



- (51) International Patent Classification:
C10G 3/00 (2006.01)
- (21) International Application Number:
PCT/US2013/053614
- (22) International Filing Date:
5 August 2013 (05.08.2013)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
13/594,139 24 August 2012 (24.08.2012) US
13/594,175 24 August 2012 (24.08.2012) US
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- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*

(54) Title: SINGLE STEP PROCESS FOR PRODUCTION OF DISTILLATE FUEL

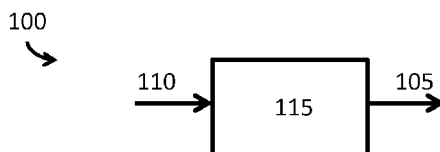


FIG. 1

(57) Abstract: The present invention is directed to preparing distillate fuel having almost no oxygen and no carbon-to-carbon double bonds. The method comprises passing biodiesel and/or lipids derived from vegetable oils, algae oils, and/or animal fats over bio-feedstock, or lipids, conversion catalyst that performs the hydrocarbon isomerization function, removes oxygen from the feedstock, cracks off the C3 backbone, and saturates double bonds. The process is a single step process eliminating the need of a separate costly hydrotreating step while producing a renewable source distillate fuel.



SINGLE STEP PROCESS FOR PRODUCTION OF DISTILLATE FUEL

[0001] This application claims priority to U.S. Patent Application Serial Numbers 13/594,139 and 13/594,175, both filed on August 24, 2012. This application claims priority to and benefits from the foregoing, the disclosures of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present application relates generally to systems and methods for producing fuels from biomass, and more particularly, to systems and methods for making distillate fuels, such as diesel and jet fuels, from biomass by subjecting the biomass to catalytic reaction.

BACKGROUND

[0003] Biofuels are of increasing interest for a number of reasons including: (1) they are a renewable resource, (2) their production is less dependent on geopolitical considerations, (3) they provide the possibility of a direct replacement of petroleum-based fuels in existing vehicles, and (4) the net greenhouse gas emissions can be substantially reduced by virtue of carbon dioxide (CO₂) uptake by biofuel precursors—particularly in the case of cellulose feedstocks.

[0004] An easily-obtainable bio-feedstock is vegetable oil, which largely comprises triglycerides and some free fatty acids. Other similar bio-feedstocks are algae oils and animal fats. However, the properties of these oils and fats generally are not sufficient for use as a direct replacement for petroleum diesel in vehicle engines, as the oils and fats can have viscosities and back-end distillation properties that are generally too high and do not burn cleanly enough, thereby leaving damaging carbon deposits on the engine. Additionally, these oils and fats gel at higher temperatures, thereby hindering their use in colder climates. These problems are mitigated when the oils and fats are blended with petroleum fuels, but still remain an impediment for long-term use in diesel engines.

[0005] Vegetable oils, algae oils, and animal fats are composed of long chain fatty acid esters of glycerol. These materials can be transesterified with methanol to produce fatty acid methyl esters (FAME), or biodiesel. Fatty acid methyl esters have some issues, though, notably poor low temperature viscometrics and poor oxidation stability, when compared to

conventional hydrocarbon or petroleum-derived diesel. Fatty acid methyl esters contain a fair amount of oxygen, generally over ten percent by weight on average, and any unsaturation in the carbon chains is retained. Depending on the animal fat or vegetable oil used to make the biodiesel, the fatty acid methyl esters would contain between one and three carbon-to-carbon double bonds. However, the greater the unsaturation present in the fatty acid methyl esters, the better the low temperature properties, but poorer oxidation stability. Poor low temperature viscometrics limit the use of fatty acid methyl esters in colder climates where the biodiesel will form wax crystals that plug fuel filters. Poor oxidation leads to the formation of insoluble gums and resins that can plug fuel filters, reducing storage stability to as little as six months as opposed to one year or longer storage stability for petroleum distillate fuel. Both of these problems can be solved by severely hydrotreating the fatty acid methyl esters or the original lipid to convert them to saturated hydrocarbons, and then isomerizing the straight chain hydrocarbons to improve their low temperature viscometrics. However, these conventional processes require a number of complex steps and the hydrotreating process is generally very costly.

[0006] Accordingly, there is a need for an improved process for high conversions of lipids and fatty acid methyl esters into acceptable distillate-compatible fuels, particularly when such a process eliminates the need for a separate hydrotreating step.

SUMMARY

[0007] Addressing the above-described problems of preparing distillate fuels, such as diesel fuels and jet fuels, from biodiesel and/or lipids, *i.e.*, vegetable oils, algae oils, and animal fats, provided is a process for preparing renewable distillate fuel which comprises passing biodiesel, lipid materials derived from vegetable oils and/or animal fats, or mixtures thereof over a bio-feedstock or lipid conversion catalyst. The process is a single step process, eliminating the need of a costly separate hydrotreating step and producing a suitable renewable distillate fuel exhibiting a cloud point of about -15°C or below.

[0008] Among other factors, it has been found that when lipid materials such as those derived from vegetable oils, algae oils, and/or animal fats, are subjected to a bio-feedstock (or lipids) conversion catalyst, such as an isomerization-type catalysts (*e.g.* Isodewaxing® registered trademark of Chevron U.S.A. Inc.), renewable distillate fuel is effectively obtained in but a single step. Specifically, it has been found that these catalysts can perform all of the

reactions required to convert the lipid materials to high quality distillate fuels. These reactions include cracking off the C₃ backbone linkages of the lipids to create individual chains, removal of oxygen, saturation of double bonds, and isomerization to create branched chains. This discovery consolidates the production of renewable distillate fuel into a single step, thus cutting the capital expense and operating costs associated with a separate hydrotreater. Biodiesel can also be subjected to the single step process, with the fatty acid methyl esters being converted in a single step to a renewable distillate fuel without the need for a separate hydrotreating step. However, by starting with the original lipid materials, one can also avoid the transesterification step of converting the lipids (vegetable oil and animal fats) to biodiesel. Overall, the present discovery allows one to prepare renewable distillate fuel in a much more simple and economical manner by consolidating the process into a single step.

1. Embodiments of the disclosure include a method of forming a distillate fuel product, comprising: subjecting a feedstock to a Group VIII metal on molecular sieve catalyst, wherein the feedstock is selected from the group consisting of biodiesels, lipids derived from vegetable oils, algae oils, animal fats, and mixtures thereof; and catalytically reacting the feedstock over the catalyst at a temperature in the range of from 650°F to 775°F to produce the distillate fuel product, wherein the step of catalytically reacting the feedstock comprises catalytically cracking off its C₃ backbone linkage to create individual chains, removing molecular oxygen from the feedstock, saturating double bonds in the chains, and isomerizing the product over the catalyst. In embodiments of the disclosure, the temperature is in the range of from about 700°F to 775°F. The reaction may produce a recoverable diesel product that has a cloud point at least as low as -15°C as low as -20°C, or as low as -30°C. In embodiments, the feedstock comprises molecular oxygen in an amount of greater than about ten percent by weight and/or the feedstock comprises unsaturation in its carbon chains, such as where molecules in the feedstock comprise between one and three carbon-to-carbon double bonds. In one example, the feedstock comprises soybean oil. The Group VIII metal on the catalyst may be platinum and/or palladium, for example. In embodiments, the Group VIII metal is present in an amount of from about 0.01% to about 10% by weight of a molecular sieve. In embodiments, the distillate fuel product contains no oxygen or low oxygen, such as less than 2.7% oxygen, less than 2% oxygen, or less than 1% oxygen. The method of claim 1, wherein molecules in the distillate fuel product contain no carbon-to-

carbon double bonds, or low amounts of carbon-to-carbon double bonds, such as less than 1%. In embodiments of the invention, molecules in the distillate fuel product comprise a secondary methyl group. The molecular sieve may be a silicoaluminophosphate molecular sieve. The molecular sieve may be a zeolitic molecular sieve. In certain embodiments, the silicoaluminophosphate molecular sieve is SM-3, SAPO-31 and/or SAPO-41. In certain embodiments, the zeolitic molecular sieve is ZSM-22, ZSM-23 and/or ZSM-35. The molecular sieve may also be an intermediate size molecular sieve, such as molecular sieve with a pore size between 5.3Å and 6.5Å, when the porous inorganic oxide is in the calcined form.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] For a more complete understanding of the exemplary embodiments of the present invention and the advantages thereof, reference is now made to the following description in conjunction with the accompanying drawings, which are briefly described as follows.

[0010] FIG. 1 is a schematic diagram of a system for producing distillate fuel, according to an exemplary embodiment.

[0011] FIG. 2 is a flowchart illustrating a method for producing distillate fuel, according to an exemplary embodiment.

DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

[0012] The present disclosure is directed to systems and methods for producing distillate fuel, wherein such implementations comprise but a single step of passing a bio-feedstock over a bio-feedstock, or lipids, conversion catalyst. The bio-feedstock can include biodiesel, lipids of vegetable oils, algae oils, animal fats, or a mixture thereof.

[0013] Illustrative embodiments of the invention are described below. In the interest of clarity, not all features of an actual implementation are described in this specification. One of ordinary skill in the art will appreciate that in the development of any such actual embodiment, numerous implementation-specific decisions must be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which will vary from one implementation to another.

[0014] The present invention may be better understood by reading the following description of non-limitative embodiments with reference to the attached drawings wherein like parts of each of the figures are identified by the same reference characters. The words and phrases used herein should be understood and interpreted to have a meaning consistent with the understanding of those words and phrases by those skilled in the relevant art. No special definition of a term or phrase, for example, a definition that is different from the ordinary and customary meaning as understood by those skilled in the art, is intended to be implied by consistent usage of the term or phrase herein. To the extent that a term or phrase is intended to have a special meaning, for example, a meaning other than that understood by skilled artisans, such a special definition will be expressly set forth in the specification in a definitional manner that directly and unequivocally provides the special definition for the term or phrase.

[0015] Referring to FIG. 1, a system 100 for producing a renewable hydrocarbon or distillate fuel 105 from a feed stream 110 is shown. In certain exemplary embodiments, the feed stream 110 includes fatty acid methyl esters, or biodiesel. In certain embodiments, the biodiesel includes oxygen (O_2) in an amount greater than about ten percent by weight. In certain embodiments, the biodiesel includes unsaturation in its carbon chains. In certain exemplary embodiments, the molecules of the biodiesel contain between one and three carbon-to-carbon double bonds. In certain other embodiments, the feed stream 110 includes lipids from vegetable oils, algae oils, and/or animal fats. Examples of suitable vegetable oils include, but are not limited to, crude or refined soybean, corn, coconut (including copra), palm, rapeseed, camelina, jatropha, and cotton oils. Examples of suitable animal fats include, but are not limited to, tallow, lard, butter, bacon grease and yellow grease. In certain exemplary embodiments, soybean oil is included in the feed stream 110. Good results for producing renewable diesel fuels may be obtained when using oils with C_{16}/C_{18} carbon chains. For renewable jet fuel production, the use of oils having lower carbon numbers, for instance, approximately C_8-C_{16} , is desired, or alternatively, the heavier carbon number molecules can be selectively cracked into the jet fuel range. In yet other embodiments, the feed stream 110 includes a combination of biodiesel and lipids of vegetable oils, algae oils, and/or animal fats.

[0016] The feed stream 110 enters a catalysis unit 115 for catalytically reacting the feed stream 110. In certain exemplary embodiments, this step includes removal of oxygen

(deoxygenation), cleavage of the C₃ glycerol backbone, hydrogenation of the double bonds, and isomerization to branched products, thus enabling a single step process. In certain embodiments, the temperature at which this step is run is generally in the range of from about 650 degrees Fahrenheit (°F) (343°C) to about 775°F (413°C). In certain exemplary embodiments, the temperature is in the range of from about 700°F (371°C) to about 775°F (413°C). By using such high temperatures, it has been found that the feed stream 110 is isomerized to the point that the recoverable diesel product, or distillate fuel 105, has a cloud point at least as low as -15°C, and in particular at least as low as -20°C, and is converted to saturated hydrocarbon chains. In certain exemplary embodiments, the feed stream 110 is subjected to the reaction step for a length of time so as to achieve a cloud point at least as low as -15°C. In certain embodiments, in a flowing reaction system, the space velocity is in a range of from about 0.25/hr to about 5.0/hr, and more preferably in the range of from about 1.0/hr to about 2.0/hr.

[0017] In certain embodiments, the feed stream 110 is in contact with a fixed stationary bed of catalyst, with a fixed fluidized bed, or with a transport bed during catalytic reaction. In one embodiment, a trickle-bed operation is employed, wherein the feed stream 110 is allowed to trickle through a stationary fixed bed, typically in the presence of hydrogen. For an illustration of the operation of such catalysts, see Miller *et al.*, United States Patent Nos. 6,204,426 and 6,723,889, for example.

[0018] The catalytic step comprises use of a bio-feedstock, or lipids, conversion catalyst. During the reaction, the triglyceride C₃ backbone linkages are cracked, the oxygen removed, and the compounds saturated, as well as the molecules being isomerized, *i.e.*, have more branching created. All of these functions are accomplished in but a single step using a bio-feedstock, or lipids, conversion catalyst at a temperature in the range of from about 650°F (343°C) to about 775°F (413°C). Despite the formation of water during the reactions, the catalyst has still been found to effectively catalyze isomerization in order to achieve the distillate fuel 105 with a cloud point at least as low as -15°C. Generally, the distillate fuel 105 produced contains almost no oxygen and no carbon-to-carbon double bonds. In certain embodiments, a majority of the molecules in the distillate fuel 105 includes a secondary methyl group. The resulting distillate fuel 105 would have increased energy content by removing the oxygen and improved oxidation stability by hydrogenating the double bonds. In addition, isomerization of the carbon chains improves low temperature performance.

[0019] Suitable catalysts include, but are not limited to platinum (Pt) or palladium (Pd) on a support such as, but not limited to SM-3, SSZ-32, ZSM-23, ZSM-22, and similar such supports. In certain embodiments, the step of catalytically isomerizing the saturated, decarboxylated biofuel intermediate comprises the use of a Pt or Pd catalyst supported on an acidic support material selected from the group consisting of beta or zeolite Y molecular sieves, SiO₂, Al₂O₃, SiO₂-Al₂O₃, and combinations thereof. In some such embodiments, the catalytic isomerization is carried out at a temperature between about 650°F (343°C) and about 750°F (413°C). The operating pressure is typically between about 200 pounds/square inch [gauge] (psig) to about 2000 psig, and more typically between about 200 psig to about 1000 psig. The hydrogen flow rate is typically between about 500 standard cubic feet/barrel (SCF/bbl) to about 5000 SCF/bbl.

[0020] The catalysts of the disclosure include an "intermediate pore size", or effective pore aperture, in the range of from about 5.3 angstroms (Å) to about 6.5 Å when the porous inorganic oxide is in the calcined form. Molecular sieves having pore apertures in this range tend to have unique molecular sieving characteristics. Unlike small pore zeolites such as erionite and chabazite, they will allow hydrocarbons having some branching into the molecular sieve void spaces. Unlike larger pore zeolites, such as the faujasites and mordenites, they can differentiate between n-alkanes and slightly branched alkanes, and larger branched alkanes having, for example, quaternary carbon atoms.

[0021] The effective pore size of the molecular sieves can be measured using standard adsorption techniques and hydrocarbonaceous compounds of known minimum kinetic diameters. See Breck, *Zeolite Molecular Sieves*. 1974 (especially Chapter 8); Anderson, *et al.*, J. Catalysis 58,114 (1979); and Lok *et al.*, United States Patent No. 4,440,871. In performing adsorption measurements to determine pore size, standard techniques are generally employed. It is convenient to consider a particular molecule as excluded if it does not reach at least 95 percent (%) of its equilibrium adsorption value on the molecular sieve in less than about 10 minutes (p/po=0.5; 25 degrees Celsius (°C)).

[0022] Intermediate pore size molecular sieves will typically admit molecules having kinetic diameters of about 5.3 Å to about 6.5 Å with little hindrance. Examples of such compounds (and their kinetic diameters in Å) are: n-hexane (4.3), 3-methylpentane (5.5), benzene (5.85), and toluene (5.8). Compounds having kinetic diameters of about 6 Å to about 6.5 Å can be admitted into the pores, depending on the particular sieve, but do not

penetrate as quickly and in some cases are effectively excluded. Compounds having kinetic diameters in the range of about 6 Å to about 6.5 Å include: cyclohexane (6.0), 2,3-dimethylbutane (6.1), and m-xylene (6.1). Generally, compounds having kinetic diameters of greater than about 6.5 Å do not penetrate the pore apertures and thus are not absorbed into the interior of the molecular sieve lattice. Examples of such larger compounds include: o-xylene (6.8), 1,3,5-trimethylbenzene (7.5), and tributylamine (8.1).

[0023] Intermediate pore size silicoaluminophosphate molecular sieves useful in the process include silicoaluminophosphate molecular sieves, such as those disclosed in detail in United States Patent No. 5,135,638. Specific intermediate pore size silicoaluminophosphate molecular sieves include SAPO-31 and SAPO-41. Another specific intermediate pore size silicoaluminophosphate is SM-3. SM-3 comprises a molecular framework of corner-sharing (SiO_2) tetrahedra, (AlO_2) tetrahedra and (PO_2) tetrahedra, (*i.e.*, $(\text{S}_x\text{Al}_y\text{P}_z)\text{O}_2$ tetrahedral units). SM-3 is disclosed in detail in Miller, United States Patent No. 5,087,347. SM-3 is a SAPO-11 type zeolite, however, its preparation and some properties are different from SAPO-11. SM-3 has an X-ray diffraction pattern that is similar to SAPO-11, however, SM-3 has the unique feature that the phosphorus, silicon, and aluminum concentrations at the molecular sieve surface is different than the concentrations in the bulk of the molecular sieve. When combined with a Group VIII metal hydrogenation component, the SM-3, for example, converts the lipids to a mixture of substantially branched hydrocarbons.

[0024] Also useful are catalysts having intermediate pore size zeolitic molecular sieves, such as ZSM-22, ZSM-23 and ZSM-35, and at least one Group VIII metal. X-ray crystallography of SAPO-31, SAPO-41, ZSM-22, ZSM-23 and ZSM-35 shows these molecular sieves to have the following major and minor axes: SAPO-11, major 6.3 Å, minor 3.9 Å; (Meier, W. H., Olson, D. H., and Baerlocher, C., *Atlas of Zeolite Structure Types*, Elsevier, 1996), SAPO-31 and SAPO-41, believed to be slightly larger than SAPO-11, ZSM-22, major 5.5 Å, minor 4.5 Å (Kokotailo et al, *Zeolites*, 5, 349(85)); ZSM-23, major 5.6 Å, minor 4.5 Å; ZSM-35, major 5.4 Å, minor 4.2 (Meier, W. M. and Olsen, D. H., *Atlas of Zeolite Structure Types*, Butterworths, 1987).

[0025] In preparing the catalyst, the intermediate pore size molecular sieve, such as SM-3, is typically used in admixture with at least one Group VIII metal. The Group VIII metal is typically selected from the group consisting of at least one of platinum and palladium and optionally, other catalytically active metals such as molybdenum, nickel, vanadium, cobalt,

tungsten, zinc and mixtures thereof. More typically, the Group VIII metal is selected from the group consisting of at least one of platinum and palladium. The amount of metal ranges from about 0.01% to about 10% by weight of the molecular sieve, preferably from about 0.2% to about 5% by weight of the molecular sieve. The techniques of introducing catalytically active metals into a molecular sieve are disclosed in the literature, and preexisting metal incorporation techniques and treatment of the molecular sieve to form an active catalyst such as ion exchange, impregnation or occlusion during sieve preparation are suitable for use in the present process. Such techniques are disclosed in United States Patent Nos. 3,236,761; 3,226,339; 3,236,762; 3,620,960; 3,373,109; 4,202,996; 4,440,781 and 4,710,485.

[0026] In the present disclosure, the term "metal" or "active metal" refers to one or more metals in the elemental state or in some form such as sulfide, oxide and mixtures thereof. Regardless of the state in which the metallic component actually exists, the concentrations are computed as if they existed in the elemental state.

[0027] It is often useful that relatively small crystal size catalyst be utilized in practicing the invention. Suitably, the average crystal size is generally no greater than about 10 microns (μm), typically no more than about 5 μm , more typically no more than about 1 μm and still more typically no more than about 0.5 μm .

[0028] The physical form of the catalyst depends on the type of catalytic reactor being employed and may be in the form of a granule or powder, and is desirably compacted into a more readily usable form (*e.g.*, larger agglomerates), usually with a silica or alumina binder for fluidized bed reaction, or pills, prills, spheres, extrudates, or other shapes of controlled size to accord adequate catalyst-reactant contact. The catalyst may be employed either as a fluidized catalyst, or in a fixed or moving bed, and in one or more reaction stages.

[0029] The intermediate pore size molecular sieve catalyst can be manufactured into a wide variety of physical forms. The molecular sieves can be in the form of a powder, a granule, or a molded product, such as an extrudate having a particle size sufficient to pass through a 2-mesh (Tyler) screen and be retained on a 40-mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion with a binder, the silicoaluminophosphate can be extruded before drying, or, dried or partially dried and then extruded.

[0030] The molecular sieve can be composited with other materials resistant to temperatures and other conditions employed in the catalytic process. Such matrix materials

include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates, sols or gels including mixtures of silica and metal oxides. Inactive materials suitably serve as diluents to control the amount of conversion in the catalytic process so that products can be obtained economically without employing other means for controlling the rate of reaction. The molecular sieve may be incorporated into naturally occurring clays, *e.g.*, bentonite and kaolin. These materials, *i.e.*, clays, oxides, etc., function, in part, as binders for the catalyst.

[0031] Naturally occurring clays which can be composited with the molecular sieve include the montmorillonite and kaolin families, which families include the sub-bentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, diokite, nacrite or anauxite. Fibrous clays such as halloysite, sepiolite and attapulgite can also be use as supports. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

[0032] In addition to the foregoing materials, the molecular sieve can be composited with porous matrix materials and mixtures of matrix materials such as silica, alumina, titania, magnesia, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, titania-zirconia as well as ternary compositions such as silica-alumina-thoria, silica-alumina-titania, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel.

[0033] The catalyst used in the methods and systems of the present invention can also be composited with other zeolites such as synthetic and natural faujasites, (*e.g.*, X and Y) erionites, and mordenites. It can also be composited with purely synthetic zeolites such as those of the ZSM series. The combination of zeolites can also be composited in a porous inorganic matrix.

[0034] FIG. 2 is a flowchart illustrating a method 200 of operation, described with respect to the system 100 of FIG. 1, according to an exemplary embodiment. In step 205, a feed stream 110 is provided. In step 210, the feed stream 110 is directed to a catalysis unit 115. In step 215, the feed stream 110 is catalytically reacted over a Group VIII metal on molecular sievecatalysts, such as SM-3. This single catalyst performs the functions of: cracking the triglyceride C₃ backbone linkages, removing the oxygen, saturating the double

bonds, and isomerizing the products without the need for a separate hydrotreating catalyst step. In step 220, the distillate fuel 105 is produced.

[0035] To further illustrate the present method, the following examples are provided. The following examples are being provided, however, to merely being illustrative, and are not meant to be limiting.

EXAMPLE

[0036] The feedstock in these experiments was a food grade 100% soybean oil purchased at the supermarket. This oil was used as purchased without further preparation.

[0037] Soybean oil was contacted with a commercially available isodewaxing catalyst available from Chevron U.S.A. Inc., and designated as ICR410 (Pt on SM-3 zeolite), at 1000 psig hydrogen pressure. The temperature of the catalyst was fixed for a given run, starting at 675°F and increasing by 25°F in the subsequent run. The temperature of the final run was jumped to 775°F. The catalyst was sulfided with DMDS in n-heptane. The isodewaxing catalyst was used as the whole extrudate.

[0038] All processed samples were sent for physical and chemical tests including cloud and pour point plus Gas Chromatography (GC), and Gas Chromatography/Mass Spectrometry (GC/MS). All chromatograms shown are Total Ion Current (TIC) from the mass spectrometer.

[0039] Chemical and physical results for the soy vegetable oil and the products from Runs 1 through 4 are summarized in Table 1.

Table 1: Isodewaxing Conditions for Soy Vegetable Oil

Run#	IDW Catalyst Temperature (°F)	Cloud Point (°C)	Pour Point (°C)	Iso-alkane to normal alkane ratio	Appearance	Figure
Soy Oil	--	-7	-9	--	Clear, yellow liquid	1
1	675	-3	-14	2.2	Clear, yellow liquid	2
2	700	-21	-22	3.5	Clear, yellow liquid	3
3	725	-17	-22	5.3	Clear, brown liquid	4
4*	775	<-30	<-30	8.3	Dark brown, fluorescent liquid	5

*The Run 4 sample is the product produced while the temperature was ramped up from 725 to 775°F

The results of each run are briefly discussed:

Run 1, 675°F

[0040] The product of the first isodewaxing of soybean oil was a clear yellow liquid. Although the cloud and pour points have not improved much over those for untreated soybean oil (Table 1), significant decarboxylation of the original fatty acids was indicated. The decarboxylated acids appear in the TIC as odd-numbered carbon chains. There are some even-numbered chains, mostly n-C₁₈ and n-C₁₆, but they are present to a lesser degree than the odd-numbered chains. The even-number chains suggest a hydrogenation mechanism removing the oxygen from the carboxylic acid, saturating the carbon with hydrogen. Generally, the greater the decarboxylation and decarbonylation that occurs, the less water formation there is, and thus less requirements for hydrogen, which can be important for many refineries.

[0041] In the GC, clustered about the major GC peaks are numerous smaller peaks from the isomerized carbon chains. These isomers differ in the position of a methyl group along the backbone as identified from our mass spectra library. Approximately 32% of the

hydrocarbon molecules remain as straight chains; the remaining 68% are present as branched chain alkanes.

Run 2, 700°F

[0042] The product from Run 2 is a clear yellow liquid. The cloud and pour points are significantly better than in the original soy oil at -21°C and -2°C, respectively.

[0043] As in Run 1, both even and odd carbon chains are present. Branching has increased to 78%.

Run 3, 725°F

[0044] The product from the isodewaxing of soybean oil at 725°F is even darker than the previous samples, certainly not water white as had been seen with the soy FAME isodewaxed products. No explanation for the dark color of the soy oil products can be provided.

[0045] Even though the product is dark in color, the cloud and pour points are very good at -17°C and -22°C, respectively. The GC/MS trace shows the expected even and odd carbon chains, all with significant branching. The Run 3 product contains 84% branched hydrocarbons.

Run 4, 775°F

[0046] Run 4 is a composite sample of the product produced as the reactor temperature was raised from 725 to 775°F. Further material was not collected at 775°F because the appearance of the product. This sample is dark brown in color but with a slight fluorescence suggesting aromaticity. GC/MS analysis indicates that a minor amount of cyclization has occurred. Low temperature properties are excellent, with cloud and pour points of <-30°C.

[0047] In addition to having good low temperature viscometrics, distillate fuels must have acceptable volatility characteristics in order to promote and sustain engine combustion. Several samples were run in the D2887 simulated distillation volatility test. Results are summarized in Table 2.

Table 2: ASTM D2887 Volatility

Sample	Distillation Temperature, °C		
	T10 ^a	T50	T90
Soybean Oil	1109	1124	1128
Run 2 product	521	578	727
Run 3 product	508	581	777
Ultra low sulfur diesel (ASTM Specifications)			540-640 ^b

^a T10 is the temperature at which 10% of the sample has distilled

^b ASTM specifications are based on values from D86, ASTM D2887 values are typically about 30°F higher.

[0048] The isodewaxed samples' volatility compares favorably with that of the ULS diesel. Further isomerization processing adjustments can fine tune the product. Also, a narrower cut of the isodewaxed product can be isolated from a distillation column in order to obtain a desired diesel product exhibiting the properties needed.

[0049] A process, such as disclosed here, which can eliminate the costly hydrotreating step and consolidate the production of renewable diesel from vegetable oils and animal fats, *i.e.*, lipids, into a single step would be of great value. A single step process would simplify the production of renewable diesel and cuts capital expense roughly in half by eliminating the need for a hydrotreater. It would also eliminate operating costs associated with the hydrotreater.

[0050] All patents and publications referenced herein are hereby incorporated by reference to the extent not inconsistent herewith. Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered

or modified and all such variations are considered within the scope and spirit of the present invention. The terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee.

CLAIMS

What is claimed is:

1. A method of forming a distillate fuel product, comprising:

 subjecting a feedstock to a Group VIII metal on molecular sieve catalyst, wherein the feedstock is selected from the group consisting of biodiesels, lipids derived from vegetable oils, algae oils, and animal fats, and mixtures thereof; and

 catalytically reacting the feedstock over the catalyst at a temperature in the range of from 650°F to 775°F to produce the distillate fuel product, wherein the step of catalytically reacting the feedstock comprises catalytically cracking off its C₃ backbone linkage to create individual chains, removing molecular oxygen from the feedstock, saturating double bonds in the chains, and isomerizing the product over the catalyst.
2. The method of claim 1, wherein the temperature is in the range of from about 700°F to 775°F.
3. The method as in any one of claims 1 or 2, wherein the reacting produces a recoverable diesel product that has a cloud point at least as low as -15°C, as low as -20°C, or as low as -30°C.
4. The method as in any one of claims 1-3, wherein the feedstock comprises molecular oxygen in an amount of greater than about ten percent by weight.
5. The method as in any one of claims 1-4, wherein the biodiesel comprises unsaturated carbon chains.
6. The method as in any one of claims 1-5, wherein the feedstock comprises soybean oil.

7. The method as in any one of claims 1-6, wherein the Group VIII metal on the catalyst comprises platinum or palladium.

8. The method as in any one of claims 1-7, wherein the Group VIII metal is present in an amount of from about 0.01% to about 10% by weight of the molecular sieve.

9. The method as in any one of claims 1-8, wherein the distillate fuel product contains no oxygen.

10. The method as in any one of claims 1-9, wherein molecules in the distillate fuel product contain no carbon-to-carbon double bonds.

11. The method as in any one of claims 1-10, wherein molecules in the distillate fuel product comprise a secondary methyl group.

12. The method as in any one of claims 1-11, wherein the molecular sieve is an intermediate size molecular sieve.

13. The method of claim 12, wherein the molecular sieve is pore size is 5.3Å to 6.5Å.

14. The method as in any one of claims 1-13, wherein the molecular sieve is a zeolite molecular sieve.

15. The method of claim 14, wherein the zeolitic molecular sieve is ZSM-22, ZSM-23, ZSM-35, or a combination thereof.

16. The method as in any one of claims 1-13, wherein the molecular sieve is a silicoaluminophosphate molecular sieve.

17. The method of claim 16, wherein the silicoaluminophosphate molecular sieve is SAPO-31, SAPO-41, or a combination thereof.

18. The method as in any one of claims 1-13, wherein the molecular sieve is SM-3

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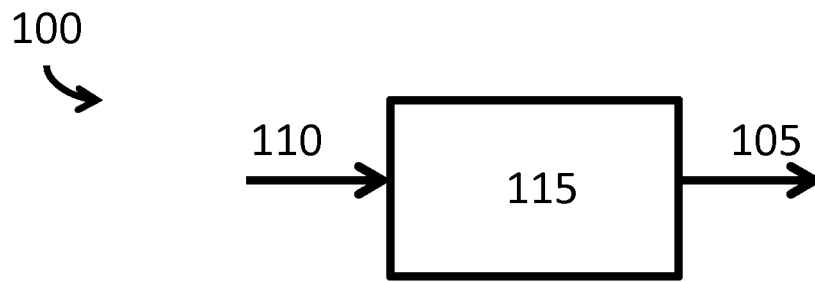


FIG. 1

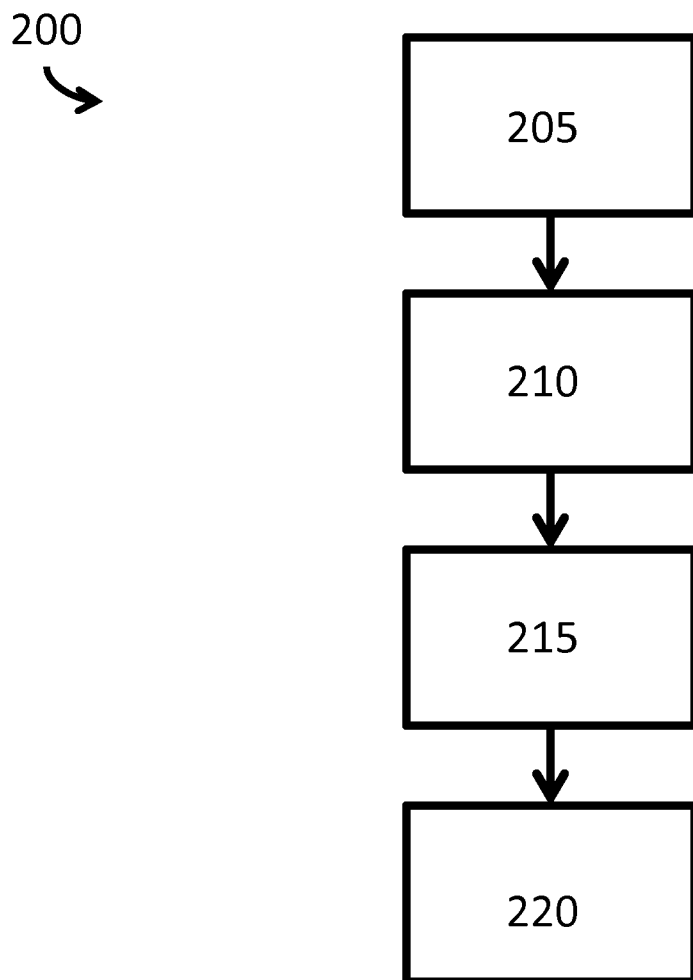


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/053614

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G3/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/207166 A1 (HERSKOWITZ MORDECHAY [IL] ET AL) 21 September 2006 (2006-09-21) example 3c -----	1-18
X	WO 2011/148045 A1 (UPM KYMMENE CORP [FI]; NOUSIAINEN JAAKKO [FI]; KNUUTTILA PEKKA [FI]; R) 1 December 2011 (2011-12-01) claims 1-4,10 -----	1-18
A	US 2008/308457 A1 (DINDI HASAN [US] ET AL) 18 December 2008 (2008-12-18) the whole document -----	1-18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

5 November 2013

Date of mailing of the international search report

13/11/2013

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/053614

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006207166 A1	21-09-2006	AU 2006226062 A1 BR PI0609771 A2 CA 2601708 A1 EP 1866266 A2 KR 20080012831 A US 2006207166 A1 US 2012149952 A1 WO 2006100584 A2	28-09-2006 18-10-2011 28-09-2006 19-12-2007 12-02-2008 21-09-2006 14-06-2012 28-09-2006
WO 2011148045 A1	01-12-2011	CA 2799643 A1 CN 102947422 A EP 2576731 A1 FI 20105585 A US 2013067801 A1 WO 2011148045 A1	01-12-2011 27-02-2013 10-04-2013 26-11-2011 21-03-2013 01-12-2011
US 2008308457 A1	18-12-2008	CA 2690193 A1 CN 101842465 A EP 2162507 A2 EP 2540804 A1 US 2008308457 A1 US 2008308458 A1 US 2008312480 A1 WO 2008157465 A2	24-12-2008 22-09-2010 17-03-2010 02-01-2013 18-12-2008 18-12-2008 18-12-2008 24-12-2008