

FUEL AND BASE OIL BLENDSTOCKS FROM A SINGLE FEEDSTOCK

TECHNICAL FIELD

[001] The invention relates generally to methods for making transportation fuel and base oil blendstocks from biomass-derived compositions.

BACKGROUND

[002] Transportation fuel and base oil blendstocks produced from biomass are of increasing interest since they are derived from renewable resources and may provide an attractive alternative and/or supplement to similar petroleum-derived products. Conventional processes for producing fuel and base oil blendstocks from biomass often employ separate fuel and base oil trains requiring duplicate reactors (and associated equipment) and the production of fuels has typically required a hydroisomerization step.

[003] Conventional approaches for converting vegetable oils or other fatty acid derivatives into transportation fuels may comprise transesterification, catalytic hydrotreatment, hydrocracking, catalytic cracking without hydrogen, and thermal cracking, among others.

[004] Triglycerides may be transesterified to produce a fatty acid alkyl ester, most commonly a fatty acid methyl ester (FAME). Conventional FAME is primarily composed of methyl esters of C_{18+} saturated fatty acids. The poor low temperature properties of conventional FAME however have limited its wider use in regions with colder climatic conditions. Generally, the introduction of at least one double bond into the FAME molecule is needed in order to improve its low temperature properties. However, FAME molecules derived from unsaturated fatty acids contribute to poor oxidation stability of the fuel and to deposit formation.

[005] Triglycerides may be hydrotreated to conventionally produce a normal C_{18+} paraffin product. However, the poor low temperature properties of the normal C_{18+} paraffin product limit the amount of product that can be blended in conventional diesel fuels in the summer time and prevent its use during the winter time. The normal C_{18+} paraffinic product may be further isomerized to a C_{18+} isoparaffinic product in order to lower the pour point.

[006] There is a need to develop methods for efficiently processing, often simultaneously, biomass-derived compositions into a broader range of lubricants and fuel types having improved low temperature properties wherein the lubricants and fuels may

be produced with reduced capital equipment requirements and with reduced hydrogen consumption.

SUMMARY OF THE INVENTION

[007] In one embodiment, the invention relates to a method comprising the steps of providing a quantity of biologically-derived oil comprising triglycerides; processing the biologically derived oil so as to transesterify at least some of the triglycerides contained therein to yield a quantity of saturated monoesters and unsaturated monoesters; oligomerizing at least some of the unsaturated monoesters to yield a quantity of fatty acid ester oligomers; separating at least some of the saturated monoesters from the fatty acid ester oligomers; and hydrotreating at least some of the fatty acid ester oligomers to yield a quantity of alkanes.

[008] The foregoing has outlined rather broadly the features of the 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

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

[010] Fig. 1 depicts a process flow diagram of an embodiment of the invention.

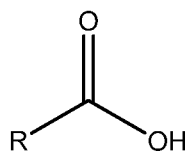
DETAILED DESCRIPTION

[011] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[012] The term “biologically-derived oil” 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, animals and combinations thereof. 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*, 72, 28-29 (1994).

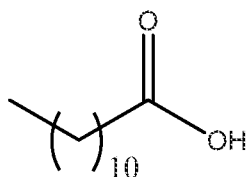
[013] The term “fatty acyl” refers to a generic term for describing fatty acids, their conjugates and derivatives, including esters, and combinations thereof. Fatty acyls encompass the esters derived from the reaction of fatty acids with alcohols. These esters may include fatty acid alkyl esters, such as fatty acid methyl esters, and fatty acid esters of glycerol, such as mono, di, and triglycerides. In the triglycerides, the three hydroxyl groups of glycerol are esterified.

[014] The term “fatty acid” refers to a class of organic acids, having between 4 and 24 carbon atoms, of the general formula:



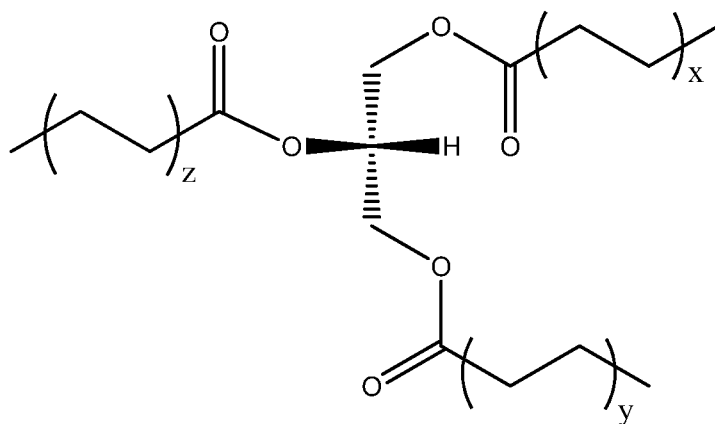
wherein R is generally a saturated (alkyl) hydrocarbon chain or a mono- or poly-unsaturated (alkenyl or olefinic) hydrocarbon chain.

[015] The term “acyl carbon atom chain” denotes the $-C(=O)R$ group, wherein R is as defined above. Thus, for example, lauric acid which has the structure



may be described as having a C_{12} acyl carbon atom chain.

[016] The term “triglyceride” 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.

[017] The term “esterification” refers to the reaction between a fatty acid and an alcohol to yield an ester species.

[018] The term “transesterification” refers to the reaction in which an alkoxy group of an ester compound is exchanged with another alkoxy group via the reaction of the ester with an alcohol, usually in presence of a catalyst. In the present invention, a transesterification occurs between triglycerides, or diglycerides, or monoglycerides, or mixtures thereof, and an alcohol (such as methanol or ethanol) to produce fatty acid alkyl esters and glycerol.

[019] The term “oligomerization” refers to the additive reaction of like or similar molecules (i.e., “mers”) to form a larger molecule. For example, unsaturated fatty acids can react or combine via the double bonds in their structures. When two such species combine to form a larger molecule, the resulting species is termed a “dimer.” When, for example, the aforementioned fatty acid components contain multiple regions of unsaturation, oligomers comprised of three or more mers are possible (e.g., “trimers”).

[020] The term “hydroprocessing” refers to processes wherein a hydrocarbon-based material reacts 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. Examples of such processes are disclosed in U.S. Pat. No. 6,630,066 and U.S. Pat. No. 6,841,063. Embodiments of the invention utilize such hydroprocessing to convert fatty acyls to paraffins. The terms “hydroprocessing” and “hydrotreating” are used interchangeably herein.

[021] The term “hydroisomerization” refers to a process in which a normal paraffin is converted at least partially into an isoparaffin by the use of hydrogen and a catalyst. Isomerization dewaxing catalysts are representative catalysts used in such processes (see U.S. Pat. No. 5,300,210; U.S. Pat. No. 5,158,665; and U.S. Pat. No. 4,859,312).

[022] The term “transportation fuels” refers to hydrocarbon-based fuels suitable for consumption by vehicles. Such fuels include, but are not limited to, diesel, gasoline, jet fuel and the like.

[023] The term diesel fuel refers to hydrocarbons having boiling points in the range of from 350°F to 700°F (177°C to 371°C).

[024] The term “base oil” refers a hydrocarbon fluid having a kinematic viscosity at 100°C between 1.5 and 74.9 mm²/s. It is a hydrocarbon fluid to which other

oils or substances may be added to produce a lubricant. Base oils are generally classified by the American Petroleum Institute (API Publication Number 1509, Appendix E) into one of five general categories: Group I base oils contain $< 90\%$ saturates and/or $> 0.03\%$ sulfur and have a viscosity index ≥ 80 and < 120 ; Group II base oils contain $\geq 90\%$ saturates and $\leq 0.03\%$ sulfur and have a viscosity index ≥ 80 and < 120 ; Group III base oils contain $\geq 90\%$ saturates and $\leq 0.03\%$ sulfur and have a viscosity index ≥ 120 ; Group IV base oils are polyalphaolefins; Group V base oils include all other base oils not included in Group I, II, III, or IV.

[025] The term “cloud point” refers to the temperature of a liquid when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions (see ASTM D2500).

[026] The term “C_n” refers to 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. The term “C₃₆₊” refers to a hydrocarbon or hydrocarbon-containing molecule or fragment having 36 or more carbon atoms in the molecule or fragment.

[027] 1. Compositions: In one embodiment, the biologically-derived oil originates from a biomass source selected from the group consisting of crops, vegetables, microalgae, animal sources and combinations thereof. Those of skill in the art will recognize that generally any biological source of fatty acyl compounds can serve as the biomass from which the biologically-derived oil 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. Exemplary biologically-derived oils/oil sources include, but are not limited to, canola, castor, soy, rapeseed, palm, coconut, peanut, jatropha, yellow grease, algae, and combinations thereof to meet the composition objectives. In one embodiment, the fatty acyl mixture is a triglyceride wherein the fatty acid groups have two or three different chain lengths to meet the composition objectives. In another embodiment, the fatty acyl mixture is a blend of triglycerides to meet the composition objectives. In yet another embodiment, the fatty acyl mixture is derived from the at least partial hydrolysis of triglycerides to meet the composition objectives.

[028] The hydrolysis, or splitting, of fats/oils to produce fatty acids and glycerol can be achieved by a number of methods: high pressure hydrolysis without a catalyst, medium-pressure autoclave hydrolysis with a catalyst, the ambient pressure Twitchell

process with a catalyst, and enzymatic hydrolysis. For more on the hydrolysis of fats/oils see, N.O.V. Sonntag, "Fat Splitting," *J. Am. Oil Chem. Soc.*, 56 (II), 729A-732A, (1979); N.O.V. Sonntag, "New Developments in the Fatty Acid Industry," *J. Am. Oil Chem. Soc.*, 56 (II), 861A-864A, (1979); V. J. Muckerheide, *Industrial Production of Fatty Acids: Fatty Acids; Their Chemistry, Properties, Production and Uses, Part 4*, 2nd ed., Interscience Publishers, 2679-2702 (1967); and M.W. Linfield et al., "Enzymatic Fat Hydrolysis and Synthesis," *J. Am. Oil Chem. Soc.*, 61, 191-195 (1984).

[029] In one embodiment, the biologically-derived oil has a C₁₀-C₁₆ acyl carbon atom chain content of at least 30 wt. % wherein at least 80% of the C₁₀-C₁₆ acyl carbon atom chains are saturated; and a C₁₈-C₂₂ acyl carbon atom chain content of at least 20 wt. % wherein at least 50% of the acyl C₁₈-C₂₂ carbon atom chains contain at least one double bond.

[030] In a first sub-embodiment, the biologically-derived oil has a C₁₀-C₁₆ acyl carbon atom chain content of at least 40 wt. %; in a second sub-embodiment, a C₁₀-C₁₆ acyl carbon atom chain content of at least 50 wt. %; in a third sub-embodiment, a C₁₀-C₁₆ acyl carbon atom chain content of at least 60 wt. %; in a fourth sub-embodiment, a C₁₀-C₁₆ acyl carbon atom chain content of at least 70 wt. %; in a fifth sub-embodiment, a C₁₀-C₁₆ acyl carbon atom chain content of no more than 80 wt. %.

[031] In a sixth sub-embodiment, the biologically derived oil has a C₁₈-C₂₂ acyl carbon atom chain content of at least 30%; in a seventh sub-embodiment, a C₁₈-C₂₂ acyl carbon atom chain content of at least 40 wt. %; in an eighth sub-embodiment, a C₁₈-C₂₂ acyl carbon atom chain content of at least 50 wt. %; in a ninth sub-embodiment, a C₁₈-C₂₂ acyl carbon atom chain content of at least 60 wt. %; in a tenth sub-embodiment, a C₁₈-C₂₂ acyl carbon atom chain content of no more than 70 wt. %.

[032] 2. Methods: Referring now to Figure 1, one embodiment of the present invention is directed to a method comprising the steps of: (Step 101) a providing a quantity of biologically-derived oil comprising triglycerides; (Step 102) processing the biologically derived oil so as to transesterify at least some of the triglycerides contained therein to yield a quantity of saturated monoesters and unsaturated monoesters; (Step 103) oligomerizing at least some of the unsaturated monoesters to yield a quantity of fatty acid ester oligomers; (Step 104) separating at least some of the saturated monoesters from the fatty acid ester oligomers; and (Step 105) hydrotreating at least some of the fatty acid ester oligomers to yield a quantity of alkanes.

[033] In some such above-described method embodiments, there is a sub-step of providing a biologically-derived oil. Such steps are generally consistent with those as described in Section 1.

[034] In some such above-described method embodiments, there is a sub-step of processing the biologically derived oil so as to transesterify at least some of the triglycerides contained therein to yield a quantity of saturated monoesters and unsaturated monoesters. Transesterification is usually accomplished by reacting a triglyceride feedstock with a molar excess of an alcohol in the presence of a catalyst. Typically, the transesterification is carried out at a temperature of between 60°C to 70°C and at a pressure of between 0.1 and 2 MPa. The catalyst may be basic (for example, NaOH, KOH, NaOMe, or KOMe) or acidic (for example, H₂SO₄ or HCl). The alcohol may be a C₁-C₄ alcohol, typically methanol or ethanol. In one embodiment, the saturated monoesters are C₁₀-C₁₆ monoesters and the unsaturated monoesters are C₁₈-C₂₂ monoesters. In one embodiment, the saturated monoesters are utilized as a transportation fuel. In another embodiment, the saturated monoesters are utilized as a component of a transportation fuel. In such embodiments wherein the saturated monoesters are operable for use as (or in) a transportation fuel, the transportation fuel is a diesel fuel. Methods for the transesterification of triglycerides are well known in the art (see, for example, U.S. Pat. Nos. 2,360,844; 2,383,632 and 2,383,633).

[035] In some such above-described method embodiments, there is a sub-step of oligomerization to yield a quantity of fatty acid ester oligomers. In one embodiment, the fatty acid ester oligomers are C₃₆₊ fatty acid ester oligomers. While not intending to be bound by theory, the above-described oligomerization is thought to occur via additive coupling reactions between fatty acid components having regions of unsaturation. Such oligomerization can be effected via thermal, catalytic, and/or chemical means. Exemplary catalysts include SiO₂-Al₂O₃, zeolites, and clays, such as bentonite and montmorillonite. In some such above-described method embodiments, the oligomerized mixture comprises an oligomer component, wherein the oligomer component of the mixture comprises at least about 50 wt. % dimer (dimeric) species (i.e., dimers resulting from the dimerization of unsaturated fatty acid components). Generally, the oligomerization is conducted over a clay catalyst, in the absence of added hydrogen, at a temperature in range of 300°F to 700°F (140°C to 371°C), at a liquid hourly space velocity in the range of 0.5-10 h⁻¹, and at a pressure such that the feed is in the liquid phase. The oligomerization may occur in the presence of added hydrogen provided that a

hydrogenating metal catalyst is not present. Methods for the oligomerization of unsaturated fatty acids are well known in the art (see, for example, U. S. Patent Nos. 2,793,219; 2,793,220; 3,422,124; 3,632,822; and 4,776,983).

[036] In some such above-described embodiments, there is a sub-step of separation. While those of skill in the art will recognize that a variety of separation techniques can be suitably employed, in some such above-described method embodiments the separating step comprises distillation. In one embodiment, the step of distilling employs a vacuum distillation unit to separate the saturated monoesters and fatty acid ester oligomers into individual fractions. Generally, the fatty acid ester oligomers are collected in a high-boiling fraction and the saturated monoesters are collected in a low-boiling fraction.

[037] In some such above-described method embodiments, there is a sub-step of hydrotreating at least some of the fatty acid ester oligomers to yield a quantity of alkanes. In one embodiment, the alkanes are C₃₆₊ alkanes. Hydrotreating removes oxygen from the fatty acyls to produce primarily a normal paraffin product. Hydrotreating involves a hydroprocessing/hydrotreating catalyst and a hydrogen-containing environment. In some such embodiments, the active hydroprocessing catalyst component is a metal or alloy selected from the group consisting of cobalt-molybdenum (Co-Mo) catalyst, nickel-molybdenum (Ni-Mo) catalyst, nickel-tungsten (Ni-W) catalyst, noble metal catalyst, and combinations thereof. Such species are typically supported on a refractory oxide support (e.g., alumina or SiO₂-Al₂O₃). Hydrotreating conditions generally include a temperature in the range of 290°C to 430°C and a hydrogen partial pressure generally in the range of 400 pounds-force per square inch gauge (psig) to 2000 psig, typically in the range of 500 psig to 1500 psig. 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*, 86, 1216-1231 (2007). Methods for hydroprocessing triglycerides to yield a paraffinic product are well known in the art (see, for example, U.S. Pat. No. 4,992,605).

[038] In one embodiment, such above-described methods further comprise a step (Step 104a) of hydrotreating at least some of the saturated monoesters to yield a quantity of diesel fuel blendstock. In one embodiment, the saturated monoesters are C₁₀-C₁₆ monoesters. Such hydrotreating steps are generally consistent with those as described previously.

[039] In conventional processes, C₁₈₊ fatty acids are hydrotreated to produce a normal paraffin product. The normal paraffin product derived from C₁₈₊ fatty acids contributes to pour point problems in diesel fuel. The normal paraffinic product derived from C₁₈₊ fatty acids can be further isomerized to lower its pour point using an isomerization dewaxing catalyst. In contrast, in some embodiments, the methods of the present invention do not require a subsequent isomerization step as the normal paraffin product may be derived from C₁₀-C₁₆ saturated monoesters which contribute less, to very little, of a pour point problem in diesel fuel. The elimination of a subsequent isomerization step also reduces cost, since that step typically requires a separate catalyst bed and/or a separate reactor. In addition, C₁₀-C₁₆ diesel fuel blendstocks can be blended into the diesel pool because the chain lengths are shorter than the normal C₁₈₊ products such that the cloud point will be low enough to have a reduced negative impact on the cloud point of the pool. By oligomerizing the unsaturated fatty acid monoesters, this not only contributes to the production of a valuable base oil product, but also removes those esters from the feed to the diesel hydrotreater, and consequently, from the diesel fuel blendstock, minimizing impact on pour and cloud points.

[040] In one embodiment, the diesel fuel blendstock produced comprises at least 70 wt. % C₁₀-C₁₆ alkanes; in a second embodiment, at least 80 wt. % C₁₀-C₁₆ alkanes; in a third embodiment, at least 90 wt. % C₁₀-C₁₆ alkanes.

[041] The cloud point of the base oil blendstock can be determined by ASTM D2500. In one embodiment, the diesel fuel blendstock has a cloud point of less than -10°C.

[042] In one embodiment, such above-described method embodiments further comprise a step of hydroisomerizing at least some of the alkanes to yield a quantity of base oil blendstock. Generally, the step of hydroisomerizing is carried out using an isomerization catalyst. Suitable such isomerization catalysts can include, but are not limited to Pt or Pd on a support such as, but further not limited to, SAPO-11, SM-3, SM-7, SSZ-32, ZSM-23, ZSM-22; and similar such supports. In some or other embodiments, the step of hydroisomerizing involves an isomerization catalyst comprising a metal selected from the group consisting of Pt, Pd, and combinations thereof. The isomerization catalyst is generally 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 isomerization is carried out at a temperature between 250°C and 400°C, and typically between 290°C and 400°C. The

operating pressure is generally 200 psig to 2000 psig, and more typically 200 psig to 1000 psig. The hydrogen flow rate is typically 50 to 5000 standard cubic feet/barrel (SCF/barrel). Other suitable hydroisomerization catalysts are disclosed in U.S. Pat. No. 5,300,210, U.S. Pat. No. 5,158,665, and U.S. Pat. No. 4,859,312.

[043] With regard to the catalytically-driven hydroisomerizing step described above, in some embodiments, the methods described herein may be conducted by contacting the 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. Illustrations of the operation of such catalysts are disclosed in U.S. Pat. No. 6,204,426 and U.S. Pat. No. 6,723,889.

[044] The viscosity index of the base oil blendstock can be determined by ASTM D2270. In one embodiment, the base oil blendstock has a viscosity index of greater than 120; in a second embodiment, a viscosity index of greater than 130; in a third embodiment, a viscosity index of greater than 140.

[045] The pour point of the base oil blendstock can be determined by ASTM D97. In one embodiment, the base oil blendstock produced has a pour point of less than -10°C .

[046] In one embodiment, the base oil blendstock may be further subjected to an optional hydrofinishing step which generally serves to improve color, and oxidation and thermal stability. In one embodiment, the base oil is utilized as a lubricating base oil blendstock.

[047] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present invention. It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural references unless expressly and unequivocally limited to one reference. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be

substituted or added to the listed items. To an extent not inconsistent herewith, all citations referred to herein are hereby incorporated by reference.

CLAIMS

1. A method comprising the steps of
 - a) providing a quantity of biologically-derived oil comprising triglycerides;
 - b) processing the biologically derived oil so as to transesterify at least some of the triglycerides contained therein to yield a quantity of saturated monoesters and unsaturated monoesters;
 - c) oligomerizing at least some of the unsaturated monoesters to yield a quantity of fatty acid ester oligomers;
 - d) separating at least some of the saturated monoesters from the fatty acid ester oligomers; and
 - e) hydrotreating at least some of the fatty acid ester oligomers to yield a quantity of alkanes.
2. The method of claim 1, wherein the biologically-derived oil has
 - a) a C₁₀-C₁₆ acyl carbon atom chain content of at least 30 wt. % wherein at least 80% of the C₁₀-C₁₆ acyl carbon atom chains are saturated; and
 - b) a C₁₈-C₂₂ acyl carbon atom chain content of at least 20 wt. % wherein at least 50% of the acyl C₁₆-C₂₂ carbon atom chains contain at least one double bond.
3. The method of claim 1, wherein the saturated monoesters are utilized as a transportation fuel.
4. The method of claim 1, wherein the saturated monoesters are utilized as a component of a transportation fuel.
5. The method of claim 1, wherein the separating step comprises distillation.
6. The method of claim 1, wherein the step of hydrotreating involves a hydroprocessing catalyst and a hydrogen-containing environment.

7. The method of claim 6, wherein the hydroprocessing catalyst is selected from the group consisting of cobalt-molybdenum (Co-Mo) catalyst, nickel-molybdenum (Ni-Mo) catalyst, nickel-tungsten (Ni-W) catalyst, noble metal catalyst, and combinations thereof.
8. The method of claim 1 further comprising a step of hydrotreating at least some of the saturated monoesters to yield a quantity of diesel fuel blendstock.
9. The method of claim 8, wherein the step of hydrotreating involves a hydroprocessing catalyst and a hydrogen-containing environment.
10. The method of claim 9, wherein the hydroprocessing catalyst is selected from the group consisting of cobalt-molybdenum (Co-Mo) catalyst, nickel-molybdenum (Ni-Mo) catalyst, nickel-tungsten (Ni-W) catalyst, noble metal catalyst, and combinations thereof.
11. The method of claim 8, wherein the diesel fuel blendstock has a cloud point of less than -10°C.
12. The method of claim 1 further comprising a step of hydroisomerizing at least some of the alkanes to yield a quantity of base oil blendstock.
13. The method of claim 12, wherein the step of hydroisomerizing involves an isomerization catalyst comprising a metal selected from the group consisting of Pt, Pd, and combinations thereof.
14. The method of claim 12, wherein the base oil blendstock has a viscosity index of greater than 120.
15. The method of claim 12, wherein the base oil blendstock is utilized as lubricating base oil blendstock.