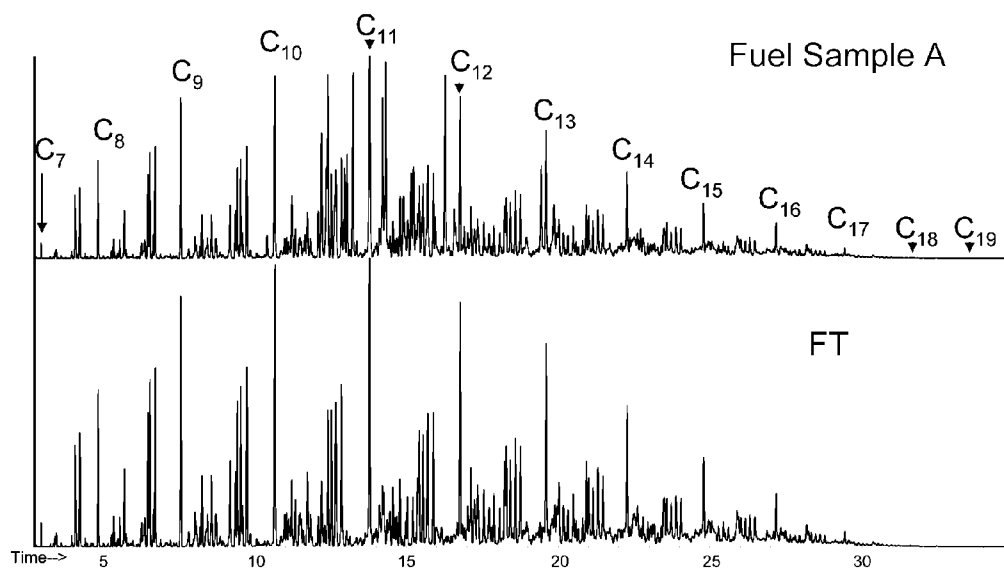


Fig. 4

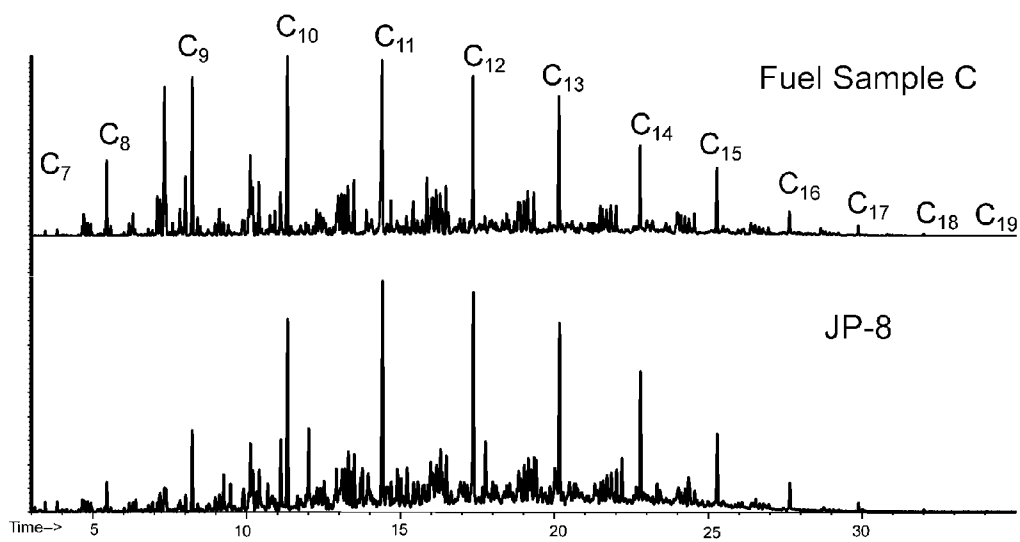


Fig. 5

AVIATION-GRADE KEROSENE FROM INDEPENDENTLY PRODUCED BLENDSTOCKS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a divisional application which claims the benefit under 35 U.S.C. §121 of U.S. patent application Ser. No. 12/147,783, filed Jun. 27, 2008, which claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Patent Application No. 60/947,126, filed Jun. 29, 2007, the disclosures of each of which are hereby incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under contract W911NF-07-C-0046 awarded by the Defense Advanced Research Projects Agency (DARPA). The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] 1. Field of the Invention

[0004] The present invention relates generally to aviation-grade high-cetane kerosene fuel. More particularly, herein disclosed is an aviation-grade kerosene fuel produced in part or fully from non-petroleum feedstocks. Specifically, the disclosed kerosene fuel comprises at least two independently produced blendstocks, with the first blendstock comprising primarily isoparaffins and normal paraffins (I/N) derived from non-petroleum feedstocks and the second blendstock comprising primarily cycloalkanes and aromatics (C/A) derived from petroleum or non-petroleum feedstocks. In embodiments, a kerosene fuel suitable for use as aviation turbine fuel having drop-in and fit-for-purpose compatibility with conventional petroleum-derived fuels comprises up to 95 volume percent (vol. %) I/N blendstock and up to 35 vol. % C/A blendstock.

[0005] 2. Background of the Invention

[0006] The generic term "kerosene" is used to describe the fraction of crude petroleum that boils approximately in the range of 293° F. to 572° F. (145° C. to 300° C.) and consists of hydrocarbons primarily in the range of C₈-C₁₆. Kerosenes are the lighter end of a group of petroleum substances known as middle distillates.

[0007] As an example, the predominant use of high-cetane kerosene in the United States is aviation turbine fuel for civilian (Jet A or Jet A-1) and military (JP-8 or JP-5) aircraft. Kerosene-based fuels differ from each other in performance specifications. Jet A and Jet A-1 are kerosene-type fuels. The primary physical difference between Jet A and Jet A-1 is freeze point (the temperature at which wax crystals disappear in a laboratory test). Jet A, which is mainly used in the United States, must have a freeze point of -40° C. or below, while Jet A-1 must have a freeze point of -47° C. or below. Jet A does not normally contain a static dissipater additive, while Jet A-1 often requires this additive. There are additional differences between the two fuels, and full specifications are outlined under the ASTM D1655 and Def Stan 91-91/5 standards, respectively.

[0008] Military turbine fuel grades such as JP-5 and JP-8 are defined by Mil-DTL-5624 and Mil-DTL-83133, respectively. These fuels are kerosene-type fuels made to more

exacting specifications than the commercial jet fuels. They also contain unique performance enhancing additives. Throughout the world, many governments have issued a variety of standards such as for TS-1 premium kerosene, TS-1 regular kerosene, and T-1 regular kerosene in Russia. The crude oil fraction for all of these aviation-grade kerosenes is basically limited to the range of 300° F. to 500° F. (149° C. to 260° C.), with additional specifications based on recovery rates at given temperature points. Hydrocarbons are primarily in the range of C₈-C₁₆.

[0009] The ready availability of crude petroleum has encouraged the establishment of the above-mentioned specifications for kerosene as the basis for fuels in engines of various types, and engines have thus been optimized to run on kerosene having these specifications. Concern has arisen regarding the reliability and availability of the petroleum supply. This concern has stimulated a search for substitutes. Liquids derived from coal, shale, tar sands, and renewable resources such as biomass, in particular, plant material, have been proposed. These processes have not adequately produced aviation-grade kerosene that complies with today's jet fuel specifications.

[0010] The failure of obtaining suitable aviation-grade kerosenes from non-petroleum feedstocks has triggered development in downstream processing of the products. For example, U.S. Pat. No. 4,645,585 discloses the production of novel fuel blends from hydroprocessing highly aromatic heavy oils such as those derived from coal pyrolysis and coal hydrogenation.

[0011] International Patent WO 2005/001002 A2 relates to a distillate fuel comprising a stable, low-sulfur, highly paraffinic, moderately unsaturated distillate fuel blendstock. The highly paraffinic, moderately unsaturated distillate fuel blendstock is prepared from a Fischer-Tropsch-derived product that is hydroprocessed under conditions during which a moderate amount of unsaturates are formed or retained to improve stability of the product.

[0012] Although many physical properties for aviation-grade kerosene can be matched and even outperformed, the fuels derived by hydroprocessing and additional upgrading as described above do not provide drop-in compatibility with conventional petroleum-derived aviation-grade kerosene, as they lack some of the major hydrocarbon constituents of typical petroleum-derived kerosene.

[0013] An attempt for better modeling of the variety of different hydrocarbon constituents was made by Violi et al. (Violi, A.; Yan, S.; Eddings, E. G.; Sarofim, A. F.; Granata, S.; Faravelli, T.; Ranzi, E.; *Combust. Sci. Technol.* 2002, 174 (11-12) 399-417). Violi et al. modeled JP-8 as a six-compound blend of well-known hydrocarbons with the following molar composition: 10% iso-octane (C₈H₁₈), 20% methylcyclohexane (C₇H₁₄), 15% m-xylene (C₈H₁₀), 30% normal-dodecane (C₁₂H₂₆), 5% tetralin (C₁₀H₁₂), and 20% tetrade-cane (C₁₄H₃₀). This surrogate blend simulates the volatility and smoke point of a practical JP-8 fuel. However, this method of reducing the fuel to a mere six-compound blend does not reproduce all required performance specifications of JP-8.

[0014] A different route was pursued in U.S. Patent Application 2006/0138025, which relates to distillate fuels or distillate fuel blendstocks comprising a blend of a Fischer-Tropsch-derived product and a petroleum-derived product that is then hydrocracked under conditions to preserve aromatics. While this may produce some required characteristics from

certain petroleum feedstocks, such as seal swell and density, this approach reduces the ability to achieve competing characteristics, such as freeze point specifications.

[0015] Accordingly, there is an ongoing need for a fuel and process that allow use of environmentally-sensitive processes as a bridge to the future and provide drop-in compatibility with existing petroleum-based aviation-grade kerosene for clean fuels produced from secure domestic resources.

SUMMARY

[0016] Herein disclosed is aviation-grade kerosene comprising: a first blendstock derived from non-petroleum feedstock and comprising primarily hydrocarbons selected from the group consisting of isoparaffins and normal paraffins, and a second blendstock comprising primarily hydrocarbons selected from the group consisting of cycloalkanes and aromatics. In embodiments, the second blendstock is derived from feedstock comprising non-petroleum feedstock. It is desirable for the aviation-grade kerosene is capable of being blended with petroleum-derived jet fuel in any proportion such that the resulting blend meets fuel grade specification of the petroleum-derived jet fuel. In embodiments, the aviation-grade kerosene comprises up to 95 vol. % of first blendstock and up to 35 vol. % of second blendstock.

[0017] In specific embodiments, the aviation-grade kerosene comprises up to 95 vol. % first blendstock, from about 0 vol. % to about 30 vol. % cycloalkanes, and from about 0 vol. % to about 15 vol. % aromatics. In embodiments, this kerosene comprising up to 95 vol. % first blendstock, from about 0 vol. % to about 30 vol. % cycloalkanes, and from about 0 vol. % to about 15 vol. % aromatics meets fit-for-purpose requirements. In embodiments, at least 50 weight percent of the kerosene is derived from coal, natural gas, or a combination thereof. In embodiments, the second blendstock is derived from coal, biomass, oil-shale, tar, oil sands, or a combination thereof. In embodiments, at least 50 weight percent of the kerosene is derived from biomass. In embodiments, at least 10 weight percent of the kerosene is derived from non-cracked bio-oil.

[0018] Also disclosed herein is a method for the production of aviation-grade kerosene comprising: producing a first blendstock from at least one non-petroleum feedstock, the first blendstock comprising primarily hydrocarbons selected from the group consisting of isoparaffins and normal paraffins; producing a second blendstock comprising primarily hydrocarbons selected from the group consisting of cycloalkanes and aromatics; and blending at least a portion of the first blendstock with at least a portion of the second blendstock to produce aviation-grade kerosene. In embodiments of the method for the production of aviation-grade kerosene, first and second blendstocks are independently-produced. In embodiments of the method, the non-petroleum feedstock is selected from the group consisting of coal, natural gas, biomass, vegetable oils, biomass pyrolysis bio-oils, biologically-derived oils and combinations thereof.

[0019] In some embodiments of the method, at least a portion of first blendstock is produced via indirect liquefaction. Indirect liquefaction may comprise Fischer-Tropsch processing of a feedstock selected from the group consisting of natural gas, coal, biomass, and combinations thereof. The kerosene may comprise up to about 90 vol. % first blendstock produced via indirect liquefaction.

[0020] In embodiments of the method for the production of aviation-grade kerosene, the at least one non-petroleum feed-

stock comprises triglyceride and/or fatty acid feedstock. The kerosene may comprise from about 65 vol. % to about 75 vol. % of first blendstock, the at least one non-petroleum feedstock for which comprises triglyceride and/or fatty acid feedstock. In embodiments, second blendstock is produced by catalytic cyclization and/or reforming of a portion of first blendstock, the at least one non-petroleum feedstock for which comprises triglyceride and/or fatty acid feedstock. The kerosene may comprise about 65 vol. % first blendstock, the at least one non-petroleum feedstock for which comprises triglyceride and/or fatty acid feedstock; and about 35 vol. % second blendstock produced by catalytic cyclization and/or reforming of a portion of first blendstock.

[0021] In some embodiments, the kerosene comprises about 70 vol. % first blendstock produced via catalytic processing of triglyceride and/or fatty acid feedstock and about 30 vol. % second blendstock produced via pyrolysis processing of high cycloalkane-content material.

[0022] In embodiments of the method for the production of aviation-grade kerosene, second blendstock is produced via pyrolysis of a feedstock selected from the group consisting of coal, oil shale, oil sands, tar, biomass, and combinations thereof. In specific embodiments, the kerosene may comprise about 80 vol. % first blendstock produced via Fischer-Tropsch processing of natural gas, coal, and/or biomass and about 20 vol. % second blendstock produced via pyrolysis processing of coal tar fraction.

[0023] In some embodiments of the method for the production of aviation-grade kerosene, the second blendstock is produced via direct liquefaction. In embodiments, the kerosene comprises about 25 vol. % second blendstock produced via direct liquefaction. In specific embodiments, the kerosene further comprises about 75 vol. % first blendstock derived from Fischer-Tropsch processing of natural gas, coal, and/or biomass.

[0024] In some embodiments of the method for the production of aviation-grade kerosene, second blendstock is produced from a biomass-derived lignin feedstock. The kerosene may comprise from about 25 vol. % to about 30 vol. % second blendstock produced from a biomass-derived lignin feedstock. In some embodiments, the kerosene comprises about 30 vol. % second blendstock produced via pyrolysis processing of biomass-derived lignin and about 70 vol. % first blendstock produced via Fischer-Tropsch processing of natural gas, coal, and/or biomass. In embodiments, the kerosene comprises about 25 vol. % second blendstock produced from a biomass-derived lignin feedstock and about 75 vol. % first blendstock derived from catalytic processing of triglyceride feedstock.

[0025] In embodiments of the method for the production of aviation-grade kerosene, the method further comprises testing the aviation grade kerosene for at least one requirement selected from the group consisting of fit-for-purpose requirements, ASTM requirements, and combinations thereof. In embodiments, the method further comprises adjusting the ratio of first blendstock and second blendstock in the kerosene to meet at least one requirement selected from the group consisting of fit-for-purpose requirements, ASTM requirements, and combinations thereof. In some embodiments, the method further comprises adjusting the amount of cycloalkanes and aromatics in the second blendstock to meet at least

one requirement selected from the group consisting of fit-for-purpose requirements, ASTM requirements, and combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] For a more detailed description of the preferred embodiment of the present invention, reference will now be made to the accompanying drawings, wherein:

[0027] FIG. 1 is a schematic of an indirect liquefaction process suitable for producing isoparaffin/n-paraffin (I/N) blendstock according to an embodiment of the present disclosure.

[0028] FIG. 2 is a schematic of a pyrolysis process suitable for producing cycloalkane/aromatic (C/A) blendstock according to an embodiment of the present disclosure.

[0029] FIG. 3 is a schematic of a direct liquefaction process suitable for producing cycloalkane/aromatic (C/A) blendstock according to an embodiment of the present disclosure.

[0030] FIG. 4 is a comparison of gas chromatography data from FT (FT derived liquid fuel from natural gas—bottom) and Fuel Sample A (top) produced from two discrete blendstocks and technological processes: (1) an isoparaffinic kerosene (IPK) produced from FT technology and natural gas feedstock and (2) an aromatic/cycloparaffinic blendstock produced from petroleum feedstock.

[0031] FIG. 5 is a comparison of gas chromatography data from typical JP-8 (bottom) and Fuel Sample C (top) produced from two discrete blendstocks and technological processes: (1) an isoparaffinic kerosene (IPK) produced from a crop oil feedstock and (2) an aromatic/cycloparaffinic blendstock produced from a crop oil feedstock.

NOTATION AND NOMENCLATURE

[0032] The term “I/N blendstock” as used herein refers to a material that comprises at least 95 weight percent of isoparaffins, normal paraffins, or a mixture thereof.

[0033] The term “C/A blendstock” as used herein refers to a material that comprises at least 95 weight percent of cycloalkanes, aromatics, or a mixture thereof.

[0034] The terms “aviation-grade kerosene” or “jet fuel” as used herein refer to kerosene-type fuels that are specified by military turbine fuel grades such as JP-5 and JP-8 and defined by Mil-DTL-5624 and Mil-DTL-83133, respectively, or civilian aviation jet fuels such as Jet A or Jet A-1 with full specifications outlined under the ASTM D1655 and Def Stan 91-91/5 standards, respectively. Throughout the world there exist a variety of similar standards that might change over time and are considered under this definition.

[0035] The term “fit-for-purpose requirements” as used herein refers to fuel property requirements that are not necessarily addressed by military or ASTM standards, but are still important to fuel performance and stability in jet engines and during fuel handling, distribution, and storage. Examples of fit-for-purpose requirements include fuel compatibility with aircraft fuel and engine system materials of construction, adequate fuel performance in compression ignition (versus turbine) engines in a wide variety of ground environments, and possible fuel performance requirements related to swelling of elastomeric seals in, for example, turbine engines.

[0036] The term “drop-in compatibility” as used herein refers to aviation-grade kerosene capable of being blended with petroleum-derived jet fuel in any proportion (i.e. from

0% to 100%) such that the resulting blend meets fuel grade specification and fit-for-purpose requirements of the equivalent petroleum-based jet fuel.

[0037] The term “I/N-C/A fuel” as used herein refers to aviation-grade kerosene derived from at least two independently produced blendstocks, with a first I/N blendstock derived from non-petroleum feedstocks and a second C/A blendstock derived from petroleum or non-petroleum feedstocks.

DETAILED DESCRIPTION

I. Overview

[0038] Herein disclosed are a fuel and a method for making the fuel whereby the fuel has drop-in compatibility with existing petroleum-derived fuels and enables production of most or all of a fuel from domestic, non-petroleum, and/or renewable feedstocks. The method of making this aviation-grade jet fuel may allow broad flexibility in fuel formulation in order to meet specific end-use requirements. The disclosed I/N-C/A fuel comprises a blend of fuel components, namely straight-chain (normal) and branched (iso-) paraffins, cycloalkanes, and/or aromatics.

[0039] Meeting a specification for aviation-grade kerosene requires providing a complex mixture of fuel chemical classes that have conflicting effects on physical properties. For example, longer carbon chain molecules serve to reduce volatility and increase density, which in turn raises freeze point above acceptable levels for high altitude flight. Balancing these characteristics along with energy density, flash point, viscosity, smoke point, seal-swelling capacity, and other characteristics makes fuel formulation difficult when derived from a single non-petroleum resource.

[0040] The aviation-grade kerosene herein disclosed is produced from at least two independently-produced blendstocks, with a first blendstock comprising primarily hydrocarbons selected from the group consisting of isoparaffins and normal paraffins (I/N) and derived from non-petroleum feedstocks and a second blendstock comprising primarily hydrocarbons selected from the group consisting of cycloalkanes and aromatics (C/A) and derived from petroleum or non-petroleum feedstocks. In embodiments, the finished I/N-C/A jet fuel comprises up to 95 volume percent (vol. %) I/N blendstock and up to 35 (vol. %) C/A blendstock.

II. Kerosene

[0041] Petroleum-based kerosene may be obtained either from the atmospheric distillation of crude oil (“straight-run” kerosene) or from cracking of heavier petroleum streams (“cracked” kerosene). The kerosene is further treated by a variety of processes to remove or reduce the level of undesirable components, e.g., aromatic hydrocarbons, sulfur, nitrogen, or olefinic materials. This additional processing also reduces compositional variation and enriches components that improve performance (cycloalkanes and isoparaffins, for example). In practice, the major processes used are hydrodesulfurization (treatment with hydrogen to remove sulfur components), washing with caustic soda solution (to remove sulfur components), and hydrogenation (to remove, for example, olefins, sulfur, metals, and/or nitrogen components). Aromatics that may have formed during the cracking process are removed via solvent extraction. For instance, hydrodesulfurized kerosene is obtained by treating a kerosene-range petroleum stock with hydrogen to convert organic sulfur to hydro-

gen sulfide, which is then removed. These subsequent treatments may blur the distinction between straight-run and cracked kerosenes.

[0042] While kerosenes are essentially similar in composition, the precise composition of a specific kerosene-range refinery stream depends on the crude oil from which the kerosene was derived and on the refinery processes used for its production. Because they are complex hydrocarbon mixtures, materials in this category are typically not defined by detailed compositional data but instead by process history, physical properties, and product-use ASTM and similar specifications.

[0043] Consequently, detailed compositional information for the streams in this category is limited. General compositional information on representative kerosene-range refinery streams and fuels, presented in Table 1, illustrates the fact that the materials in this category are similar in physical properties and composition. Regardless of crude oil source or processing history, major components of kerosenes comprise branched and straight-chain paraffins (iso- and normal or n-alkanes) and naphthenes (cycloparaffins or cycloalkanes), which normally account for at least 75 vol. % of a finished fuel. Aromatic hydrocarbons in this boiling range, such as alkylbenzenes (single ring) and alkyl-naphthalenes (double ring) do not normally exceed 25 vol. % of a kerosene product. Olefins are usually not present at more than 5% by volume. The distillation range of kerosenes is such that benzene (80° C. boiling point) and normal-hexane (69° C. boiling point) concentrations are generally less than 0.01% by mass. The boiling points of the 3-7 fused-ring polycyclic aromatic compounds (PACs) are well above the boiling range of straight-run kerosene streams. Consequently, the concentrations of PACs found in kerosenes are very low, if not below the limits of detection of the available analytical methods. A detailed analysis of a hydrodesulfurized kerosene illustrates this and is presented as Table 2.

TABLE 1

General Kerosene Compositional Information			
	Hydrodesulfurized Kerosene	Jet A	JP-8
API Gravity	39-45.5	37.2-46.1	37.0-46.7
Aromatic Content, vol. %	18-21.4	11.6-24.0	13.6-22.1
Olefin Content, vol. %	1.0-1.66	0.0-4.1	0.6-3.0
Saturates Content, vol. %	77.2-82	71.9-88.4	74.9-85.8
10% Distillation, ° F.	329-406	294-394	333-390
FBP Distillation, ° F.	451-568	404-510	419-474
(Final Boiling Pt.)		(90%)	(90%)

TABLE 2

Hydrodesulfurized Kerosene	
Component	Weight Percent
Nonaromatics	80.27
Saturates	78.61
Olefins	1.66
Aromatics	19.72
Less than Three-Ring PAC	19.72
Three- to Seven-Ring PAC	<0.01

III. I/N Blendstock

[0044] The herein disclosed I/N-C/A blend fuel comprises at least one I/N blendstock comprising primarily hydrocar-

bons selected from the group consisting of isoparaffins and normal paraffins, the hydrocarbons derived from non-petroleum feedstock. The finished I/N-C/A jet fuel comprises up to 95 vol. % of I/N blendstock. In embodiments, I/N blendstock comprises isoparaffin and/or normal paraffin compounds containing primarily from eight to sixteen carbon atoms per molecule (C8 to C16 compounds). In embodiments, these compounds are produced directly via a chemical process such as, but not limited to, Fischer-Tropsch condensation of synthesis gas ('syngas'), thermocatalytic processing of vegetable oils, pyrolysis, liquefaction, and gas-to-liquids processing.

[0045] In embodiments, I/N blendstock is derived from one or a combination of the following feedstocks: natural gas, coal, biomass, vegetable oils, biomass pyrolysis bio-oils, and other biologically-derived oils. I/N blendstock can be produced by several routes. In a specific embodiment, as shown in FIG. 1, indirect liquefaction is used to produce I/N blendstock. Indirect liquefaction feedstock, such as coal or biomass, **10** is gasified in gasifier **40** with steam **20** and/or oil **30**. Gasifier effluent **50**, may comprise carbon monoxide, hydrogen, carbon dioxide, hydrogen sulfide, and/or ammonia. Gasifier effluent **50** is purified and upgraded in step **60**, whereby a contaminant stream(s) **70** comprising, for example, hydrogen sulfide, ammonia, and/or carbon dioxide is removed. Syngas stream **80**, comprising primarily CO and H₂, undergoes liquefaction **90** to yield liquid products **100**. In embodiments, liquid products **100** are synthesized from syngas **80** by catalytic Fischer-Tropsch (F-T) processing. The Fischer-Tropsch reactions produce a wide spectrum of oxygenated compounds, in particular, alcohols and paraffins ranging in carbon numbers from C₁-C₃ (gases) to C₃₅₊ (solid waxes). These Fischer-Tropsch products yield distillate fuels that comprise C₈-C₁₆ paraffins and, through isomerization, C₈-C₁₆ isoparaffins that have excellent cetane numbers and very low sulfur and aromatic content. These properties make F-T products suitable for use as I/N blendstock. However, because of the lack of adequate cycloalkanes and aromatics, Fischer-Tropsch distillate fuels are typically unable to meet all military and ASTM specifications and fit-for-purpose requirements. Therefore, as described further hereinbelow, I/N blendstock is blended with C/A blendstock to obtain aviation-grade I/N-C/A fuel. In embodiments, I/N-C/A fuel comprises up to 95 vol. % I/N blendstock, alternatively about 90 vol. % I/N blendstock derived from Fischer-Tropsch processing of natural gas, coal, and/or biomass. In embodiments, the I/N-C/A fuel comprises about 80 vol. % I/N blendstock derived from Fischer-Tropsch processing of natural gas, coal, and/or biomass. In alternative embodiments, I/N-C/A fuel comprises about 70 vol. % I/N blendstock derived from Fischer-Tropsch processing of natural gas, coal, and/or biomass.

[0046] In embodiments, I/N blendstock is produced from triglyceride and/or fatty acid feedstocks. I/N blendstock n-paraffins may be produced, for example, via: (1) catalytic triglyceride dissociation into fatty acids and glycerol, (2) glycerol removal, and (3) oxygen removal from fatty acids (e.g., via catalytic decarboxylation and/or reduction) to yield normal paraffins. I/N blendstock isoparaffins may be produced via (4) catalytic isomerization of a portion of these normal paraffins to yield isoparaffins.

[0047] In embodiments, I/N-C/A fuel comprises from about 65 vol. % to about 95 vol. % I/N blendstock derived from catalytic processing of triglyceride feedstock. In specific embodiments, I/N-C/A fuel comprises about 75 vol. % I/N blendstock derived from catalytic processing of triglyceride

eride feedstock. In alternative embodiments, I/N-C/A fuel comprises about 80 vol. % I/N blendstock derived from catalytic processing of triglyceride feedstock. In alternative embodiments, I/N-C/A fuel comprises about 80 to 90 vol. % I/N blendstock derived from catalytic processing of triglyceride feedstock.

IV. C/A Blendstock

[0048] As mentioned hereinabove, I/N blendstock typically has a density below minimum requirements. For example, the I/N blendstock typically has a density below the MIL-DTL-83133-specified minimum requirement of 0.775 kg/L and may be very near to exceeding or may exceed the freeze point maximum requirement of less than -47° C. As it is desirable for the I/N-C/A fuel to meet standard (for example, MIL-DTL-83133-specified) density, freeze point, and flash point requirements, the disclosed I/N-C/A fuel further comprises at least one independently-produced C/A blendstock to obtain required density and cold-flow performance. The C/A blendstock comprises primarily hydrocarbons selected from the group consisting of cycloalkanes and aromatics. The aviation-grade I/N-C/A fuel comprises an appropriate blend of aromatics and cycloalkanes whereby requisite density and freeze point specifications of the resulting high cetane kerosene fuel are met. In embodiments, the hydrocarbons of the C/A blendstock are derived from petroleum feedstocks. In embodiments, the hydrocarbons of the C/A blendstock are derived from non-petroleum feedstocks. In embodiments, the hydrocarbons of the C/A blendstock are derived from a combination of petroleum and non-petroleum feedstocks. In embodiments, the I/N-C/A fuel comprises up to 35 vol. % C/A blendstock.

[0049] In embodiments, the C/A blendstock comprises aromatics. In embodiments, the C/A blendstock comprises aromatics selected primarily from the group consisting of C₉ to C₁₅ aromatics which provide the requisite density. In embodiments, the aromatics are primarily alkylated benzene compounds. In addition to providing density, aromatics may also contribute to beneficial seal swelling and may provide needed lubricity and viscosity. In embodiments, the C/A blendstock comprises less than about 15 vol. % aromatics. In embodiments, the C/A blendstock comprises from about 0 vol. % to about 15 vol. % aromatics.

[0050] In embodiments, C/A blendstock comprises cycloalkanes. In embodiments, the C/A blendstock comprises cycloalkanes primarily selected from the group consisting of C₉ to C₁₅ cycloalkanes which reduce freeze point (to counteract the freeze point increase resulting from aromatic addition) without adversely decreasing flash point. In embodiments, C/A blendstock comprises less than about 30 vol. % cycloalkane. In embodiments, suitable freeze point are obtained in the I/N-C/A fuel by selection of aromatics (i.e. having high density and low freeze point) for the C/A blendstock such that the C/A blendstock comprises 0% cycloalkanes. In embodiments, C/A blendstock comprises from about 0 vol. % to about 30 vol. % cycloalkane. In embodiments, jet-fuel compliant I/N-C/A fuel comprises up to 95 vol. % of paraffins selected from isoparaffins and normal paraffins, from about 0 vol. % to about 30 vol. % cycloalkanes, and from about 0 vol. % to about 15 vol. % aromatics. In embodiments, I/N-C/A fuel comprises about 95 vol. % I/N blendstock and about 5% high density low freeze point aromatic.

[0051] Without limitation, C/A blendstock may be derived from one or a combination of the following feedstocks: petroleum, oil shale, oil sands, natural gas, coal, biomass, vegetable oil, biomass pyrolysis bio-oil, and other biologically-derived oils. In embodiments, aviation-grade I/N-C/A kerosene comprises at least 50 weight percent of hydrocarbons selected from cycloalkanes and aromatics, said hydrocarbons derived from coal, biomass, or a combination thereof.

[0052] C/A blendstock may be produced by several methods. FIG. 2 shows an embodiment for the production of C/A blendstock via pyrolysis (heating in a deficiency of oxygen). Pyrolysis may be performed by any method known to one of skill in the art. In FIG. 2, pyrolysis feedstock **110** undergoes pyrolysis **120**. Suitable pyrolysis feedstock **110** includes, without limitation, coal, oil shale, oil sands, biomass, and combinations thereof. Gases **140** and char/ash/minerals **130** are removed. Pyrolysis oil vapors are condensed, the resulting pyrolysis oil **150** is hydrotreated as is known to those of skill in the art. In embodiments, catalytic hydrotreating is used to reduce the level of at least one contaminant selected from the group consisting of nitrogen, sulfur, oxygen, and metals. In embodiments, pyrolysis oil **150** is treated with hydrogen **180** and the level of sulfur and/or nitrogen in pyrolysis oil **150** is reduced via elimination of gas stream(s) **170** comprising, for example, hydrogen sulfide and/or ammonia. Via hydrotreating **160**, contaminant-reduced liquid products **190** are obtained. This procedure is similar to the procedure used in upgrading crude oil in a refinery to produce a variety of liquid fuels, as known to those of skill in the art. Table 3 presents a comparison of pyrolyzed coal tar fractions based on typical boiling range and major hydrocarbon constituents.

TABLE 3

Typical Coal Tar Fractions		
Fraction	Boiling Range, ° C.	Typical HC Constituents and Carbon Numbers
Ammoniacal Liquor	~100	—
Light Oil	<170	Benzene, C ₆ ; Toluene, C ₇ ; Xylene, C ₈
Middle Oil or Carbolic Oil	170-230	Naphthalene, C ₁₀
Heavy Oil or Creosote Oil	230-270	Naphthalene, C ₁₀
Green Oil or Anthracene Oil	270-360	Anthracene, C ₁₄
Residue or Pitch	>360	—

[0053] In particular, low-temperature tar and light oils formed from sub-bituminous and bituminous coals at temperatures below about 700° C. as relatively fluid, dark brown oils that comprise phenols, pyridines, paraffins, and/or olefins. The oils are heterogeneous, with any one component constituting only a fraction of a percent of the total mass. The lignite tars may also contain up to 10% of paraffin waxes, so the product has a “butter-like consistency” and solidifies at temperatures as high as 6° C. to 8° C. The primary high-temperature tar vapors formed above 700° C. are more homogeneous. The light oils are predominantly benzene, toluene, and xylenes (BTX) and the tars are bitumen-like viscous mixtures that contain high proportions of polycondensed aromatics. For the most part, the pyrolysis tars and oils are not suitable final fuel products. Often they are unstable, and when warmed, they polymerize and become more viscous. Ash and mineral matter **130** is removed in pyrolysis **120**, which increases the heating value, but sulfur and nitrogen are not

completely removed in pyrolysis **120**. A more stable and useful product is obtained by hydrogenating **160** and removing the sulfur and/or nitrogen from the fuel as hydrogen sulfide and/or ammonia in stream(s) **170**. These procedures are, as noted previously, similar to the various refinery procedures used to upgrade natural crude oils. The hydrotreated liquid products **190** may be further refined and upgraded, by any methods known to one of skill in the art, to yield a mix of cycloalkanes and aromatics of which the C/A blendstock is comprised.

[0054] In embodiments, the I/N-C/A fuel comprises about 20 vol. % C/A blendstock derived from pyrolysis processing of a coal tar fraction. In embodiments, the I/N-C/A fuel comprises about 80 vol. % I/N blendstock derived from Fischer-Tropsch processing of natural gas, coal, and/or biomass, and about 20 vol. % C/A blendstock derived from pyrolysis processing of coal tar fraction. In embodiments, I/N-C/A fuel comprises about 30 vol. % C/A blendstock derived from pyrolysis processing of a high cycloparaffin-content material derived from oil shale or oil sand feedstock. In embodiments, I/N-C/A fuel comprises about 70 vol. % I/N blendstock derived from catalytic processing of triglyceride feedstock and about 30 vol. % C/A blendstock derived from pyrolysis processing of a high cycloparaffin-content material derived from an oil shale or oil sand feedstock.

[0055] In another embodiment of the invention, shown in FIG. 3, direct liquefaction **220** of liquefaction feedstock **210** is used to produce C/A blendstock. Liquefaction feedstock **210** may comprise, for example, coal and/or biomass. There are two basic procedures: hydroliquefaction and solvent extraction. In hydroliquefaction, coal **210** is mixed with recycled coal oil **230** and, together with hydrogen **240**, fed to high-pressure catalytic reactor **220** where hydrogenation of coal **210** takes place. In solvent extraction, also termed "solvent refining," coal **210** and hydrogen **240** are dissolved at high pressure in a recycled coal-derived solvent **230** which transfers hydrogen **240** to coal **210**. After phase separation **260**, wherein gases **270** and ash **280** may be removed from coal liquid **250** which may be further cleaned and upgraded by refinery procedures, liquid fuels **290** are produced. In solvent refining, with a low level of hydrogen transfer, a solid, relatively clean fuel termed "solvent refined coal" **290** is obtained. As in pyrolysis, the compounds are similar to the coal tars and highly aromatic in nature. Hydrogenation and selective catalytic processing, as known to one of skill in the art, may be performed to yield a mix of cycloalkanes and aromatics that provide the C/A blendstock.

[0056] In embodiments, the I/N-C/A fuel comprises about 20 vol. % C/A blendstock derived from direct liquefaction of a coal feedstock. In embodiments, the I/N-C/A fuel comprises about 80 vol. % I/N blendstock derived from Fischer-Tropsch processing of natural gas, coal, and/or biomass, and about 20 vol. % C/A blendstock derived from direct liquefaction of a coal feedstock.

[0057] In an embodiment, C/A blendstock comprises cycloalkanes obtained by separation (e.g., via distillation or extraction) of cycloalkanes selected from the group consisting of C9-C15 cycloalkanes from petroleum feedstocks. In embodiments, C/A blendstock comprises aromatic compounds obtained by separation (e.g., via distillation or extraction) of aromatic compounds selected from the group consisting of C9-C15 single-ring aromatic compounds from

petroleum feedstocks. Suitable petroleum feedstocks comprise oil sand- and/or oil shale-derived products that are inherently rich in cycloalkanes.

[0058] In an embodiment, C/A blendstock is produced by catalytic cyclization and/or reforming of I/N blendstock prepared from triglyceride and/or fatty acid feedstocks as disclosed hereinabove. In this embodiment, I/N blendstock may be produced via: (1) catalytic triglyceride dissociation into fatty acids and glycerol, (2) glycerol removal, (3) oxygen removal from fatty acids (via catalytic decarboxylation and/or reduction) to yield normal paraffins, and, to the extent desired, (4) catalytic isomerization of a portion of these normal paraffins to yield isoparaffins. In embodiments, I/N-C/A fuel comprises about 35 vol. % C/A blendstock derived from catalytic processing of triglyceride feedstock. In embodiments, I/N-C/A fuel comprises about 65 vol. % I/N blendstock derived from catalytic processing of triglyceride feedstock and about 35 vol. % C/A blendstock derived from catalytic processing of triglyceride feedstock.

[0059] In another embodiment of the invention, C/A blendstock is produced from biomass-derived lignin feedstock. C/A blendstock may be produced via catalytic depolymerization of biomass-derived lignin feedstock followed by hydroprocessing as required to yield a desired proportion (for example, JP-8-quality) of cycloalkanes and aromatics. In embodiments, the I/N-C/A fuel comprises about 20 vol. % C/A blendstock derived from pyrolysis of biomass-derived lignin. In alternative embodiments, I/N-C/A fuel comprises about 15 vol. % C/A blendstock derived from catalytic processing of lignin. In embodiments, I/N-C/A fuel comprises about 80 vol. % I/N blendstock derived from Fischer-Tropsch processing of natural gas, coal, and/or biomass, and about 20 vol. % C/A blendstock derived from pyrolysis processing of biomass-derived lignin. In embodiments, I/N-C/A fuel comprises about 85 vol. % I/N blendstock derived from catalytic processing of triglyceride feedstock and about 15 vol. % C/A blendstock derived from catalytic processing of lignin.

V. I/N-C/A Fuel

[0060] A finished I/N-C/A fuel may have "drop-in compatibility" with its petroleum-derived counterpart, i.e. the I/N-C/A fuel may be blended in any proportion, from 0 vol. % to 100 vol. % with a petroleum-derived counterpart. The disclosed I/N-C/A fuel provides for the blending of fuel components (including isoparaffins, normal paraffins, cycloalkanes, and/or aromatics), at least two of which are derived from disparate processes, to create UN-C/A fuel. In embodiments, at least 50 weight percent of an aviation-grade UN-C/A kerosene fuel is derived from coal, natural gas, or a combination thereof. In embodiments, at least 50 weight percent of an I/N-C/A fuel is derived from biomass. In embodiments, at least 10 weight percent of an I/N-C/A fuel is derived from non-cracked bio-oil. In embodiments, UN-C/A fuel has a cetane number of greater than about 70.

[0061] In embodiments, the I/N-C/A fuel complies with specifications for Jet A and/or another civilian jet fuel. In embodiments, the I/N-C/A fuel complies with a military jet fuel specification selected from JP-8 and other military-grade jet fuel specifications.

[0062] In addition to meeting fuel property and performance requirements listed in U.S. military and ASTM (American Society for Testing and Materials) International aviation jet fuel specifications, in embodiments, an I/N-C/A-blended fuel will also meet applicable U.S. military-specified fit-for-purpose requirements that address a variety of fuel performance and materials compatibility issues. As mentioned hereinabove, fit-for-purpose requirements refers to fuel property requirements that are not necessarily addressed by military or ASTM standards, but are important to fuel performance and stability in jet engines and during fuel handling, distribution, and storage. Examples of fit-for-purpose requirements include fuel compatibility with aircraft fuel and engine system materials of construction, adequate fuel performance in compression ignition (versus turbine) engines in a wide variety of ground environments, and possible fuel performance requirements related to swelling of elastomeric seals in, for example, turbine engines. These fit for purpose requirements, in addition to feedstock properties and ASTM standards are used to determine the optimal ratio of the I/N blendstock to the C/A blendstock.

VI. EXAMPLES

Example 1

Fuel Sample A

[0063] A FT fuel produced from natural gas and containing iso-paraffinic and normal paraffin hydrocarbons did not comply with density requirement of the JP-8 military specification (MIL-DTL-83133E). In this example, a mixture of aromatic hydrocarbon fluid containing aromatic hydrocarbons ranging in carbon chain length from 8-16, was blended to a concentration of 23% by weight with the FT fuel. A summary

TABLE 4-continued

Results from Jet Fuel Specification Tests of Fuel Sample A Comprising Blend of Aromatic Hydrocarbon and Fischer-Tropsch Derived Fuel		
Specification Test	Sample A	Military Spec
Sulfur, mass %	0.0	0.30 max
Heat of Combustion, Btu/lb	18500	18400
Distillation:		
10% recovered, ° C.	172	205 max
Endpoint, ° C.	274	300 max
Residue, vol %	1.4	1.5 max
Loss, vol %	0.4	1.5 max
Flash Point, ° C.	48	>38
Freeze Point, ° C.	-57	-47 max
Hydrogen Content, mass %	14.0	13.4 min
API Gravity @ 60° F.	48.2	37.0-51.0
Specific Gravity @ 15° C., g/mL	0.787	0.775-0.84

[0064] As seen in the data presented in Table 2, the resulting fuel had a density of 0.788 g/mL achieving the minimum specification requirement of 0.775 g/mL as defined by MIL-DTL-83133E while complying with all of the parameters contained within the specification. Data from gas chromatography of Sample A and a typical FT fuel is provided in FIG. 4.

Example 2

Fuel Sample B

[0065] The same FT fuel as used in Example 1 was blended at 82% wt. with 8% wt. of a mixed aromatic fluid and 10% wt. cycloparaffinic fluid. A summary of Fuel Sample B results from key specification parameters is provided in Table 5.

TABLE 5

Results for Key Jet Fuel Specification Tests of Fuel Sample B Comprising Blend of Aromatic and Cycloparaffin Hydrocarbons with Fischer-Tropsch Derived Fuel				
	Specific Gravity, g/mL	Freeze Point, ° C.	Flash Point, ° C.	HHV, MJ/kg
Mil Spec	0.775-0.84	-47	>38 C.	>42.8
Sample B	0.779	-61.4	48	46.1
FT Fuel	0.755	-56.7	48	46.6

of results from Fuel Sample A compared to specification requirements outlined in MIL-DTL-83133E is provided in Table 4.

TABLE 4

Results from Jet Fuel Specification Tests of Fuel Sample A Comprising Blend of Aromatic Hydrocarbon and Fischer-Tropsch Derived Fuel		
Specification Test	Sample A	Military Spec
Acid Number, mg KOH/gm	0.003	0.015 max
Aromatics, vol %	19.4	25 vol % max
Olefins, vol %	0.0	5 vol % max

Example 3

Fuel Sample C

[0067] Two hydrocarbon blendstocks, one consisting of normal- and iso-paraffinic hydrocarbon and the second consisting of a mixture of aromatic and cycloparaffinic hydrocarbons, were produced exclusively from crop oil and blended to achieve a fuel sample complying with the requirements of MIL-DTL-83133E. In this example, neither fuel blendstock possessed, on its own, the physical characteristics required by the specification; however, through blending at a ratio of 44%

normal and iso-paraffinic blendstock, and 66% aromatic and cycloparaffinic blendstock, the resulting fuel achieved the necessary characteristics. A summary of results from Fuel Sample C compared to specification parameters outlined in MIL-DTL-83133E is provided in Table 6. Data from gas chromatography of Sample C and a typical JP-8 fuel is provided in FIG. 5.

TABLE 6

Results from Jet Fuel Specification Tests of Fuel Sample C Comprising a Blend of Two Discrete Hydrocarbon Blendstocks Produced from Crop Oil		
Specification Test	Sample C	Military Spec
Aromatics, vol %	19.8	25 vol % max
Olefins, vol %	1.9	5 vol % max
Heat of Combustion, Btu/lb	18400	18400
Distillation:		
10% recovered, ° C.	171	205 max
Endpoint, ° C.	255	300 max
Residue, vol %	1.2	1.5 max
Loss, vol %	0.4	1.5 max
Flash Point, ° C.	49	>38
Freeze Point, ° C.	-52	-47 max
API Gravity @ 60° F.	44.3	37.0-51.0
Specific Gravity @ 15° C., g/mL	0.805	0.775-0.84

[0068] While preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the disclosure. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). Use of the term “optionally” with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0069] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the preferred embodiments of the present invention. The discussion of a reference is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent they provide exemplary, procedural or other details supplementary to those set forth herein.

What is claimed is:

1. Aviation-grade kerosene comprising:

a first blendstock derived from non-petroleum feedstock and comprising primarily hydrocarbons selected from the group consisting of isoparaffins and normal paraffins; and

a second blendstock comprising primarily hydrocarbons selected from the group consisting of cycloalkanes and aromatics.

2. The aviation-grade kerosene of claim 1 wherein the second blendstock is derived from feedstock comprising non-petroleum feedstock.

3. The aviation-grade kerosene of claim 1 that is capable of being blended with petroleum-derived jet fuel in any proportion such that the resulting blend meets fuel grade specification of the petroleum-derived jet fuel.

4. The aviation-grade kerosene of claim 3 comprising up to 95 volume percent of first blendstock and up to 35 volume percent of second blendstock.

5. The aviation-grade kerosene of claim 4, comprising up to 95 volume percent first blendstock, from about 0 volume percent to about 30 volume percent cycloalkanes, and from about 0 volume percent to about 15 volume percent aromatics.

6. The aviation-grade kerosene as in claim 5 wherein fit-for-purpose requirements are met.

7. The aviation-grade kerosene of claim 6 wherein at least 50 weight percent of the kerosene is derived from coal, natural gas, or a combination thereof.

8. The aviation-grade kerosene of claim 6 wherein the second blendstock is derived from coal, biomass, oil-shale, tar, oil sands, or a combination thereof.

9. The aviation-grade kerosene of claim 6 wherein at least 50 weight percent of the kerosene is derived from biomass.

10. The aviation-grade kerosene of claim 1 wherein at least 10 weight percent of the kerosene is derived from non-cracked bio-oil.

11. The aviation-grade kerosene of claim 1 having a specific density in the range of from about 0.775 g/mL to about 0.84 g/mL.

12. The aviation-grade kerosene of claim 11 having a freeze point below -47° C.

13. The aviation-grade kerosene of claim 12 having a flash point of greater than 38° C.

14. The aviation-grade kerosene of claim 1 having a cetane number of greater than about 70.

15. The aviation-grade kerosene of claim 1 wherein the non-petroleum feedstock is selected from the group consisting of coal, natural gas, biomass, vegetable oils, biomass pyrolysis bio-oils, biologically-derived oils and combinations thereof.

16. The aviation-grade kerosene of claim 1 wherein the non-petroleum feedstock comprises at least one component selected from the group consisting of triglycerides and fatty acids.

17. The aviation-grade kerosene of claim 16 comprising from about 65 volume percent to about 95 volume percent first blendstock.

18. The aviation-grade kerosene of claim 17 wherein the second blendstock comprises pyrolysis products derived from pyrolysis of a second feedstock comprising at least one component selected from the group consisting of high-cycloalkane content oil shales and oil sands.

19. The aviation-grade kerosene of claim 17 wherein the non-petroleum feedstock comprises at least one component selected from the group consisting of triglycerides and fatty

acids and wherein at least a portion of the second blendstock is produced by subjecting a portion of the non-petroleum feedstock to cyclization, reforming, or both.

20. The aviation-grade kerosene of claim **19** wherein the kerosene comprises about 65 volume percent first blendstock and about 35 volume percent second blendstock.

21. The aviation-grade kerosene of claim **1** wherein the non-petroleum feedstock comprises at least one component selected from the group consisting of natural gas, coal, and biomass and wherein the first blendstock comprises at least one Fischer-Tropsch conversion product thereof.

22. The aviation-grade kerosene of claim **1** wherein the second blendstock comprises at least one product of pyrolysis of a feedstock selected from the group consisting of coal, oil shale, oil sands, tar, biomass and combinations thereof.

23. The aviation-grade kerosene of claim **1** wherein the second blendstock comprises at least one product of pyrolysis of biomass-derived lignin.

24. The aviation-grade kerosene of claim **23** comprising from about 15 volume percent to about 30 volume percent of the second blendstock.

25. The aviation-grade kerosene of claim **23** wherein the first blendstock comprises at least one catalytic processing product of a component selected from the group consisting of triglycerides and fatty acids.

26. The aviation-grade kerosene of claim **23** wherein the non-petroleum feedstock comprises at least one component selected from the group consisting of natural gas, coal and biomass and wherein the first blendstock comprises at least one Fischer-Tropsch conversion product thereof.

27. The aviation-grade kerosene of claim **1** comprising about 95 volume percent of the first blendstock and about 5 volume percent of the second blendstock, wherein the second blendstock comprises primarily high density, low freeze point aromatics.

28. The aviation-grade kerosene of claim **1** comprising at least 50 weight percent of hydrocarbons selected from cycloalkanes and aromatics, said hydrocarbons derived from coal, biomass, or a combination thereof.

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