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(54) **CO-PROCESSING DIESEL FUEL WITH VEGETABLE OIL TO GENERATE A LOW CLOUD POINT HYBRID DIESEL BIOFUEL**

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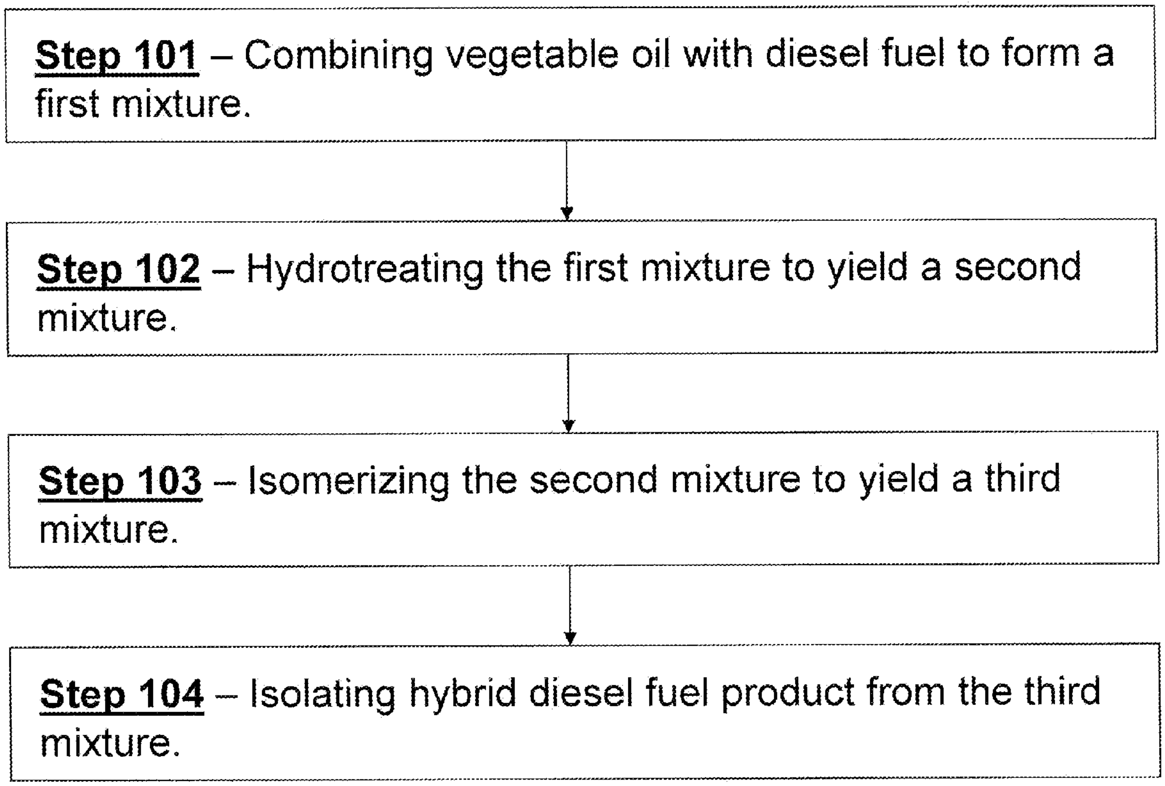
(57) **ABSTRACT**

The foregoing describes methods and systems for co-processing vegetable oil and petroleum diesel to yield a hybrid diesel biofuel composition. As previously stated, in some embodiments the present invention is directed to methods/systems by/with which a mixture of vegetable oil and petroleum diesel is co-processed in two stages: the mixture is first hydrotreated to yield a reduced-sulfur hybrid intermediate, and then the hybrid intermediate is processed in an isomerization unit to yield a low cloud point hybrid diesel product that is partially derived from biomass. A notable benefit of at least some such methods/systems is that interstage removal of H_2S and NH_3 is not required between the stages of hydrotreating and isomerizing, wherein such benefit is afforded by sulfur- and nitrogen-tolerant isomerization catalysts.



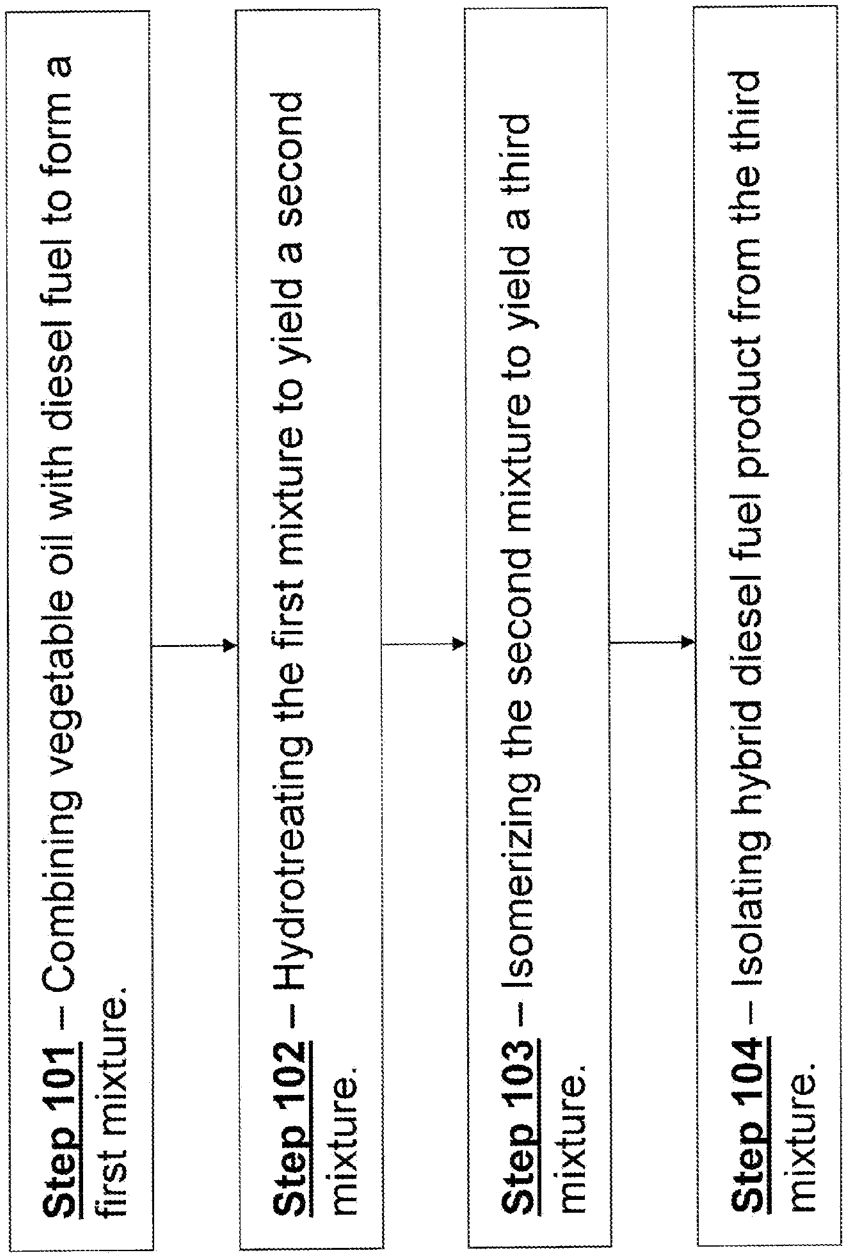

Step 101 – Combining vegetable oil with diesel fuel to form a first mixture.
Step 102 – Hydrotreating the first mixture to yield a second mixture.
Step 103 – Isomerizing the second mixture to yield a third mixture.
Step 104 – Isolating hybrid diesel fuel product from the third mixture.

Fig. 1

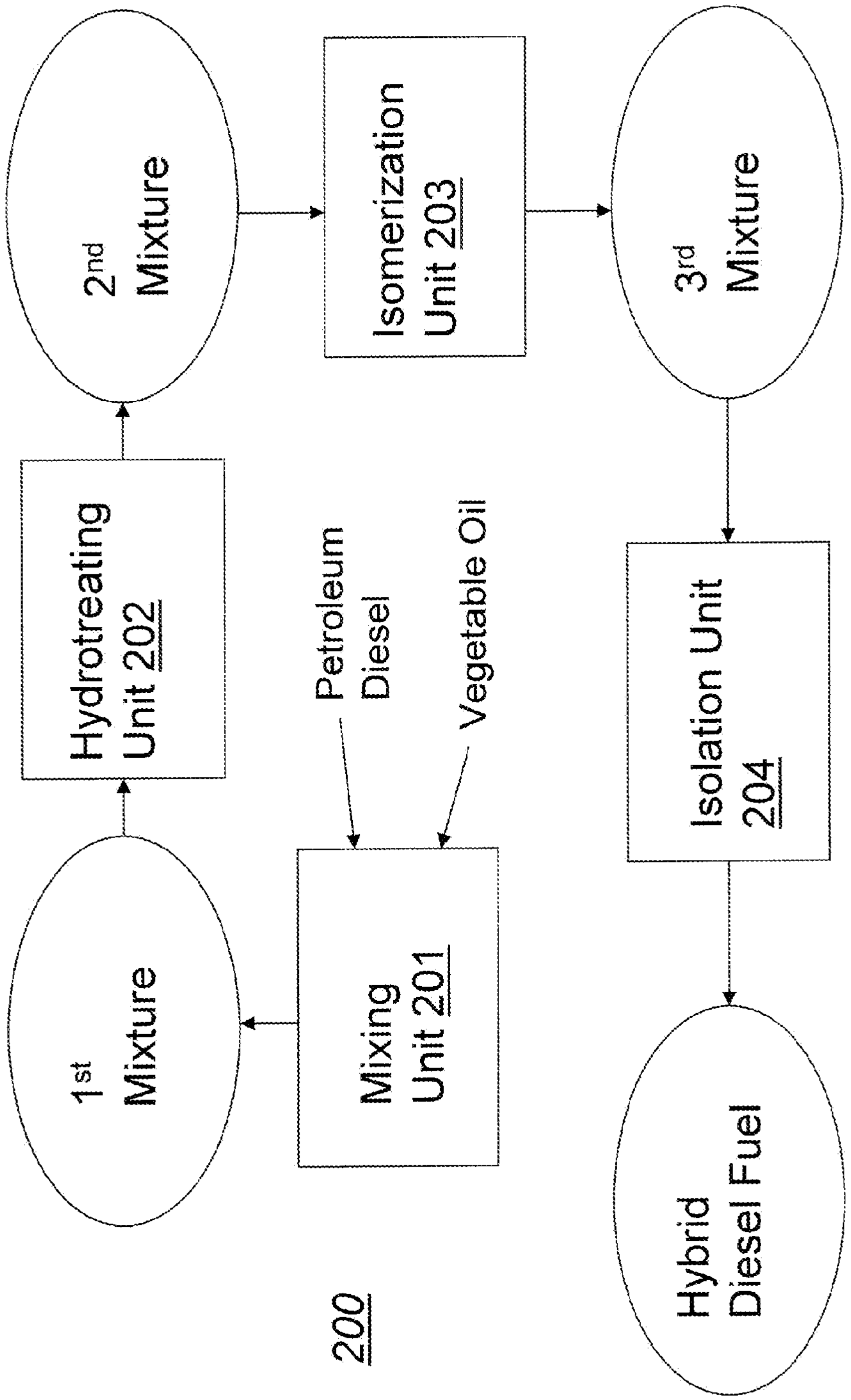

200
Petroleum Diesel
Vegetable Oil
Mixing Unit 201
1st Mixture
Hydrotreating Unit 202
2nd Mixture
Isomerization Unit 203
3rd Mixture
Isolation Unit 204
Hybrid Diesel Fuel

Fig. 2

CO-PROCESSING DIESEL FUEL WITH VEGETABLE OIL TO GENERATE A LOW CLOUD POINT HYBRID DIESEL BIOFUEL

FIELD OF THE INVENTION

[0001] This invention relates generally to diesel fuels and specifically to methods and systems for efficiently making low-sulfur hybrid diesel biofuels by co-processing blends of petroleum diesel and vegetable or crop oils.

BACKGROUND

[0002] 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 CO_2 uptake by biofuel precursors —particularly in the case of cellulosic feedstocks. See Pearce, “Fuels Gold,” New Scientist, September 23 pp. 36-41, 2006.

[0003] An easily-obtainable biofuel is vegetable oil, which largely comprises triglycerides and some free fatty acids. The properties of vegetable oil, however make it generally inappropriate for use as a direct replacement for petroleum diesel in vehicle engines, as the vegetable oils’ viscosities are generally too high and do not burn cleanly enough, thereby leaving damaging carbon deposits on the engine. Additionally, vegetable oils tend to gel at lower temperatures, thereby hindering their use in colder climates. These problems are mitigated when the vegetable oils are blended with petroleum fuels, but still remain an impediment for long-term use in diesel engines. See Pearce, 2006; Huber et al., “Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering,” Chem. Rev., vol. 106, pp. 4044-4098, 2006.

[0004] Transesterification is currently a method used to convert vegetable oils into diesel-compatible fuels (i.e., conventional biodiesel) that can be burned in conventional diesel engines. However, a similar cold flow problem with conventional biodiesel fuels still remains. This problem is at least partly due to the fact that at lower temperatures, e.g., around freezing (ca. 0° C.), conventional biodiesel often thickens and does not flow as readily. Therefore a limitation of biodiesel produced in this way is that it generally possesses a higher cloud point (and pour point) that renders it unusable in some, particularly colder, climates.

[0005] An alternative to the above-described transesterification, and as described herein, is to mix a vegetable oil (e.g., canola oil) with conventional diesel to form a mixture, and to then hydrotreat the mixture to yield a hybrid diesel biofuel. Generally, the vegetable oil is present in the mixture in an amount that is less than that of the conventional diesel. Depending on the embodiment, the vegetable oil typically comprises less than about 10 weight percent of the mixture.

[0006] When a vegetable oil is added to the diesel going to a hydrotreater, the cloud point is typically increased, driving the diesel “off-spec.” This requires readjustment of the diesel cut point, thereby reducing yield. While the prior art teaches isomerization dewaxing catalysts to lower cloud point, these catalysts either require removal of H_2S and NH_3 from the hydrotreater effluent ahead of the dewaxing reactor, or else have to operate at high temperature where life of the dewaxing catalyst is short. Accordingly, a method that could economically-utilize biomass in the production of hydrotreated diesel fuels, while still maintaining a relatively low cloud point, is still very much needed and would be highly beneficial.

BRIEF DESCRIPTION OF THE INVENTION

[0007] In some embodiments, the present invention is directed to methods (i.e., processes) and systems for co-processing vegetable oil and petroleum diesel to yield a hybrid diesel product comprising a biomass-derived component. Typically, such methods and systems work to provide a hybrid diesel product that benefits from a (partial) biomass-derived component, but without the poor low-temperature properties of conventional ester-based biodiesel.

[0008] So as to address at least some of the above-described limitations and/or recognized needs of biofuels and/or their processing, in some embodiments the present invention is directed to methods by which a mixture of vegetable oil and petroleum diesel is first hydrotreated to yield a reduced-sulfur hybrid intermediate, and then the hybrid intermediate is processed in an isomerization unit to yield a low cloud point hybrid (bio)diesel product that is partially derived from biomass. The low cloud point hybrid diesel product ideally possesses a cloud point within (or at least close to) the standard diesel range. Typically, such embodiments utilize a sulfur- and/or nitrogen-tolerant isomerization catalyst such that H_2S and NH_3 are generally not removed from the hybrid intermediate stream prior to isomerization. By forgoing interstage removal of H_2S and NH_3, such sulfur- and/or nitrogen-tolerant isomerization catalysts can enable the favorable economics of such methods/systems. Such isomerization catalysts are described in Miller, U.S. patent application Ser. No. 12/181,652, filed Jul. 29, 2008, and incorporated by reference herein.

[0009] In some embodiments, the present invention is directed to one or more methods for producing a hybrid diesel (bio)fuel product, such methods comprising the steps of: (a) combining vegetable oil with diesel fuel to form a first mixture, wherein the vegetable oil comprises not more than 10 weight percent of said first mixture; (b) hydrotreating the first mixture to yield a second mixture, wherein triglyceride components of the first mixture are deoxygenated, and wherein at least 95 atomic percent of the sulfur present in the first mixture is converted to H_2S in the second mixture; (c) isomerizing the second mixture in the presence of an isomerization catalyst to yield a third mixture comprising hybrid diesel fuel having a cloud point that is lower than that of the second mixture, wherein H_2S in the second mixture has not been removed prior to isomerizing; and (d) isolating the hybrid diesel fuel of the third mixture to yield a hybrid diesel fuel product.

[0010] So as to facilitate the production of such above-described hybrid diesel fuel and/or to implement any or all of the aforementioned methods, in some or other embodiments, the present invention is directed to one or more systems for generating a hybrid diesel fuel product, such systems generally comprising: (a) a mixing unit for combining vegetable oil with diesel fuel so as to form a first mixture, wherein the vegetable oil comprises not more than 10 weight percent of said first mixture; (b) a hydrotreating unit for hydrotreating the first mixture to yield a second mixture, wherein said unit is operable for deoxygenating triglyceride components of the first mixture, and wherein at least 95 atomic percent of the sulfur present in the first mixture is converted to H_2S in the second mixture; and (c) an isomerization unit for isomerizing the second mixture in the presence of an isomerization catalyst to yield a third mixture comprising hybrid diesel fuel having a cloud point that is lower than that of the second mixture, wherein H_2S in the second mixture has not been removed prior to isomerizing.

[0011] The foregoing has outlined rather broadly the features of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

[0013] FIG. **1** illustrates, in flow diagram form, methods for producing hybrid diesel biofuel compositions, in accordance with some embodiments of the present invention; and

[0014] FIG. **2** depicts, schematically, systems for implementing methods such as illustrated in FIG. **1**, in accordance with some embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

1. INTRODUCTION

[0015] Embodiments of the present invention are directed to methods (processes) and systems for co-processing vegetable oil and petroleum diesel to yield a hybrid diesel (bio) fuel composition. In some such embodiments, the present invention is directed to methods (and systems for implementing such methods) by which a mixture of vegetable oil and petroleum diesel is co-processed in two stages: the mixture is first hydrotreated to yield a reduced-sulfur hybrid intermediate, and then the hybrid intermediate is processed in an isomerization unit to yield a low cloud point hybrid diesel product that is partially derived from biomass. The low cloud point hybrid diesel product generally possesses a cloud point within (or at least close to) the standard diesel range.

[0016] A unique aspect of at least some such above-described embodiments of the present invention is that between the steps/stages of hydrotreating and isomerizing, there is no interstage removal of H_2S and NH_3. In some such embodiments, this elimination of H_2S/NH_3 interstage removal is enabled via use of sulfur- and nitrogen-tolerant/resistant isomerization catalysts, such as those described in Miller, U.S. patent application Ser. No. 12/181,652, filed Jul. 29, 2008, and incorporated by reference herein. By eliminating such H_2S/NH_3 interstage removal, the efficiency of such large-scale co-processing can be greatly increased, thereby reducing overall production costs.

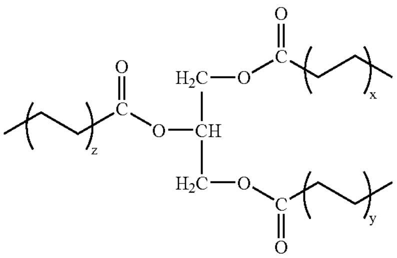
2. DEFINITIONS

[0017] Certain terms and phrases are defined throughout this description as they are first used, while certain other terms used in this description are defined below:

[0018] The prefix "bio," as used herein, refers to an association with a renewable resource of biological origin, such resources generally being exclusive of fossil fuels.

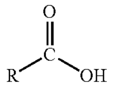
[0019] A "biologically-derived oil," as defined herein, refers to any triglyceride-containing oil that is at least partially derived from a biological source such as, but not limited to, crops, vegetables, microalgae, and the like. Such oils may further comprise free fatty acids. The biological source is henceforth referred to as "biomass." For more on the advantages of using microalgae as a source of triglycerides, see R. Baum, "Microalgae are Possible Source of Biodiesel Fuel," Chem. & Eng. News, vol. 72(14), pp. 28-29, 1994. Herein, the terms "vegetable oil," "crop oil," and "biologically-derived oil" will generally be used interchangeably.

[0020] "Triglyceride," as defined herein, refers to a class of molecules having the following molecular structure:



where x, y, and z can be the same or different, and wherein one or more of the branches defined by x, y, and z can have unsaturated regions.

[0021] A "carboxylic acid" or "fatty acid," as defined herein, is a class of organic acids having the general formula:



where "R" is generally a saturated (alkyl)hydrocarbon chain or a mono- or polyunsaturated (alkenyl) hydrocarbon chain.

[0022] "Lipids," as defined herein, broadly refers to the class of molecules comprising fatty acids, and tri-, di-, and monoglycerides.

[0023] "Hydrolysis" of triglycerides yields free fatty acids and glycerol, such fatty acid species also commonly referred to as carboxylic acids (see above).

[0024] "Transesterification," or simply "esterification," refers to the reaction between a fatty acid and an alcohol to yield an ester species.

[0025] "Hydroprocessing" or "hydrotreating" refers to processes or treatments that react a hydrocarbon-based material with hydrogen, typically under pressure and with a catalyst (hydroprocessing can be non-catalytic). Such processes include, but are not limited to, hydrodeoxygenation (of oxygenated species), hydrotreating, hydrocracking, hydroisomerization, and hydrodewaxing. For examples of such processes, see Cash et al. U.S. Pat. No. 6,630,066; and Elomari, U.S. Pat. No. 6,841,063. Embodiments of the present invention utilize such hydroprocessing to convert triglycerides to paraffins. The terms "hydroprocessing" and "hydrotreating" are used interchangeably herein.

[0026] "Isomerizing," as defined herein, refers to catalytic processes that typically convert n-alkanes to branched isomers. ISODEWAXING (Trademark of CHEVRON U.S.A. INC.) catalysts are representative catalysts used in such processes. See, e.g., Zones et al., U.S. Pat. No. 5,300,210; Miller, U.S. Pat. No. 5,158,665, and Miller, U.S. Pat. No. 4,859,312.

[0027] "Transportation fuels," as defined herein, refer to hydrocarbon-based fuels suitable for consumption by vehicles. Such fuels include, but are not limited to, diesel, gasoline, jet fuel and the like.

[0028] "Diesel fuel," as defined herein, is a material suitable for use in diesel engines and conforming to the current version at least one of the following specifications: ASTM D 975—"Standard Specification for Diesel Fuel Oils"; European Grade CEN 90; Japanese Fuel Standards JIS K 2204; The United States National Conference on Weights and Measures (NCWM) 1997 guidelines for premium diesel fuel; and The United States Engine Manufacturers Association recommended guideline for premium diesel fuel (FQP-1A).

[0029] The term "biodiesel," as used herein, refers to diesel fuel that is at least significantly derived from a biological source, and which is generally consistent with ASTM International Standard Test Method D-6751. Often, biodiesel is blended with conventional petroleum diesel. B20 is a blend of 20 percent biodiesel with 80 percent conventional diesel. B100 denotes pure biodiesel.

[0030] "Conventional biodiesel," as defined herein, refers to ester-based biodiesel produced via a transesterification of triglyceride-containing vegetable oils.

[0031] The term "hybrid diesel biofuel," as used herein, specifically refers to diesel produced via the co-processing (hydrotreating+isomerizing) of vegetable oil and conventional (petroleum) diesel, in accordance with methods and system of the present invention.

[0032] "Pour point," as defined herein, represents the lowest temperature at which a fluid will pour or flow. See, e.g., ASTM International Standard Test Methods D 5950-96, D 6892-0.3, and D 97.

[0033] "Cloud point," as defined herein, represents the temperature at which a fluid begins to phase separate due to crystal formation. See, e.g., ASTM Standard Test Methods D 5773-95, D 2500, D 5551, and D 5771.

[0034] As defined herein, "C_n," where "n" is an integer, describes a hydrocarbon or hydrocarbon-containing molecule or fragment (e.g., an alkyl or alkenyl group) wherein "n" denotes the number of carbon atoms in the fragment or molecule—irrespective of linearity or branching.

3. METHODS

[0035] As mentioned previously, and with reference to FIG. **1**, in some embodiments the present invention is directed to one or more methods for co-processing vegetable oil with conventional diesel to yield a hybrid (bio)diesel fuel product, said methods generally, comprising the steps of: (Step **101**) combining vegetable oil with diesel fuel to form a first mixture, wherein the vegetable oil comprises not more than 10 weight percent of said first mixture; (Step **102**) hydrotreating the first mixture to yield a second mixture, wherein triglyceride components of the first mixture are deoxygenated, and wherein at least 95 atomic percent of the sulfur present in the first mixture is converted to H_2S in the second mixture; (Step **103**) isomerizing the second mixture in the presence of an isomerization catalyst to yield a third mixture comprising hybrid diesel fuel having a cloud point that is lower than that of the second mixture, wherein H_2S in the second mixture has not been removed prior to isomerizing; and (Step **104**) isolating the hybrid diesel fuel of the third mixture to yield a hybrid diesel fuel product.

[0036] In some such above-described method embodiments, the isomerization catalyst is sufficiently-tolerant of sulfur so as to make it unnecessary to remove the H_2S (from the second mixture) prior to isomerizing. In some such embodiments, the first mixture comprises a nitrogen content greater than 50 ppm. In some or other such embodiments, the first mixture comprises a nitrogen content of up to about 500 ppm.

[0037] In some such above-described embodiments, the step of isomerizing results in superior fuel properties relative to those of the non-isomerized paraffinic (i.e., n-paraffin or n-alkane) product—although the n-paraffinic product itself could find use as a fuel or other commodity. One such fuel property that can be improved by isomerization is cloud point, i.e., isomerization can lower the cloud point of a mixture.

[0038] Typically, isomerization is carried out using an isomerization catalyst. Such isomerization catalysts have traditionally comprised Pt or Pd on a support such as SAPO-11, SM-3, SSZ-32, ZSM-23, ZSM-22, and similar such supports; and/or on an acidic support material such as beta or zeolite Y molecular sieves, SiO_2, Al_2O_3, SiO2-Al_2O_3, and combinations thereof. Traditionally, the isomerization is carried out at a temperature between about 500° F. and about 750° F. The operating pressure is typically 200 to 2000 pounds-force per square inch gauge (psig), and more typically 200 psig to 1000 psig. Hydrogen flow rate is typically 50 to 5000 standard cubic feet/barrel (SCF/barrel). For other suitable isomerization catalysts, see, e.g., Zones et al., U.S. Pat. No. 5,300,210; Miller, U.S. Pat. No. 5,158,665; and Miller. U.S. Pat. No. 4,859,312.

[0039] An important advantage of the present invention is the ability to eliminate interstage removal of H_2S/NH_3 between hydrotreating and isomerization, this ability provided by an isomerization catalyst that is sulfur- and nitrogen-tolerant. Accordingly, in some such above-described embodiments, the isomerization catalyst comprises an active metal catalyst (e.g., Pt) on a support such as any of those described in Miller, U.S. patent application Ser. No. 12/181,652, filed Jul. 29, 2008, and incorporated by reference herein. Generally, the silicoaluminophosphate support described in Miller is designated as SM-7, this support being isostructural with conventional SAPO-11. Accordingly, in some or other such above-described embodiments, the isomerization catalyst comprises Pt (and/or other active metal, such as Pd) on an SAPO-11 support. Reaction conditions for such isomerizing are typically within the parameters of traditional isomerization methods (see above).

[0040] With regard to the catalytically-driven isomerizing step described above, in some embodiments, the methods described herein may be conducted by contacting the n-paraffinic product with a fixed stationary bed of catalyst, with a fixed fluidized bed, or with a transport bed. In one presently contemplated embodiment, a trickle-bed operation is employed, wherein such feed 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., U.S. Pat. Nos. 6,204,426 and 6,723,889.

[0041] In some such above-described method embodiments, the vegetable oil originates from a biomass source selected from the group consisting of crops, vegetables, microalgae, and combinations thereof. Accordingly, the term "vegetable oil" is actually quite broad and can generally be extended to include any biologically-derived oil (see above definitions). Those of skill in the art will recognize that generally any biological source of lipids can serve as a biomass source from which a biologically-derived oil (e.g., vegetable oil) comprising triglycerides can be obtained. It will be further appreciated that some such sources are more economical and more amenable to regional cultivation, and also that those sources from which food is not derived may be additionally attractive (so as not to be seen as competing with food). Exemplary vegetable oils/oil sources include, but are not limited to, canola, soy, rapeseed, palm, peanut, jatropha, yellow grease, algae, and the like.

[0042] In some such above-described method embodiments, the step of hydrotreating involves a hydroprocessing/hydrotreating catalyst and a hydrogen-containing environment. For a general review of hydroprocessing/hydrotreating, see, e.g., Rana et al., "A Review of Recent Advances on Process Technologies for Upgrading of Heavy Oils and Residua," Fuel, vol. 86, pp. 1216-1231, 2007. For an example of how triglycerides can be hydroprocessed to yield a paraffinic product, see Craig et al., U.S. Pat. No. 4,992,605.

[0043] In some such above-described method embodiments, the step of hydrotreating involves or otherwise utilizes a hydrotreating catalyst comprising an active metal or metal-alloy hydrotreating catalyst component that is operationally integrated with a refractory support material. In some such embodiments, active metal catalyst component is selected from the group consisting of cobalt-molybdenum (Co—Mo) catalyst, nickel-molybdenum (Ni—Mo) catalyst, noble metal catalyst, and combinations thereof. In these or other embodiments, the refractory support material typically comprises a refractory oxide support such as, but not limited to, Al_2O_3, SiO_2—Al_2O_3, and combinations thereof. In some particular embodiments, the hydrotreating step makes use of an alumina-supported nickel-molybdenum catalyst.

[0044] In some such above-described method embodiments, the hydrotreating is carried out at a temperature between 550° F. and 800° F. In some such embodiments, the hydrotreating is carried out under a H_2 partial pressure of between 400 psig and 2000 psig. In some or other such embodiments, the hydrotreating is carried out under a H_2 partial pressure of between 500 psig and 1500 psig.

[0045] As hydrotreating effectively removes sulfur (in the form of H_2S), in some embodiments the second mixture has, exclusive of H_2S, a reduced sulfur content of typically not more than 20 ppm, and of preferably not more than 10 ppm. Note that hydrotreating also permits the removal of oxygen (in the form of H_2O).

[0046] Hydrotreating can also affect the cloud point, typically lowering the cloud point of the second mixture relative to that of the first mixture. In some such embodiments, the second mixture has cloud point of −6° C. or less, while in some or other embodiments, the second mixture has a cloud point of −8° C. or less.

[0047] Isolation of the hybrid diesel (bio)fuel from the third mixture is achieved simply by removing any H_2S present, where H_2S removal at this stage is typically easier than its removal between the hydrotreating and isomerizing steps. In some embodiments, isolation of the hybrid diesel fuel is at least partly achieved by stripping the third mixture of H_2S.

[0048] Typically, the method embodiments of the present invention produce a hybrid diesel (bio)fuel that is low in sulfur content. In some embodiments, the hybrid diesel fuel has, exclusive of H_2S, a sulfur content of not more than 20 ppm, and in some such embodiments of not more than 10 ppm.

[0049] Isomerization of the second mixture, as described in method embodiments above, can reduce its pour point so as to yield a hybrid diesel biofuel with a pour point that is less than that of the second mixture. In some such embodiments, the hybrid diesel fuel has a cloud point of −10 ° C. or less.

4. SYSTEMS

[0050] As already mentioned in a previous section, and with reference to FIG. **2**, in some embodiments the present invention is directed to one or more systems **200** for co-processing vegetable oil with petroleum diesel so as to afford the production of such above-described hybrid diesel fuel and/or to implement any or all of the aforementioned methods. Accordingly, and still referring to FIG. **2**, in some or other such embodiments, the present invention is generally directed to one or more systems for generating a hybrid diesel fuel product, such systems generally comprising: a mixing unit **201** for combining vegetable oil with diesel fuel so as to form a first mixture, wherein the vegetable oil comprises not more than 10 weight percent of said first mixture; a hydrotreating unit **202** for hydrotreating the first mixture to yield a second mixture, wherein said unit is operable for deoxygenating triglyceride components of the first mixture, and wherein at least 95 atomic percent of the sulfur present in the first mixture is converted to H_2S in the second mixture; and an isomerization unit **203** for isomerizing the second mixture in the presence of an isomerization catalyst to yield a third mixture comprising hybrid diesel fuel having a cloud point that is lower than that of the second mixture, wherein H_2S in the second mixture has not been removed prior to isomerizing.

[0051] In some such above-described system embodiments, system **100** further comprises an isolation unit **204** for isolating the hybrid diesel fuel in the third mixture so as to yield a hybrid diesel fuel product. In some or other such embodiments, the isolation unit comprises an H_2S stripping unit.

[0052] A preferred isomerization unit is one that utilizes an ISODEWAXING catalyst, preferably containing SM-7 or SSZ-32. In some or other such embodiments, the isomerization catalyst comprises Pt on an SM-7 support.

[0053] Generally, all of the above-described system units are configured for processing a vegetable oil in accordance with the methods described in Section 3. Further, there is typically a proximal relationship between the various units that comprise system **200**, but this need not always be the case. Such relationships may be influenced by existing infrastructure and other economic considerations.

5. VARIATIONS

[0054] In some variously-contemplated alternative embodiments, the intermediate (second) mixture is catalytically-isomerized to an isomerized intermediate mixture prior to separation into various components. Accordingly, method/system parameters cain be configured to produce hybrid (bio) fuels other than diesel. Such variation results in additional method and corresponding system embodiments having alternative step and component sequences, but otherwise generally as described for the embodiments above.

[0055] As stated and/or implied above, persons of skill in the art will recognize that other vegetable or crop oils and/or algae-derived oils could also be used, and that even animal fats (e.g., beef tallow) could be used, at least in part, in the methods/systems of the present invention in a manner analogous to that of the vegetable oil. Additionally, there can be a delicate interplay of economics, renewables, and fuel properties (e.g., cloud point) in determining the composition of the starting mixture and, as a result, the final product.

6. EXAMPLE

[0056] The following example is provided to demonstrate particular embodiments of the present invention. It should be appreciated by those of skill in the art that the methods/systems disclosed in the example which follows merely represent exemplary embodiments of the present invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present invention.

EXAMPLE

[0057] This Example serves to illustrate an exemplary system for implementing a method embodiment of the present invention, so as to produce a hybrid diesel biofuel.

[0058] Using for isomerization a catalyst of Pt on SM-7, a 95/5 diesel/canola oil mixture, having approximately 500 ppm sulfur (S), was hydroprocessed (hydrodesulfurization, HDS) in a hydrotreating unit to yield a hybrid diesel intermediate. Note that, upon hydrotreating, diesel processed Without canola oil is much reduced in sulfur content (below 6 ppm), but has a relatively high cloud point (i.e., −7° C.; see Table 1, vide infra). With canola oil added, this hybrid diesel intermediate mixture was processed in an isomerization unit employing an ISODEWAXING (IDW) catalyst (Pt on SM-7) to yield a hybrid diesel product having a relatively low cloud point (−13° C.). This lower cloud point allows the diesel to be used in colder climates. No interstage removal of H_2S and NH_3 was required, with the total effluent from the first (hydrotreating) stage going to the second (isomerizing) stage.

[0059] Table 1 below compares yields/properties of products that resulted from diesel and diesel/canola oil feeds having been processed in accordance with some embodiments of the present invention. Processing conditions were as follows: HDS at 0.7 LHSV, ISODEWAXING at 1.8 LHSV 700 psig total pressure, 525 psig H_2 pressure, and 1300 SCFB H_2.

TABLE 1

		Diesel	Diesel	95/5 Wt % Diesel/Canola Oil
HDS Catalyst		65 Co—Mo/Al_2O_3 35 Ni—Mo/Al_2O_3	65 Co—Mo/Al_2O_3 35 Ni—Mo/Al_2O_3	65 Co—Mo/Al_2O_3 35 Ni—Mo/Al_2O_3
HDS Temperature (° F.)		650	650	650
IDW Catalyst			Pt/SM-7	Pt/SM-7
IDW Temperature (° F.)			670	684
Conversion < 350° F.		0.6	2.6	3.5
Yields (Wt. %)	CO_2			0.03
	H_2O			0.5
	C_1-C_2	0.05	0.08	0.18
	C_3	0.06	0.16	0.36
	C_4	0.08	0.26	0.20
	C_5 - 180° F.	0.25	0.95	0.81
	180-350° F.	7.99	8.79	9.17
	350° F.+	91.88	90.11	89.20
Pour Point (° F.)		−11	−17	−14
Cloud Point (° F.)		−7	−13	−13

[0060] Because of the high activity of the isomerization catalyst, it can be operated at 684° F., not much higher than the 650° F. of the hydrotreating catalyst. This will extend the run life of the system, and also makes possible the use of the isomerization catalyst downstream of the hydrotreating catalyst in the same reactor (although separate reactors are preferred).

7. CONCLUSION

[0061] The foregoing describes methods and systems for co-processing vegetable oil and petroleum diesel to yield a hybrid diesel biofuel composition. As previously stated, in some embodiments the present invention is directed to methods/systems by/with which a mixture of vegetable oil and petroleum diesel is co-processed in two stages; the mixture is first hydrotreated to yield a reduced-sulfur hybrid intermediate, and then the hybrid intermediate is processed in an isomerization unit to yield a low cloud point hybrid diesel product that is partially derived from biomass. A notable benefit of at least some such methods/systems is that interstage removal of H_2S and NH_3 is not required between the stages of hydrotreating and isomerizing.

[0062] All patents and publications referenced herein are hereby incorporated by reference to the extent not inconsistent herewith. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.

What I claimed:

1. A method comprising the steps of:

a) combining vegetable oil with diesel fuel to form a first mixture, wherein the vegetable oil comprises riot more than 10 weight percent of said first mixture;

b) hydrotreating the first mixture to yield a second mixture, wherein triglyceride components of the first mixture are deoxygenated, and wherein at least 95 atomic percent of the sulfur present in the first mixture is converted to H_2S in the second mixture;

c) isomerizing the second mixture in the presence of an isomerization catalyst to yield a third mixture comprising hybrid diesel fuel having a cloud point that is lower than that of the second mixture, wherein H_2S in the second mixture has not been removed prior to isomerizing; and

d) isolating the hybrid diesel fuel of the third mixture to yield a hybrid diesel fuel product.

2. The method of claim **1**, wherein the first mixture comprises a nitrogen content greater than 50 ppm.

3. The method of claim **1**, wherein the first mixture comprises a nitrogen content of up to about 500 ppm.

4. The method of claim **1**, wherein the isomerization catalyst comprises Pt on an SM-7 support.

5. The method of claim **1**, wherein the isomerization catalyst comprises Pt on an SAPO-11 support.

6. The method of claim **1**, wherein the vegetable oil comprises one or more biologically-derived oils selected from the group consisting of canola, soy, rapeseed, palm, peanut, jatropha, yellow grease, algae, and combinations thereof.

7. The method of claim **1**, wherein the step of hydrotreating involves a hydrotreating catalyst comprising a metal or metal-alloy active hydrotreating catalyst component selected from the group consisting of cobalt-molybdenum (Co—Mo) catalyst, nickel-molybdenum (Ni—Mo) catalyst, noble metal catalyst, and combinations thereof.

8. The method of claim **7**, wherein the hydrotreating catalyst comprises a refractory oxide support.

9. The method of claim **7**, wherein the hydrotreating catalyst comprises a support component selected from the group consisting of Al_2O_3 and SiO_2—Al_2O_3.

10. The method of claim **1**, wherein the hydrotreating utilizes an alumina-supported nickel-molybdenum catalyst.

11. The method of claim **1**, wherein the hydrotreating is carried out at a temperature between 550° F. and 800° F.

12. The method of claim **1**, wherein the hydrotreating is carried out under a H_2 partial pressure of between 400 psig and 2000 psig.

13. The method of claim **1**, wherein the hydrotreating is carried out under a H_2 partial pressure of between 500 psig and 1500 psig.

14. The method of claim **1**, wherein the second mixture has, exclusive of H_2S, a sulfur content of not more than 20 ppm.

15. The method of claim **1**, wherein the second mixture has cloud point of −8° C. or less.

16. The method of claim **1**, wherein the hybrid diesel fuel has, exclusive of H_2S, a sulfur content of not more than 10 ppm.

17. The method of claim **1**, wherein the hybrid diesel fuel has a cloud point of −10° C. or less.

18. The method of claim **1**, wherein isolation of the hybrid diesel fuel is at least partly achieved by stripping the third mixture of H_2S.

19. A system for generating a hybrid diesel fuel product, said system comprising:

a) a mixing unit for combining vegetable oil with diesel fuel so as to form a first mixture, wherein the vegetable oil comprises not more than 10 weight percent of said first mixture;

b) a hydrotreating unit for hydrotreating the first mixture to yield a second mixture, wherein said unit is operable for deoxygenating triglyceride components of the first mixture, and wherein at least 95 atomic percent of the sulfur present in the first mixture is converted to H_2S in the second mixture; and

c) an isomerization unit for isomerizing the second mixture in the presence of an isomerization catalyst to yield a third mixture comprising hybrid diesel fuel having a cloud point that is lower than that of the second mixture, wherein H_2S in the second mixture has not been removed prior to isomerizing.

20. The system of claim **19** further comprising an isolation unit for isolating the hybrid diesel fuel in the third mixture so as to yield a hybrid diesel fuel product.

21. The system of claim **20**, wherein the isomerization catalyst comprises Pt on an SM-7 support.

22. The system of claim **20**, wherein the isolation unit comprises an H_2S stripping unit.

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