

FUEL PRODUCTION FROM FEEDSTOCK
CONTAINING LIPIDIC MATERIAL

FIELD OF THE INVENTION

[0001] This invention relates to the production of a fuel composition from a feedstock that includes a lipidic material. More particularly, this invention relates to the production of a dewaxed and/or hydroisomerized fuel composition that includes a step of hydrotreating a feedstock containing the lipidic material.

BACKGROUND OF THE INVENTION

[0002] Rising costs and threats of shortages and supply interruptions have recently highlighted the need for alternative fuel sources to petroleum-based products. Biofuels have particularly been a focus for alternative fuels.

[0003] U.S. Patent Publication No. 2009/0158637 discloses a process for producing aviation fuel from renewable feedstocks. The feedstocks include plant oils and animal fats and oils. The process involves treating a renewable feedstock by hydrogenating and deoxygenating to provide n-paraffins having from about 8 to about 24 carbon atoms. At least some of the n-paraffins are isomerized to improve cold flow properties. At least a portion of the paraffins are selectively cracked to provide paraffins meeting specifications for different aviation fuels such as JP-8.

[0004] U.S. Patent Publication No. 2009/0088351 discloses a method for processing triglyceride-containing, biologically-derived oils to produce lubricants and transportation fuels. The method comprises converting triglycerides to free fatty acids and the separating the fatty acids by saturation type. Such separation by type enables the preparation of both lubricants and transportation fuels.

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[0005] U.S. Patent Publication No. 2008/0244962 discloses a method for producing an isoparaffinic product useful as jet fuel from a renewable feedstock. The method also includes co-producing a jet fuel and a liquefied petroleum gas (LPG) fraction from a renewable feedstock. The method includes hydrotreating the renewable feedstock to produce a hydrotreating unit heavy fraction that includes n-paraffins and hydroisomerizing the hydrotreating unit heavy fraction to produce a hydroisomerizing unit heavy fraction that includes isoparaffins. The method also includes recycling the hydroisomerizing unit heavy fraction through the hydroisomerization unit to produce an isoparaffinic product that may be fractionated into a jet fuel and an LPG fraction. The produced product is a jet fuel produced from a renewable feedstock having specified cold flow properties.

[0006] There are particular problems associated with producing fuels from any variety of renewable feedstocks. In particular, in the manufacture and recovery of jet fuel and diesel fuel, various desirable characteristics of the fuels. In the case of jet fuel such desirable characteristics of freeze point and smoke point are especially difficult to achieve. Accordingly, there is desired a process in which renewable type feedstocks can be effectively used to make high quality fuels.

SUMMARY OF THE INVENTION

[0007] This invention produces high quality fuel from sources that are considered renewable feedstocks. The process is specifically directed to producing a fuel composition from a lipidic biomass.

[0008] According to one aspect of the invention, there is provided a method for producing a dewaxed and/or hydroisomerized fuel composition. A feedstock is prepared or provided in which the feedstock contains lipidic biomass. Preferably, the feedstock further comprises mineral oil. The feedstock can be hydrotreated to produce a hydrotreated material. At least a

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portion of the hydrotreated material can then be only dewaxed to produce a dewaxed fuel composition, only hydroisomerized to produce a hydroisomerized fuel composition, or both dewaxed and hydroisomerized to produce a dewaxed and hydroisomerized fuel composition.

[0009] In one embodiment, at least a portion of the dewaxed and/or hydroisomerized fuel composition can be recovered as jet fuel or diesel fuel, *e.g.*, following distillation. In a particular embodiment, the recovered fuel composition can exhibit one or more of the following properties: a smoke point of at least 25.0 mm; a freeze point of not higher than -35°C; an ASTM D86 90% distillation point within the range of from 250°C to 290°C; an ASTM D86 90% distillation point within the range of from 200°C to 240°C; and an ASTM D86 90% distillation point within the range of from 260°C to 350°C.

DETAILED DESCRIPTION OF THE INVENTION

[0010] This invention provides a process for producing high quality fuel compositions from a feedstock that includes a lipidic material. The process can advantageously result in the high quality fuels by aligning the appropriate type of feedstock composition with the appropriate type of processing steps. The fuel can tailored for a variety of end uses such as jet fuel or diesel fuel, and is particularly suited for use as jet fuel.

[0011] The feedstock that is used in this invention comprises lipidic biomass. In one embodiment, the feedstock comprises lipidic biomass and mineral oil. When the feedstock comprises both lipidic biomass and mineral oil, in one embodiment, the lipidic biomass can comprise from 5 wt% to 50 wt% of the feedstock, for example from 5 wt% to 35 wt%, from 5 wt% to 25 wt%, from 10 wt% to 40 wt%, from 10 wt% to 30 wt%, from 20 wt% to 40 wt%, from 25 wt% to 50 wt%, from 25 wt% to 40 wt%, or from 35 wt% to 50 wt%. When the feedstock comprises both lipidic

biomass and mineral oil, in another embodiment, the lipidic biomass can comprise from 50 wt% to 95 wt% of the feedstock, for example from 50 wt% to 85 wt%, from 50 wt% to 75 wt%, from 55 wt% to 85 wt%, from 60 wt% to 90 wt%, from 60 wt% to 75 wt%, from 70 wt% to 90 wt%, from 75 wt% to 95 wt%, or from 80 wt% to 95 wt%.

[0012] The term "lipidic biomass" as used according to the invention is a composition comprised of biological materials. Generally, these biological materials include vegetable fats/oils, animal fats/oils, fish oils, pyrolysis oils, and algae lipids/oils, as well as components of such materials. More specifically, the lipidic biomass includes one or more type of lipid compounds. Lipid compounds are typically biological compounds that are insoluble in water, but soluble in nonpolar (or fat) solvents. Non-limiting examples of such solvents include alcohols, ethers, chloroform, alkyl acetates, benzene, and combinations thereof.

[0013] Major classes of lipids include, but are not necessarily limited to, fatty acids, glycerol-derived lipids (including fats, oils and phospholipids), sphingosine-derived lipids (including ceramides, cerebroside, gangliosides, and sphingomyelins), steroids and their derivatives, terpenes and their derivatives, fat-soluble vitamins, certain aromatic compounds, and long-chain alcohols and waxes.

[0014] In living organisms, lipids generally serve as the basis for cell membranes and as a form of fuel storage. Lipids can also be found conjugated with proteins or carbohydrates, such as in the form of lipoproteins and lipopolysaccharides.

[0015] Examples of vegetable oils that can be used in accordance with this invention include, but are not limited to rapeseed (canola) oil, soybean oil, coconut oil, sunflower oil, palm oil, palm kernel oil, peanut oil, linseed oil, tall oil, corn oil, castor oil, jatropha oil, jojoba oil, olive oil, flaxseed oil,

camelina oil, safflower oil, babassu oil, tallow oil and rice bran oil. In the processes of the present invention, coconut, palm, palm kernel and babassu oils are preferred.

[0016] Vegetable oils as referred to herein can also include processed vegetable oil material. Non-limiting examples of processed vegetable oil material include fatty acids and fatty acid alkyl esters. Alkyl esters typically include C₁-C₅ alkyl esters. One or more of methyl, ethyl and propyl esters are preferred.

[0017] Examples of animal fats that can be used in accordance with the invention include, but are not limited to, beef fat (tallow), hog fat (lard), turkey fat, fish fat/oil, and chicken fat. The animal fats can be obtained from any suitable source including restaurants and meat production facilities.

[0018] Animal fats as referred to herein also include processed animal fat material. Non-limiting examples of processed animal fat material include fatty acids and fatty acid alkyl esters. Alkyl esters typically include C₁-C₅ alkyl esters. One or more of methyl, ethyl and propyl esters are preferred.

[0019] Algae oils or lipids are typically contained in algae in the form of membrane components, storage products and metabolites. Certain algal strains, particularly microalgae such as diatoms and cyanobacteria, contain proportionally high levels of lipids. Preferably, algal sources for the algae oils contain from 2 wt% to 40 wt% of lipids, based on total weight of the biomass itself.

[0020] Algal sources for algae oils include, but are not limited to, unicellular and multicellular algae. Examples of such algae include a rhodophyte, chlorophyte, heterokontophyte, tribophyte, glaucophyte,

chlorarachniophyte, euglenoid, haptophyte, cryptomonad, dinoflagellum, phytoplankton, and the like, and combinations thereof. Preferred are algae of the class Chlorophyceae and/or Haptophyta. Specific species include, but are not limited to, *Neochloris oleoabundans*, *Scenedesmus dimorphus*, *Euglena gracilis*, *Phaeodactylum tricornutum*, *Pleurochrysis carterae*, *Prymnesium parvum* and *Tetraselmis chui*, *Chlamydomonas reinhardtii*.

[0021] In one embodiment, the feedstock is comprised of lipidic biomass in which the lipidic biomass has a total triglyceride content of at least 2 wt%, based on total weight of the lipidic biomass included in the feedstock. Preferably, the feedstock is comprised of lipidic biomass in which the lipidic biomass has a total triglyceride content of at least 10 wt %, for example at least 40 wt % or at least 60 wt %, based on total weight of the lipidic biomass included in the feedstock.

[0022] Types of triglycerides can be determined according to the fatty acid constituents. The fatty acid constituents can be readily determined using Gas Chromatography (GC) analysis. This analysis involves extracting the fat or oil, saponifying (hydrolyzing) the fat or oil, preparing an alkyl (*e.g.*, methyl) ester of the saponified fat or oil, and determining the type of (methyl) ester using GC analysis.

[0023] In one embodiment of the invention, a majority of triglyceride present in the lipidic biomass is comprised of C₈ to C₁₈ fatty acids, based on total weight of triglyceride present in the lipidic biomass. For clarity, when a fatty acid or fatty acid ester molecule is specified as a “C_{xx}” fatty acid or fatty acid ester, what is meant is that “xx” is the number of carbons on the carbon side of the carboxylate linkage, *i.e.*, including the carboxylate carbon, whereas, in fatty acid esters, the ester carbons are not included in the “C_{xx}” and are the carbons on the oxygen side of the carboxylate linkage, *i.e.*, stopping at the carboxylate oxygen. Further, a triglyceride is a

molecule having a structure identical to the reaction product of glycerol and three fatty acids. Thus, although a triglyceride is described herein as being comprised of fatty acids, it should be understood that the fatty acid component does not necessarily contain an carboxylic acid hydrogen. In the processes of the present invention, a majority of triglyceride present in the lipidic biomass is preferably comprised of C₁₀ to C₁₆, for example C₁₂ to C₁₄ fatty acids, based on total weight of triglyceride present in the lipidic biomass.

[0024] In another embodiment of the invention, at least 60 wt% of triglyceride present in the lipidic biomass is comprised of C₈ to C₁₈ fatty acids, based on total weight of triglyceride present in the lipidic biomass. Preferably, at least 60 wt% of triglyceride present in the lipidic biomass is comprised of C₁₀ to C₁₆, for example at least 60 wt% of triglyceride present in the lipidic biomass is comprised of C₁₂ to C₁₄ fatty acids, based on total weight of triglyceride present in the lipidic biomass.

[0025] In another embodiment of the invention, at least 80 wt% of triglyceride present in the lipidic biomass is comprised of C₈ to C₁₈ fatty acids, based on total weight of triglyceride present in the lipidic biomass. Preferably, at least 80 wt% of triglyceride present in the lipidic biomass is comprised of C₁₀ to C₁₆, for example at least 80 wt% of triglyceride present in the lipidic biomass is comprised of C₁₂ to C₁₄ fatty acids, based on total weight of triglyceride present in the lipidic biomass.

[0026] In a particular embodiment, the feedstock comprises triglyceride, with the triglyceride comprising lauric acid (C 12:0). Using the notation "C xx:yy" indicates a compound having "xx" carbons on the main chain, *i.e.*, on the carbon side of the carboxylate group including the carboxylate carbon, and having "yy" unsaturations (double bonds) on the main chain. Preferably, the triglyceride is comprised of 40% to 60% lauric

acid constituents, for example from 42% to 58% or from 44% to 55% lauric acid constituents. Unless otherwise unambiguously specified, percentages expressed herein are percentages based on a number total of elements or constituents.

[0027] In another embodiment, the feedstock comprises triglyceride, with the triglyceride comprising myristic acid (C 14:0). Preferably, the triglyceride is comprised of 10% to 28% myristic acid constituents, for example from 12% to 26% or from 14% to 24% myristic acid constituents.

[0028] In yet another embodiment of the invention, the lipidic biomass present in the feedstock is comprised of at least 20 wt% fatty acid alkyl esters (*e.g.*, methyl or ethyl, corresponding to FAME or FAEE, respectively, based on total weight of the lipidic biomass. Preferably, the fatty acid alkyl ester is a composition that includes at least one fatty acid alkyl ester in which the fatty acid constituent component is selected from the group consisting of capric acid (C 10:0), lauric acid (C 12:0), myristic acid (C 14:0), palmitic acid (C 16:0) and stearic acid (C 18:0). More preferably, the lipidic biomass present in the feedstock is comprised of at least 30 wt%, for example at least 40 wt%, of the fatty acid alkyl esters such as FAME, based on total weight of the lipidic biomass.

[0029] The lipidic biomass portion of the feedstock used in this invention can include at least one terpene. Terpenes are considered a class of biosynthetic hydrocarbons comprising multiple units of isoprene (2-methyl-1,3-butadiene), which is a five-carbon hydrocarbon. The isoprene units can be linked together to form an acyclic (including branched or linearly arranged carbon atoms) or cyclic framework.

[0030] Non-limiting examples of terpenes include hemiterpenes, which consist of one isoprene unit (for example, isoprene); monoterpenes, which consist of two isoprene residues (for example, limonene and myrcene);

sesquiterpenes, which consist of three isoprene residues and include, but are not limited to, acyclic sesquiterpenes (for example, farnesene) and cyclic sesquiterpenes (for example, cuparene, curcumene, zingiberene, and bisabolene); diterpenes, which consist of four isoprene residues (for example, cembrene and taxadiene); triterpenes, which consist of six isoprene residues (for example, squalene); tetraterpenes, which consist of eight isoprene residues (for example, carotene, acyclic lycopene, monocyclic gamma-carotene, and bicyclic alpha- and beta-carotenes).

Terpenes particularly suitable for use as a feedstock or feedstock component include at least one compound selected from the group consisting of isoprene, myrcene, ocimene, limonene, terpinolene, phellandrene, farnesene, cuparene, cuprenene, isobazzanene, sesquiphellandrene, abisabolene, curcumene, zingiberene and barbatene.

[0031] In one embodiment of the invention, the feedstock can include at least 5 wt% terpenes, based on total weight of the lipidic biomass. For instance, the feedstock can include at least 10 wt%, *e.g.*, at least 20 wt% or at least 30 wt% terpenes, based on total weight of the lipidic biomass.

[0032] The feedstock, in one embodiment, comprises lipidic biomass having a saponification value particularly suited to forming jet fuel. The saponification value of a lipidic biomass such as an oil or fat is defined as the number of milligrams of potassium hydroxide required to neutralize the fatty acids resulting from the complete hydrolysis of 1 gram of the lipidic biomass sample. In one embodiment, the feedstock comprises lipidic biomass in which the lipidic biomass has a saponification value from 180 mg KOH/g oil to 300 mg KOH/g oil, for example from 200 mg KOH/g oil to 280 mg KOH/g oil or from 215 mg KOH/g oil to 270 mg KOH/g oil.

[0033] In one embodiment of the invention, the feedstock comprises lipidic biomass having an iodine value particularly suited to forming jet

fuel. The iodine value of a lipidic biomass such as an oil or fat is defined as the number of grams of iodine absorbed by 100 grams of the lipidic biomass sample. The iodine value is preferably determined according to standard method EN 14111 (2003):1. In one embodiment, the feedstock comprises lipidic biomass in which the lipidic biomass has an iodine value of not greater than 130, preferably not greater than 120, for example not greater than 110 or not greater than 100. In a particular embodiment, the feedstock comprises lipidic biomass in which the lipidic biomass has an iodine value of from 1 to 130, preferably from 1 to 120, for example from 1 to 100.

[0034] The process of this invention can advantageously be performed without having to convert any substantial quantity of lipid by pretreatment prior to hydrotreating. For example, the process is beneficial in that it is not necessary to convert triglycerides to free fatty acids or ultimately to esters of free fatty acids such as FAME by such techniques as transesterification. A particular benefit of this embodiment is that the feedstock can include a limited amount of glycerol, which can be considered an undesirable by-product from the transesterification process.

[0035] In one embodiment, the feedstock of the invention comprises not greater than 10 wt% glycerol, based on total weight of the feedstock. In a preferred embodiment, the feedstock of the invention comprises not greater than 5 wt%, for example not greater than 3 wt% or not greater than 2 wt% glycerol, based on total weight of the feedstock.

[0036] In one embodiment, the feedstock can include at least 0.05 wt% lipidic biomass, based on total weight of the feedstock. In a preferred embodiment, the feedstock includes at least 0.5 wt%, for example at least 1 wt%, at least 2 wt%, or at least 4 wt% lipidic biomass, based on total weight of the feedstock.

[0037] Additionally or alternately, the feedstock can include not more than 90 wt% lipidic biomass, based on total weight of the feedstock. In a preferred embodiment, the feedstock includes not more than 60 wt%, for example not more than 40 wt% or not more than 20 wt% lipidic biomass, based on total weight of the feedstock.

[0038] The feedstock used in this invention can further comprise a mineral oil. Examples of mineral oils can include, but are not limited to, straight run (atmospheric) gas oils, vacuum gas oils, demetallized oils, coker distillates, cat cracker distillates, heavy naphthas (optionally but preferably at least partially denitrogenated and/or at least partially desulfurized), diesel boiling range distillate fraction (optionally but preferably at least partially denitrogenated and/or at least partially desulfurized), jet fuel boiling range distillate fraction (optionally but preferably at least partially denitrogenated and/or at least partially desulfurized), kerosene boiling range distillate fraction (optionally but preferably at least partially denitrogenated and/or at least partially desulfurized), and coal liquids. Preferably, the feedstock does not contain any appreciable asphaltenes. In one embodiment, the mineral oil can be mixed with the lipidic biomass and then hydrotreated to form a hydrotreated material. In another embodiment, the mineral oil can be hydrotreated to reduce the nitrogen and/or sulfur content before being mixed with the lipidic biomass.

[0039] The mineral oil component can contain nitrogen-containing compounds (abbreviated as “nitrogen”). Such nitrogen can typically be present as organonitrogen compounds and typically in amounts from 1 wppm to 1.0 wt%, based on total weight of the mineral oil component.

[0040] The mineral oil will typically contain sulfur-containing compounds (abbreviated as “sulfur”). Such sulfur can typically be present

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in the mineral oil as organosulfur compounds and, in untreated mineral oils, typically in amounts from greater than 0.15 wt%, based on total weight of the mineral oil.

[0041] In one embodiment, the feedstock can include not greater than 99 wt% mineral oil, based on total weight of the feedstock. Preferably, the feedstock can include not greater than 98 wt%, for example not greater than 95 wt%, not greater than 90 wt%, or not greater than 80 wt% mineral oil, based on total weight of the feedstock.

[0042] Additionally or alternately, the feedstock can include at least 5 wt% mineral oil, based on total weight of the feedstock. In one embodiment, the feedstock can include at least 10 wt%, for example at least 20 wt%, at least 30 wt%, or at least 40 wt% mineral oil, based on total weight of the feedstock.

[0043] According to one aspect of the invention, the feedstock can have a boiling range less than that of typical vacuum gas oil. The basic test method of determining the boiling range of such feedstock, as well as the fuel compositions produced according to this invention, can be by performing batch distillation according to ASTM D86-09e1, Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure.

[0044] In one embodiment, the feedstock can have an initial boiling point of at least 100°C, preferably at least 150°C, for example at least 180°C or at least 200°C.

[0045] Additionally or alternately, the feedstock can have a final boiling point of not greater than 500°C, preferably not greater than 450°C, for example not greater than 400°C.

[0046] The process of this invention includes a step of hydrotreating the feedstock to produce a hydrotreated material. Hydrotreating refers to a

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process in which a feed to be hydrotreated and a hydrogen-containing treat gas are contacted optionally but preferably in the presence of one or more hydrotreating catalysts.

[0047] In one embodiment, the hydrotreating catalyst can comprise a hydrotreating catalyst effective for removing various metal contaminants, such as arsenic, nickel, and vanadium. In another embodiment, the hydrotreating catalyst is also effective in removing heteroatoms, such as sulfur, and nitrogen. In yet another embodiment, the hydrotreating catalyst is further effective in saturating aromatics and other unsaturates with hydrogen. Generally, in hydrotreating operations cracking of the hydrocarbon molecules in the feedstock, *i.e.*, breaking the larger hydrocarbon molecules into smaller hydrocarbon molecules, is minimized, and the unsaturated hydrocarbons are either fully or partially hydrogenated.

[0048] Any catalyst capable of effectively hydrotreating feedstock can be used. Non-limiting examples include catalysts comprising a Group VIB metal and/or a Group VIII metal, optionally on a support. Suitable metals can include cobalt, nickel, iron, molybdenum, tungsten, and combinations thereof. Suitable supports can include relatively high specific surface area metal oxides such as silica, silica-alumina, alumina, and titania. While one preferred embodiment includes a catalyst comprising a Group VIB metal and a Group VIII metal (*e.g.*, in oxide form, or preferably after the oxide form has been sulfidized under appropriate sulfidization conditions), optionally on a support, the catalyst may additionally or alternately contain additional components, such as other transition metals (*e.g.*, Group V metals such as niobium), rare earth metals, organic ligands (*e.g.*, as added or as precursors left over from oxidation and/or sulfidization steps), phosphorus compounds, boron compounds, fluorine-containing compounds, silicon-containing compounds, promoters, binders, fillers, or like agents, or combinations thereof. The Groups referred to herein refer to Groups of the

CAS Version found in the Periodic Table of the Elements in Hawley's Condensed Chemical Dictionary, 13th Edition. By way of illustration, suitable Group VIII/VIB catalysts are described, for example, in one or more of U.S. Patent Nos. 6,156,695, 6,162,350, 6,299,760, 6,582,590, 6,712,955, 6,783,663, 6,863,803, 6,929,738, 7,229,548, 7,288,182, 7,410,924, and 7,544,632, U.S. Patent Application Publication Nos. 2005/0277545, 2006/0060502, 2007/0084754, and 2008/0132407, and International Publication Nos. WO 04/007646, WO 2007/084437, WO 2007/084438, WO 2007/084439, and WO 2007/084471, *inter alia*.

[0049] Other suitable hydrotreating catalysts can include zeolitic catalysts, as well as noble metal catalysts, *e.g.*, wherein the noble metal is selected from Pd, Pt, and a combination thereof. In one embodiment of the invention, more than one type of hydrotreating catalyst may be used in the same reaction stage or zone. Additionally or alternately, there may be only one hydrotreating reaction stage or zone, or there may be multiple (*e.g.*, at least two).

[0050] Other hydrotreating catalysts that can be specifically used are those hydrotreating catalysts useful for saturating aromatics. Non-limiting examples of such catalysts include nickel, cobalt-molybdenum, nickel-molybdenum, nickel-tungsten and noble metal (*e.g.*, platinum and/or palladium) catalysts, with the noble metal catalysts being sulfur sensitive, but more selective for aromatics removal. Typical non-noble metal hydrotreating catalysts include, for example, Ni/Mo on alumina, Co/Mo on alumina, Co/Ni/Mo on alumina.

[0051] Hydrotreating is preferably carried out at an average reactor temperature of at least 40°C. In another preferred embodiment, hydrotreating is carried out at an average reactor temperature of not greater than 440°C. In a particular embodiment, hydrotreating is carried out within

a temperature range from 40°C to 440°C. More preferably, hydrotreating can be carried out at an average reactor temperature from 100°C to 425°C, for example from 125°C to 400°C.

[0052] It is also preferred to carry out hydrotreating at an average reactor pressure from 6.8 atm (100 psia, or 690 kPaa) to 204 atm (3000 psia, or 20.7 MPaa). In another preferable embodiment, hydrotreating can be carried out at an average reactor pressure from 13.6 atm (200 psia, or 1.4 MPaa) to 81.7 atm (1200 psia, or 8.3 MPaa).

[0053] Hydrotreating can also be effectively carried out at a liquid hourly space velocity (LHSV) from 0.3 V/V/Hr to 10 V/V/Hr. In one preferred embodiment, hydrotreating can be carried out at a LHSV from 1 hr⁻¹ to 5 hr⁻¹.

[0054] Preferably, hydrotreating can be carried out at a hydrogen treat gas rate in the range from 35.6 Nm³/m³ to 1780 Nm³/m³ (200 scf/bbl to 10000 scf/bbl). In another preferable embodiment, hydrotreating can be carried out at a hydrogen treat gas rate in the range from 90 Nm³/m³ to 890 Nm³/m³ (500 scf/bbl to 5000 scf/bbl).

[0055] According to one aspect of the invention, at least a portion of the hydrotreated material can be dewaxed. Dewaxing in this invention refers to catalytic dewaxing in which a heavier hydrocarbon reacts with hydrogen in the presence of a dewaxing catalyst at reaction conditions. The catalytic dewaxing process is, in essence, a type of hydrocracking process. Dewaxing is more particularly based on selective hydrocracking, typically of predominantly normal paraffins.

[0056] The dewaxing process can incorporate the use of a molecular sieve-based catalyst in which active hydrocracking sites are accessible to contact with the paraffin molecules, preferably excluding larger aromatic

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type compounds. The reactions conditions in dewaxing can preferably be effective to further improve the cold flow properties of the hydrotreated material, such as freeze point, cloud point, pour point, and/or cold filter plug point.

[0057] Any catalyst effective in dewaxing hydrocarbon can be used. In one embodiment, hydrotreating catalyst compositions that include one or more of Co, Ni, and Fe and include one or more of Mo and W, as well as Pt and Pd noble metals on an acidic support, can be effectively used in dewaxing. In another embodiment, the dewaxing catalyst can include an (acidic) oxide support or carrier. Non-limiting examples of such carrier can include silica, alumina, silica-alumina, and other shape selective molecular sieves. Preferably, the carrier can be combined with at least one catalytic component such as a silicoaluminophosphate (SAPO), titania, zirconia, vanadia, and other Group II, IV, V or VI oxides, ferrierite, mordenite, ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-22 (also known as theta one or TON), ZSM-48, SAPO-11, SAPO-36, SAPO-37, SAPO-40, and zeolite Y sieves such as ultra stable Y, and like. If stripping is not available prior to dewaxing and/or if the sulfur content of the hydrotreated and separated heavy fraction is high enough to result in dewaxing catalyst activity reduction or loss, zeolites containing framework transition metals having improved sulfur resistance (for example, in U.S. Patent Nos. 5,185,136, 5,185,137, and 5,185,138) may be employed.

[0058] The dewaxing can be carried out at reaction conditions including an average reaction temperature from 300°F (149°C) to 900°F (482°C). Preferably, dewaxing can be carried out at reaction conditions including an average reaction temperature from 550°F (289°C) to 800°F (427°C).

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[0059] Dewaxing can also be preferably carried out at an average reaction pressure from 27.2 atm (400 psia, or 2.8 MPaa) to 136 atm (2000 psia, or 13.8 MPaa).

[0060] The hydrogen containing treat gas rate in dewaxing can range from 300 scf/bbl ($53 \text{ Nm}^3/\text{m}^3$) to 5000 scf/bbl ($890 \text{ Nm}^3/\text{m}^3$). Preferably, the hydrogen containing treat gas rate can be from 2000 scf/bbl ($356 \text{ Nm}^3/\text{m}^3$) to 4000 scf/bbl ($712 \text{ Nm}^3/\text{m}^3$).

[0061] Liquid hourly space velocity in dewaxing, in volumes/volume/hour (V/V/Hr), can range from 0.1 to 10. Preferably liquid hourly space velocity can be from 1 V/V/Hr to 5 V/V/Hr.

[0062] According to another aspect of invention, at least a portion of the hydrotreated material can be hydroisomerized. In a preferred embodiment, at least a portion of the hydrotreated material is dewaxed to form a dewaxed fuel composition and then hydroisomerized to produce a dewaxed and hydroisomerized fuel composition.

[0063] The terms “hydroisomerize” and “hydroisomerization” as used in this invention refers to a catalytic process in which feed is contacted with catalyst in the presence of hydrogen and a substantial portion of waxy paraffinic compounds in the feed can be converted to non-waxy isoparaffinic compounds, while at the same time reducing and/or minimizing conversion of (normal) paraffins by cracking. The use of the hydroisomerization step can effectively increase the volume of the jet/diesel fuel formed in the overall process. In particular, the use of the hydroisomerization step can reduce the heavier portion of a feedstock by transforming that component into an additional volume of jet/diesel fuel.

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[0064] Hydroisomerization can be carried out using a catalyst such as a shape selective molecular sieve catalyst. Large pore crystalline molecular sieves or intermediate pore molecular sieves are particularly effective.

[0065] Large pore crystalline molecular sieves useful in the hydroisomerization step of this invention preferably have a Constraint Index of less than 2. Intermediate pore crystalline molecular sieves useful in the hydroisomerization step of this invention preferably have a Constraint Index of at least 2. The method by which the Constraint Index is determined is fully described in U.S. Patent No. 4,016,218, which is incorporated herein by reference.

[0066] In one embodiment, the molecular sieves used in the isomerization step of this invention have an alpha value of less than 100. The alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant = 0.016 sec^{-1}). The alpha test is described in U.S. Patent No. 3,354,078 and in *J. Catalysis*, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980), to which reference is made for a description of the test. The experimental conditions of the test used to determine the alpha values referred to in this specification include a constant temperature of 538°C and a variable flow rate as described in detail in *J. Catalysis*, 61, 395 (1980).

[0067] Non-limiting examples of large pore molecular sieve catalysts can include, but are not limited to, molecular sieves selected from the group consisting of zeolite beta, mordenite, zeolite Y, ZSM-20, ZSM-4 (omega), zeolite L, VPI-5, SAPO-37, MeAPO-37, AlPO-8, cloverite, and combinations thereof. Non-limiting examples of intermediate pore

molecular sieves can include, but are not limited to, ZSM-22, ZSM-23, ZSM-48, SAPO-11, SAPO-5, MeAPO-11, MeAPO-5, and combinations thereof; and an example of a non-intersecting two-dimensional intermediate pore molecular sieve is ZSM-35 (synthetic ferrierite).

[0068] Catalysts useful in the hydroisomerization step preferably contain a hydrogenation metal, which can be one or more noble metals, one or more non-noble metals, or a combination thereof. Suitable noble metals include Group VIII noble metals, such as platinum and other members of the platinum group, such as iridium, palladium, and rhodium, and combinations of these metals. Suitable non-noble metals include those of Groups VB, VIB, and (the non-noble metals of) VIII of the Periodic Table. Preferred non-noble metals include, but are not limited to, chromium, molybdenum, tungsten, cobalt, nickel, and combinations of these metals, including cobalt-molybdenum, nickel-tungsten, nickel-molybdenum, cobalt-nickel-molybdenum, nickel-molybdenum-tungsten, cobalt-molybdenum-tungsten, and cobalt-nickel-tungsten. The non-noble metals can be pre-sulfided prior to use by exposure to a sulfur-containing gas such as hydrogen sulfide at an elevated temperature to effect conversion (*e.g.*, of the oxide form) to the corresponding sulfide form of the metal.

[0069] The metal can be incorporated into the catalyst by any suitable method or combination of methods, such as by impregnation or ion exchange into the zeolite. The metal can be incorporated in the form of a cationic, anionic, or neutral complex. Cationic complexes of the type $\text{Pt}(\text{NH}_3)_4^{++}$ can be used for exchanging metals onto the zeolite. Anionic complexes such as the molybdate or metatungstate ions can also be useful for impregnating metals into the catalysts.

[0070] In one embodiment, the hydroisomerization catalyst can comprise a zeolite and a hydrogenation metal. In one preferred

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embodiment, the catalyst can comprise from 0.01 wt% to 20 wt%, for example from 0.1 wt% to 15 wt%, of hydrogenation metal, based on total weight of the catalyst.

[0071] The molecular sieve, in one embodiment, can include a binder (or matrix) material. Binder materials are preferably metal oxides. Non-limiting examples of metal oxide binders can include, but are not limited to, alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia-zirconia, and the like, and combinations thereof. In one embodiment, the catalysts are ZSM-23, ZSM-48 or SAPO-11, and zeolite beta, which are combined with alumina, and formed into a useable shape by methods such as extrusion or tableting.

[0072] Hydroisomerization can be carried out in the presence of hydrogen gas under hydroprocessing conditions of elevated temperature and pressure. Particular reaction conditions for hydroisomerization can depend on the feed used, the catalyst used, whether or not the catalyst is sulfided, the desired yield, and the desired properties of the desired product, *inter alia*. Conditions under which the hydroisomerization process of this invention can be carried out include temperatures from 600°F to 750°F (315°C to 399°C), for example from 600°F to 700°F (315°C to 371°C), and pressures from 1.7 atm to 204 atm (25 psia to 3000 psia, or 170 kPaa to 20.7 MPaa), for example 6.8 atm to 170 atm (100 psia to 2500 psia, or 1.4 MPaa to 17.3 MPaa). Hydroisomerization pressures in this context refer to the hydrogen partial pressure within the hydroisomerization reactor, although the hydrogen partial pressure is the same as or substantially the same as the total pressure when the treat gas is 100% or substantially 100% hydrogen. However, the total pressure will be greater than the hydrogen

partial pressure when the treat gas contains hydrogen and other usually relatively inert gases.

[0073] Liquid hourly space velocity during contacting can generally be from 0.1 hr^{-1} to 20 hr^{-1} , for example from 0.1 hr^{-1} to 5 hr^{-1} . The hydrogen to hydrocarbon ratio can fall within a range from 1.0 mole H_2 to 50 moles H_2 per mole hydrocarbon feed, for example from 10 mole H_2 to 20 moles H_2 per mole hydrocarbon feed.

[0074] Treat gas is used in hydrotreating, as well as dewaxing and hydroisomerization. The terms “hydrogen”, “hydrogen treat gas”, and “treat gas” are used synonymously herein, and may be either pure hydrogen or a hydrogen-containing treat gas which is a treat gas stream containing hydrogen in an amount at least sufficient for the intended reaction(s), plus one or more other gases (*e.g.*, including nitrogen and light hydrocarbons such as methane) that generally do not adversely interfere with or affect either the reactions or the products. Impurities, such as H_2S and NH_3 , are generally undesirable and would typically be removed from the treat gas before it is conducted to the reactor. The treat gas stream introduced into a reaction stage can preferably contain at least about 50 vol% and more preferably at least about 75 vol% hydrogen.

[0075] Various reactor configurations can be used for the inventive process. The feedstock can contact a fixed bed of catalyst, a fluidized bed or an ebullating bed. An example of one configuration is a trickle-bed operation in which a liquid feedstock trickles through a stationary fixed bed. Another example of a reactor configuration is a countercurrent process, *i.e.*, where the hydrocarbon feed flows down over a fixed catalyst bed while H_2 flows in the opposite direction. In this configuration, H_2S and/or NH_3 can be removed overhead.

[0076] Light or heavy fractions of one or more of the hydrotreated, dewaxed and hydroisomerized material can be removed to produce or recover the desired fuel composition. In one embodiment, separation of light or heavy components or fractions of the hydrotreated material can be carried out prior to dewaxing. In another embodiment, separation of light or heavy components or fractions of dewaxed material can be carried out. In yet another embodiment, separation of light or heavy components or fractions of hydroisomerized material can be carried out. In these embodiments, the separation can be carried out so as to affect fuel quality, and in particular to provide at least one jet fuel or diesel fuel having high quality characteristics. Separation can be carried out using any appropriate means. Fractionation and/or distillation is(are) preferred. Atmospheric distillation, vacuum distillation, or a combination of atmospheric and vacuum distillation can be used.

[0077] Hydrotreating, dewaxing, hydroisomerizing, separation of components, or any combination thereof can be carried out to produce a fuel composition, particularly at least one jet fuel or diesel fuel, having highly desirable fuel characteristics. The process steps are particularly effective in producing a jet fuel composition.

[0078] The process steps of the invention can be carried out under predetermined conditions effective to provide at least one jet fuel having one or more of the predetermined characteristics of smoke point, freeze point, or one or more other properties as set forth in ASTM D1655–08a Standard Specification for Aviation Turbine Fuels, the contents of which are incorporated herein by reference.

[0079] In one embodiment, the feedstock can be hydrotreated, dewaxed, hydroisomerized, or a combination thereof, so as to form a fuel composition having a smoke point of at least 25.0 mm, preferably at least

25.5 mm, for example at least 26.0 mm or at least 26.5 mm. The smoke point as described is determined according to ASTM D 1322. The fuel is preferably jet fuel.

[0080] In another embodiment, the feedstock can be hydrotreated, dewaxed, hydroisomerized, or a combination thereof, so as to form a fuel composition having a freeze point of not higher than -35°C , preferably not higher than -45°C , for example not higher than -50°C or not higher than -55°C . The freeze point as described is determined according to ASTM D 4529. The fuel is preferably jet fuel.

[0081] In one embodiment, the process can be carried out to produce or recover a kerosene type or a gasoline type jet fuel. In one embodiment, the process can be carried out to produce or recover a kerosene type jet fuel having an ASTM D86 90% distillation point within the range from 250°C to 290°C , preferably within the range from 260°C to 280°C . In another embodiment, the process can be carried out to produce or recover a gasoline type jet fuel having an ASTM D86 90% distillation point within the range from 200°C to 240°C , preferably within the range from 210°C to 230°C .

[0082] In one embodiment, the process can be carried out to produce or recover a kerosene type jet fuel having an ASTM D86 10% distillation point within the range from 150°C to 200°C , preferably within the range from 160°C to 180°C . In another embodiment, the process can be carried out to produce or recover a gasoline type jet fuel having an ASTM D86 10% distillation point within the range from 110°C to 140°C , preferably within the range from 120°C to 130°C .

[0083] In one embodiment, the process can be carried out to produce or recover a diesel fuel. In a particular embodiment, the process can be carried out to produce or recover diesel fuel having an ASTM D86 90% distillation

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point within the range from 260°C to 350°C, preferably within the range from 280°C to 340°C.

[0084] In another embodiment, the process can be carried out to produce or recover a diesel fuel having an ASTM D86 10% distillation point within the range from 200°C to 240°C, preferably within the range from 210°C to 230°C.

[0085] While these fuel characteristics are mentioned in separate embodiments, it is contemplated that fuels produced or recovered can have any combination of two or more, or even all, of the characteristics/properties disclosed herein.

[0086] Additionally or alternately, the present invention includes the following embodiments.

[0087] Embodiment 1. A method for producing a dewaxed fuel composition comprising: providing a feedstock containing lipidic biomass; hydrotreating the feedstock to produce a hydrotreated material; and dewaxing and/or hydroisomerizing at least a portion of the hydrotreated material to produce the dewaxed and/or hydroisomerized fuel composition.

[0088] Embodiment 2. The method of embodiment 1, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel or diesel fuel.

[0089] Embodiment 3. The method of embodiment 1 or embodiment 2, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel having a smoke point of at least 25.0 mm.

[0090] Embodiment 4. The method of any of the previous embodiments, wherein at least a portion of the dewaxed and/or

hydroisomerized fuel composition is recovered as jet fuel having a freeze point of not higher than 35°C.

[0091] Embodiment 5. The method of any of the previous embodiments, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel having an ASTM D86 90% distillation point within the range of from 250°C to 290°C.

[0092] Embodiment 6. The method of any of the previous embodiments, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel having an ASTM D86 90% distillation point within the range of from 200°C to 240°C.

[0093] Embodiment 7. The method of any of the previous embodiments, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as diesel fuel having an ASTM D86 90% distillation point within the range of from 260°C to 350°C.

[0094] Embodiment 8. The method of any of the previous embodiments, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is distilled and at least one jet fuel or at least one diesel fuel is recovered following distillation.

[0095] Embodiment 9. The method of any of the previous embodiments, wherein the feedstock further comprises mineral oil.

[0096] Embodiment 10. The method of any of the previous embodiments, wherein at least a portion of the hydrotreated material is dewaxed but not hydroisomerized.

[0097] Embodiment 11. The method of any of the previous embodiments, wherein at least a portion of the hydrotreated material is hydroisomerized but not dewaxed.

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[0098] The principles and modes of operation of this invention have been described above with reference to various exemplary and preferred embodiments. As understood by those of skill in the art, the overall invention, as defined by the claims, encompasses other preferred embodiments not specifically enumerated herein.

CLAIMS:

1. A method for producing a dewaxed fuel composition comprising: providing a feedstock containing lipidic biomass; hydrotreating the feedstock to produce a hydrotreated material; and dewaxing and/or hydroisomerizing at least a portion of the hydrotreated material to produce the dewaxed and/or hydroisomerized fuel composition.
2. The method of claim 1, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel or diesel fuel.
3. The method of claim 1 or embodiment 2, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel having a smoke point of at least 25.0 mm.
4. The method of any of the previous claims, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel having a freeze point of not higher than 35°C.
5. The method of any of the previous claims, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel having an ASTM D86 90% distillation point within the range of from 250°C to 290°C.
6. The method of any of the previous claims, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as jet fuel having an ASTM D86 90% distillation point within the range of from 200°C to 240°C.
7. The method of any of the previous claims, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is recovered as diesel fuel having an ASTM D86 90% distillation point within the range of from 260°C to 350°C.

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8. The method of any of the previous claims, wherein at least a portion of the dewaxed and/or hydroisomerized fuel composition is distilled and at least one jet fuel or at least one diesel fuel is recovered following distillation.

9. The method of any of the previous claims, wherein the feedstock further comprises mineral oil.

10. The method of any of the previous claims, wherein at least a portion of the hydrotreated material is dewaxed but not hydroisomerized.

11. The method of any of the previous claims, wherein at least a portion of the hydrotreated material is hydroisomerized but not dewaxed.