

**APPLICATION-SPECIFIC FINISHED LUBRICANT
COMPOSITIONS COMPRISING A BIO-DERIVED ESTER
COMPONENT AND METHODS OF MAKING SAME**

FIELD OF THE INVENTION

[0001] This invention relates to finished lubricant compositions and their manufacture, and specifically to application-specific finished lubricant compositions comprising a diester component—particularly wherein the diester component is at least partially derived from biomass.

BACKGROUND

[0002] Esters have been used as lubricating oils for over 50 years. They are used in a variety of applications ranging from jet engines to refrigeration. In fact, esters were the first synthetic crankcase motor oils in automotive applications. However, esters have largely given way to polyalphaolefins (PAOs) due to the lower cost of PAOs and their formulation similarities to mineral oils. In fully synthetic motor oils, however, esters are almost always used in combination with PAOs to balance the effect on seals, additive solubility, volatility reduction, and energy efficiency improvement by enhanced lubricity.

[0003] Ester-based lubricants, in general, have excellent lubrication properties due to the polarity of the ester molecules of which they are comprised. Due to the polarity of the ester functionality, esters have a stronger affinity for metal surfaces than PAOs and mineral oils. As a result, they are very effective in establishing protective films on metal surfaces, such protective films serving to mitigate the wear of such metals. Such lubricants are less volatile than the traditional lubricants and tend to have much higher flash points and much lower vapor pressures. Ester lubricants are excellent solvents and dispersants, and can readily solvate and disperse the degradation by-products of oils, i.e., they greatly reduce sludge buildup. While ester lubricants are relatively stable to thermal and oxidative processes, the ester functionalities give microbes a handle with which to do their biodegrading more efficiently and more effectively than their mineral oil-based

analogues—thereby rendering them more environmentally-friendly. However, as previously alluded to, the preparation of esters is more involved and more costly than that of their PAO counterparts.

[0004] Recently, novel diester-based lubricant compositions and their corresponding manufacture have been described in Miller et al., United States Patent Application Publication No. 20080194444 A1, published Aug. 14, 2008; and in Miller et al., United States Patent Publication No. 20090198075 A1, published Aug. 6, 2009. The diester syntheses described in these patent applications render the economics of diester lubricant formulations more favorable.

[0005] In view of the foregoing, and notwithstanding such above-described advances, further integration of such diester-based lubricant synthesis with one or more other processes, particularly those further involving the conversion of low value by-products into application-specific finished lubricant compositions, can further shift the economics of ester-based lubricant manufacture in a favorable direction.

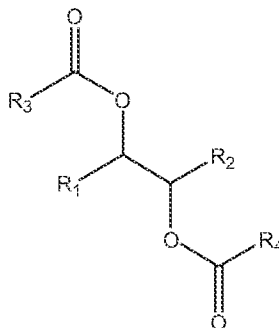
BRIEF DESCRIPTION OF THE INVENTION

[0006] The present invention is generally directed to methods of making application-specific finished lubricant compositions comprising bio-derived diester species. In some embodiments, bio-derived fatty acid moieties are reacted with Fischer-Tropsch (FT)/gas-to-liquids (GTL) reaction products and/or by-products (i.e., α -olefins) to yield bio-derived diester species that can then be selectively blended with base stock (oil) and one or more additive species to yield an application-specific finished lubricant product having a biomass-derived component.

[0007] In some embodiments, the present invention is directed to processes for making such above-mentioned finished lubricant compositions, said processes generally comprising the steps of: (a) preparing a quantity of epoxidized olefins, wherein said step of preparing comprises the sub-steps of: (i) isolating alpha-olefins (α -olefins) made from a gas-to-liquids process to yield isolated α -olefins; (ii) isomerizing at least a majority of the isolated α -olefins to yield a quantity of internalized olefins; and (iii) epoxidizing at least a majority of the internalized olefins to form a quantity of epoxidized olefins comprising an epoxide ring; and (b) obtaining a quantity of esterification agents, the

esterification agents being derived from triglyceride-borne fatty acid moieties, whereby said derivation yields esterification agents selected from the group consisting of carboxylic acids, acyl halides, acyl anhydrides, and combinations thereof; wherein the step of obtaining comprises the sub-steps of: (i') selecting a biomass source comprising triglycerides, said triglycerides comprising fatty acid moieties of appropriate length; (ii') liberating a majority of the fatty acid moieties from the triglyceride molecules of which they are a component so as to yield esterification agents; (c) esterifying at least a majority of the epoxidized olefins with the esterification agents so as to yield a quantity of diester species; and (d) combining the quantity of diester species with a quantity of base oil and an additive component comprising at least one additive selected from the group consisting of antioxidants, detergents, anti-wear agents, metal deactivators, corrosion inhibitors, rust inhibitors, friction modifiers, anti-foaming agents, viscosity index improvers, demulsifying agents, emulsifying agents, tackifiers, complexing agents, extreme pressure additives, pour point depressants, and combinations thereof; wherein selection of the at least one additive is directed largely by the end-use of the lubricant composition being made, wherein said lubricant composition can be of a type selected from the group consisting of turbine oils, metalworking fluids, hydraulic fluids, compressor oils, chain oils, farm equipment engine oils, tractor hydraulic fluids, marine oils, paper machine oils, spindle and textile oils, trailer wheel bearing greases, and combinations thereof.

[0008] Typically, the finished lubricant compositions produced by the above-mentioned processes comprise, together with a base oil (base stock) and one or more additive species, a quantity of at least one diester species, the diester species generally having the following structure:



wherein R_1 , R_2 , R_3 , and R_4 are the same or independently selected from C_2 to C_{17} hydrocarbon groups (*vide infra*).

[0009] 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

[0010] 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:

[0011] FIG. 1 depicts exemplary diester species that can be used to form at least part of the diester component of at least some of the lubricant compositions described herein, said lubricant compositions being made in accordance with some embodiments of the present invention;

[0012] FIG. 2 is a flow diagram illustrating an exemplary method of making a lubricant composition, in accordance with some embodiments of the present invention;

[0013] FIG. 3 (Scheme 1) illustrates how at least some of the diesters of the diester component of finished lubricant compositions can be generated from an epoxide species by proceeding through a diol (dihydroxy) intermediate species, in accordance with some embodiments of the present invention;

[0014] FIG. 4 (Scheme 2) illustrates how at least some of the diesters of the diester component of finished lubricant compositions can be generated via direct esterification of epoxide species, in accordance with some embodiments of the present invention;

[0015] FIG. 5 (Scheme 3) illustrates how at least some of the diesters of the diester component of finished lubricant compositions can be generated via an enzyme-facilitated pathway, in accordance with some embodiments of the present invention;

[0016] FIG. 6 (Scheme 4) illustrates how fractional crystallization can be used to tailor the diester component of the finished lubricant composition, in accordance with some variational embodiments of the present invention; and

[0017] FIG. 7 (Scheme 5) illustrates how fractional crystallization can be used to tailor the diester component of the finished lubricant composition, in accordance with some other variational embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

1. Introduction

[0018] As mentioned in a preceding section, the present invention is directed to methods of making application-specific lubricant compositions having a biomass-derived component. In some embodiments, bio-derived (i.e., derived from a renewable biomass source) fatty (carboxylic) acid moieties are reacted with Fischer-Tropsch (FT)/gas-to-liquids (GTL) reaction products and/or by-products (i.e., α -olefins) to yield bio-derived diester species that can then be selectively blended with base stock (oil) and one or more additive species to yield an application-specific finished lubricant product having a biomass-derived component.

[0019] Because biolubricants and biofuels are increasingly capturing the public's attention and becoming topics of focus for many in the oil industry, the use of biomass in the making of such above-mentioned finished lubricants could be attractive from several different perspectives (e.g., renewability, regulatory, economic, etc.). As biomass is utilized in the making of the diester component of the finished lubricants described herein, such lubricants are deemed to be biolubricants—or at the very least, they are deemed to comprise a bio-derived component.

2. Definitions

[0020] “Lubricants,” as defined herein, are substances (usually a fluid under operating conditions) introduced between two moving surfaces so to reduce the friction and wear between them. This definition is intended to include greases, whose viscosity drops dramatically upon application of shear.

[0021] Herein, “base oil” will be understood to mean the single largest component (by weight) of a lubricant composition. Base oils are categorized into five groups (I-V) by the American Petroleum Institute (API). See API Publication Number 1509. The API

Base Oil Category, as shown in the following table (**Table 1**), is used to define the compositional nature and/or origin of the base oil.

Table 1.

Base Oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	>0.03	and/or	<90	80 to 120
Group II	<0.03	and	>90	80 to 120
Group III	<0.03	and	>90	>120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III or IV (e.g., esters)			

[0022] “Mineral base oils,” as defined herein, are those base oils produced by the refining of a crude oil.

[0023] “Pour point,” as defined herein, represents the lowest temperature at which a fluid will pour or flow. See, e.g., ASTM International Standard Test Method D 5950-02 (R 2007).

[0024] “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 Method D 5771-05.

[0025] “Centistoke,” abbreviated “cSt,” is a unit for kinematic viscosity of a fluid (e.g., a lubricant), wherein 1 centistoke equals 1 millimeter squared per second (1 cSt = 1 mm²/s). See, e.g., ASTM Standard Guide and Test Method D 2270-04. Herein, the units cSt and mm²/s are used interchangeably.

[0026] With respect to describing molecules and/or molecular fragments herein, “R_m,” where “m” is an index, refers to a hydrocarbon group, wherein the molecules and/or molecular fragments can be linear and/or branched.

[0027] As defined herein, “C_n,” where “n” is an integer, describes a hydrocarbon molecule or fragment (e.g., an alkyl group) wherein “n” denotes the number of carbon atoms in the fragment or molecule.

[0028] The term “carbon number” is used herein in a manner analogous to that of “C_n.” A difference, however, is that carbon number refers to the total number of carbon atoms in a molecule (or molecular fragment) regardless of whether or not it is purely hydrocarbon in nature. Linoleic acid, for example, has a carbon number of 18.

[0029] The term “internal olefin,” as used herein, refers to an olefin (i.e., an alkene) having a non-terminal carbon-carbon double bond (C=C). This is in contrast to “α-olefins” which do bear a terminal carbon-carbon double bond.

[0030] The term “vicinal,” as used herein, refers to the attachment of two functional groups (substituents) to adjacent carbons in a hydrocarbon-based molecule, e.g., vicinal diesters.

[0031] The term “fatty acid moiety,” as used herein, refers to any molecular species and/or molecular fragment comprising the acyl component of a fatty (carboxylic) acid.

[0032] The prefix “bio,” as used herein, refers to an association with a renewable resource of biological origin, such as resource generally being exclusive of fossil fuels. Such an association is typically that of derivation, i.e., a bio-ester derived from a biomass precursor material.

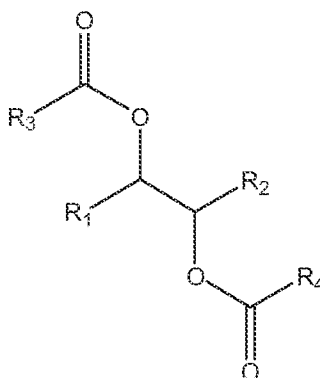
[0033] “Fischer-Tropsch products,” as defined herein, refer to molecular species derived from a catalytically-driven reaction between CO and H₂ (i.e., “syngas”). See, e.g., Dry, “The Fischer-Tropsch process: 1950-2000,” vol. 71(3-4), pp. 227-241, 2002; Schulz, “Short history and present trends of Fischer-Tropsch synthesis,” Applied Catalysis A, vol. 186, pp. 3-12, 1999; Claeys and Van Steen, “Fischer-Tropsch Technology,” Chapter 8, pp. 623-665, 2004.

[0034] “Gas-to-liquids,” as used herein, refers to Fischer-Tropsch processes for generating liquid hydrocarbons and hydrocarbon-based species (e.g., oxygenates).

[0035] “Application-specific finished lubricant compositions,” as described herein, refers to lubricant compositions formulated for a specific end-use.

3. Finished Lubricant Compositions

[0036] Methods of the present invention (*vide infra*) generally provide for application-specific finished lubricant compositions comprising a bio-derived diester component, the diester component comprising a quantity of (vicinal) diester species having the following chemical structure:



where R_1 , R_2 , R_3 , and R_4 are the same or independently selected from a C_2 to C_{17} carbon fragment. Depending on the embodiment, such resulting diester species can have a molecular mass between 340 atomic mass units (a.m.u.) and 780 a.m.u.

[0037] In some embodiments, the diester component of such above-described lubricant compositions is substantially homogeneous. In some or other embodiments, the diester component of such compositions comprises a variety (i.e., a mixture) of diester species. In some embodiments, the diester component of the finished lubricant composition comprises a quantity of at least one diester species derived from a C_8 to C_{14} olefin and a C_6 to C_{14} carboxylic acid.

[0038] In some embodiments, the finished lubricant composition comprises a quantity of at least one diester species selected from the group consisting of decanoic acid 2-decanoyloxy-1-hexyl-octyl ester and its isomers, tetradecanoic acid 1-hexyl-2-tetradecanoyloxy-octyl esters and its isomers, dodecanoic acid 2-dodecanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-hexyl-octyl ester and its isomers, octanoic acid 2-octanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-pentyl-heptyl ester and isomers, octanoic acid 2-octanoyloxy-1-

pentyl-heptyl ester and isomers, decanoic acid 2-decanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid-2-decanoyloxy-1-pentyl-heptyl ester and its isomers, dodecanoic acid 2-dodecanoyloxy-1-pentyl-heptyl ester and isomers, tetradecanoic acid 1-pentyl-2-tetradecanoyloxy-heptyl ester and isomers, tetradecanoic acid 1-butyl-2-tetradecanoyloxy-hexyl ester and isomers, dodecanoic acid-1-butyl-2-dodecanoyloxy-hexyl ester and isomers, decanoic acid 1-butyl-2-decanoyloxy-hexyl ester and isomers, octanoic acid 1-butyl-2-octanoyloxy-hexyl ester and isomers, hexanoic acid 1-butyl-2-hexanoyloxy-hexyl ester and isomers, tetradecanoic acid 1-propyl-2-tetradecanoyloxy-pentyl ester and isomers, dodecanoic acid 2-dodecanoyloxy-1-propyl-pentyl ester and isomers, decanoic acid 2-decanoyloxy-1-propyl-pentyl ester and isomers, octanoic acid 2-octanoyloxy-1-propyl-pentyl ester and isomers, hexanoic acid 2-hexanoyloxy-1-propyl-pentyl ester and isomers, and mixtures thereof.

[0039] Referring to **Fig. 1**, shown are exemplary diester compounds **1-7** that can be generated by steps/sub-steps of the methods described hereinafter, wherein all of such compounds can be formed from a 1-tetradecene α -olefin and a dodecanoic acid (C_{12} fatty acid), and wherein structural diversity arises from the extent to which the 1-tetradecene has been “internalized.” Compound **1**, for example, arises from the epoxidation of 1-tetradecene directly. Any or all of compounds **1-7** could be present in the diester component of the application-specific finished lubricant compositions of the present invention.

4. Methods of Making Finished Lubricant Compositions

[0040] As mentioned in the preceding sections, the present invention is generally directed to methods of making application-specific finished lubricant compositions comprising a bio-derived diester component such as described above.

[0041] Referring to the flow diagram shown in **Fig. 2**, in some embodiments, the present invention is directed to at least one process for making lubricant compositions, said process comprising the steps of: (201) preparing a quantity of epoxidized olefins, wherein said step of preparing comprises the sub-steps of: (201a) isolating α -olefins made from a gas-to-liquids (GTL) process to yield isolated α -olefins; (201b) isomerizing at least a majority of the isolated α -olefins to yield a quantity of internalized olefins; and

(201c) epoxidizing at least a majority of the internalized olefins to form a quantity of epoxidized olefins comprising an epoxide ring; and (202) obtaining a quantity of esterification agents, the esterification agents being derived from triglyceride-borne fatty acid moieties, whereby said derivation yields esterification agents selected from the group consisting of carboxylic acids, acyl halides, acyl anhydrides, and combinations thereof; wherein the step of obtaining comprises the sub-steps of: (202a) selecting a biomass source comprising triglycerides, said triglycerides comprising fatty acid moieties of appropriate length (being proportional to carbon number); (202b) liberating a majority of the fatty acid moieties from the triglyceride molecules of which they are a component so as to yield esterification agents; (203) esterifying at least a majority of the epoxidized olefins with the esterification agents so as to yield a quantity of diester species; and (204) combining the quantity of diester species with a quantity of base oil and an additive component comprising at least one additive selected from the group consisting of antioxidants, detergents, anti-wear agents, metal deactivators, corrosion inhibitors, rust inhibitors, friction modifiers, anti-foaming agents, viscosity index improvers, demulsifying agents, emulsifying agents, tackifiers, complexing agents, extreme pressure additives, pour point depressants, and combinations thereof; wherein selection of the at least one additive is directed largely by the end-use of the lubricant composition being made, wherein said lubricant composition can be of a type selected from the group consisting of turbine oils, metalworking fluids, hydraulic fluids, compressor oils, chain oils, farm equipment engine oils, tractor hydraulic fluids, marine oils, paper machine oils, spindle and textile oils, trailer wheel bearing greases, and combinations thereof.

[0042] The GTL process by which the α -olefins are produced can be a low-temperature (200-300°C) Fischer-Tropsch (LTFT) process, a high-temperature Fischer-Tropsch (HTFT) process (>300°C), or some combination of the two. In addition, in some such embodiments, the GTL process may further include one or more additional processes subsequent to the initial Fischer-Tropsch synthesis.

[0043] In some such above-described processes, the sub-step of isolating the α -olefins comprises their separation from a largely paraffinic GTL product. Such separation can be effected via a variety of techniques including, but not limited to, distillation, fractionation, membrane separation, phase separation, and combinations thereof.

[0044] In some such above-described processes, the sub-step of isomerizing involves use of an olefin isomerization catalyst such as, but not limited to, crystalline aluminosilicate and like materials and aluminophosphates. See, e.g., Schaad, United States Patent No. 2,537,283, issued Jan. 9, 1951; Holm et al., United States Patent No. 3,211,801, issued Oct. 12, 1965; Noddings et al., United States Patent No. 3,270,085, issued Aug. 30, 1966; Noddings, United States Patent No. 3,327,014, issued Jun. 20, 1967; Mitsutani et al., United States Patent No. 3,304,343, issued Feb. 14, 1967; Holm et al., United States Patent No. 3,448,164, issued Jun. 3, 1969; Johnson et al., United States Patent No. 4,593,146, issued Jun. 3, 1986; Tidwell et al., United States Patent No. 3,723,564, issued Mar. 27, 1973; and Miller, United States Patent No. 6,281,404, issued Aug. 28, 2001; the last of which claims a crystalline aluminophosphate-based catalyst with 1-dimensional pores of size between 3.8 Å and 5 Å.

[0045] Regarding the above-mentioned sub-step of epoxidizing (i.e., the epoxidation step), in some embodiments, the above-described olefin (having been internalized from an α -olefin) can be reacted with a peroxide (e.g., H_2O_2) or a peroxy acid (e.g., peroxyacetic acid) to generate an epoxide. See, e.g., Swern et al., "Epoxidation of Oleic Acid, Methyl Oleate and Oleyl Alcohol with Perbenzoic Acid," J. Am. Chem. Soc., vol. 66(11), pp. 1925-1927, 1944.

[0046] In some such above-described processes, the sub-step of liberating triglyceride-borne fatty acid moieties comprises hydrolyzing the triglycerides to yield glycerol and carboxylic acids, the latter being operable for use as esterification agents (see, e.g., Huber et al., "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," Chem. Rev., vol. 106, pp. 4044-4098, 2006). In some such embodiments, there further comprises a sub-step of substantially separating the carboxylic acids on the basis of their degree of unsaturation so that the esterification agents used in the subsequent step of esterifying are substantially homogeneous in terms of their degree of unsaturation. See Miller, United States Patent Application Publication No. 20090285728 A1, published Nov. 19, 2009.

[0047] In some such above-described processes, the step of esterifying the epoxidized olefins proceeds through a diol intermediate (see Miller et al., United States Patent Application Publication No. 20080194444 A1, published Aug. 14, 2008). Such a diol intermediate can be generated via epoxide ring opening to yield the corresponding diol,

wherein this ring opening is effected via acid-catalyzed or based-catalyzed hydrolysis. Exemplary acid catalysts include, but are not limited to, mineral-based Brønsted acids (e.g., HCl, H₂SO₄, H₃PO₄, perhalogenates, etc.), Lewis acids (e.g., TiCl₄ and AlCl₃) solid acids such as acidic aluminas and silicas or their mixtures, and the like. See, e.g., Parker et al., "Mechanisms of Epoxide Reactions," Chem. Rev., vol. 59(4), pp. 737-799, 1959; and Paterson et al., "*meso* Epoxides in Asymmetric Synthesis: Enantioselective Opening by Nucleophiles in the Presence of Chiral Lewis Acids," Angew. Chem. Int. Ed., vol. 31(9), pp. 1179-1180, 1992. Based-catalyzed hydrolysis typically involves the use of bases such as aqueous solutions of sodium or potassium hydroxide.

[0048] In some such embodiments, the diol intermediate is reacted with the esterification agent in the presence of an acid catalyst. Shown in Scheme 1 (Fig. 3), is an exemplary such pathway that proceeds through a diol species en route to a diester species, wherein in some such embodiments the diester species so formed can subsequently be incorporated, as the diester component or a portion thereof, into a finished lubricant composition.

[0049] In some such above-described processes, the step of esterifying the epoxidized olefins is carried directly via reaction between the epoxidized olefin and the esterification agent (see Miller et al., United States Patent Application Publication No. 20090198075 A1, published Aug. 6, 2009). In some such embodiments, the step of esterifying the epoxidized olefins is carried out in the presence of an acid catalyst, wherein the acid catalyst can be selected from the group consisting of H₃PO₄, H₂SO₄, sulfonic acid, Lewis acids, silica and alumina-based solid acids, amberlyst, tungsten oxide, and combinations thereof. In some embodiments, during the step of directly esterifying, efforts are made to remove water produced as a result of the esterifying process. Such efforts can positively impact the diester yield. Shown in Scheme 2 (Fig. 4) is an exemplary such pathway that proceeds via direct esterification of the epoxide species en route to a diester species.

[0050] In some such above-described processes, the sub-step of epoxidizing is enzymatically-facilitated (see Miller et al., United States Patent Application Serial No. 12/270,235, filed Nov. 13, 2008). Shown in Scheme 3 (Fig. 5) is an exemplary such pathway, wherein the epoxidation of the internalized olefin is enzymatically-facilitated or mediated. While Scheme 3 depicts an exemplary pathway that proceeds via direct

esterification of the epoxide species (en route to a diester species), such epoxidation could alternatively proceed through a diol species.

[0051] In some such above-described processes, the diester species formed is selected from the group consisting of decanoic acid 2-decanoyloxy-1-hexyl-octyl ester and its isomers, tetradecanoic acid-1-hexyl-2-tetradecanoyloxy-octyl esters and its isomers, dodecanoic acid 2-dodecanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-hexyl-octyl ester and its isomers, octanoic acid 2-octanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-pentyl-heptyl ester and isomers, octanoic acid 2-octanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid 2-decanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid-2-decanoyloxy-1-pentyl-heptyl ester and its isomers, dodecanoic acid 2-dodecanoyloxy-1-pentyl-heptyl ester and isomers, tetradecanoic acid 1-pentyl-2-tetradecanoyloxy-heptyl ester and isomers, tetradecanoic acid 1-butyl-2-tetradecanoyloxy-hexyl ester and isomers, dodecanoic acid 1-butyl-2-dodecanoyloxy-hexyl ester and isomers, decanoic acid 1-butyl-2-decanoyloxy-hexyl ester and isomers, octanoic acid 1-butyl-2-octanoyloxy-hexyl ester and isomers, hexanoic acid 1-butyl-2-hexanoyloxy-hexyl ester and isomers, tetradecanoic acid 1-propyl-2-tetradecanoyloxy-pentyl ester and isomers, dodecanoic acid 2-dodecanoyloxy-1-propyl-pentyl ester and isomers, decanoic acid 2-decanoyloxy-1-propyl-pentyl ester and isomers, octanoic acid 2-octanoyloxy-1-propyl-pentyl ester and isomers, hexanoic acid 2-hexanoyloxy-1-propyl-pentyl ester and isomers, and mixtures thereof.

[0052] In some such above-described processes, wherein, in the step of combining, the base oil is selected from the group consisting of GTL base oils, mineral base oils, diester-based base oils, and mixtures thereof. In some such embodiments, the base fluid is a GTL base oil or a diester-based base oil.

[0053] In some embodiments, all or part of the additive component is provided as an additive package. In some or other embodiments, some or all of the diester component is combined with some or all of the additive component to collectively form an additive package. In some embodiments, the quantity of diester component, or a portion thereof, serves to facilitate dispersion of all or part of the additive component into the base oil. For more on the variety of lubricant additives that exist, and on the properties they impart, see, e.g., Rudnick, L.R. *Lubricant Additives: Chemistry and Applications*, 2nd ed., CRC Press, Boca Raton, 2009.

[0054] In some such above-described processes, the sub-step of selecting a biomass source comprising triglycerides is based on identification and sufficient content of triglyceride molecules bearing fatty acid moieties of length more desirably suitable for use as a particular lubricant composition. For example, in its hydrolyzed form, palm oil comprises approximately 44 percent palmitic acid, a saturated fatty acid with a carbon number of 16.

[0055] In some such above-described processes, the lubricant composition is a hydraulic fluid having a pour point of from about -80°C to about 0°C.

[0056] In some such above-described processes, the lubricant composition is a turbine oil having a viscosity index (VI) of from at least 90 to at most 130, and having an RPVOT oxidative stability of from at least 250 min. to at most 2300 min. See ASTM Standard Guide and Test Method D 2272-02

[0057] In some such above-described processes, the lubricant composition is a metalworking fluid having a pour point of from about -20°C to about 0°C. Such metalworking fluids typically have a viscosity in the range of from about 32 centistokes (cSt) to about 220 cSt—measured at 40°C.

[0058] In some such above-described processes, the lubricant composition is a compressor oil having a VI of from at least 90 to at most 130, and having a pour point of from at least -60°C to at most 0°C. Such compressor oil typically has a viscosity in the range of from about 32 cSt to about 220 cSt—measured at 40°C.

[0059] In some such above-described processes, the lubricant composition is a chain oil having a VI in the range of from at least 50 to at most 130, and having an aniline point in the range of from at least 0°C to at most 130°C.

5. Variations

[0060] Variations (i.e., alternate embodiments) on the above-described methods of making application-specific lubricant compositions include, but are not limited to, integrating such methods with one or more other processes to produce one or more other

related or different products, and/or to enhance the products being made by one or more of the above-described method embodiments.

[0061] As an example of such an above-described variational embodiment, Scheme 4 (Fig. 6) illustrates an exemplary method embodiment of the present invention, wherein diester synthesis proceeds via a direct esterification of an epoxide species. In this scheme, a fractional crystallization process is used to separate saturated fatty acids from unsaturated fatty acids, whereby the saturated fatty acids are used in the direct esterification (see Miller, United States Patent Application Publication No. 20090285728 A1, published Nov. 19, 2009). In some such contemplated variational embodiments, the unsaturated fatty acids can be hydroprocessed to yield saturated fatty acids that are subsequently recycled back into the direct esterification sub-process. Additionally or alternatively, the unsaturated fatty acids can be reacted to form triester and/or diester species that are used in other compositions or in the finished lubricant compositions described herein (see, e.g., Elomari et al., United States Patent Application Serial No. 12/480,032, filed June 8, 2009; and Elomari et al., United States Patent Application Serial No. 12/498,663, filed July 7, 2009).

[0062] Naturally, the above-described variational embodiment could be modified such that the esterification proceeds through a diol species, as is depicted in Scheme 5 (Fig. 7). Additionally, either of these variational embodiments depicted in Schemes 4 and 5 could utilize enzymes to facilitate the epoxidation of the internalized olefins.

[0063] Additionally or alternatively, in some variational embodiments the FT/GTL process can be tuned or otherwise tailored to produce α -olefins as the primary product stream, and/or with high yields of α -olefins of specific chain length/carbon number. Separation sub-processes can be employed to further refine the α -olefin type that is ultimately epoxidized en route to diester formation, in accordance with some embodiments of the present invention.

6. Examples

[0064] The following examples are provided to demonstrate, and/or more fully illustrate, particular embodiments of the present invention. It should be appreciated by those of skill in the art that the methods disclosed in the examples which follow 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 1

[0065] This Example serves to illustrate how various aspects of such above-described methods might be tailored to yield a hydraulic fluid (oil), in accordance with some embodiments of the present invention.

[0066] In some such above-cited embodiments, hydraulic oils can be prepared by blending a quantity of the bio-derived diester species (*vide supra*) with base oil and the following: zinc-based or ashless metal-free antiwear additives, antioxidants, metal deactivators, and rust inhibitor additives. Such hydraulic fluids can be engineered so as to keep metal-to-metal contact at a minimum, as required by all anti-wear hydraulic fluids, thereby helping to extend equipment life. Furthermore, these hydraulic oils can be designed for use in vane-, piston-, and gear-type pumps. These hydraulic oils will typically have a viscosity ranging from about 5 cSt to about 360 cSt—measured at 40°C, and they will typically have viscosity indices (VIs) ranging from about 95 to about 350, flash points ranging from about 120°C to about 400°C, and pour points ranging from about -80 °C to about 0 °C.

EXAMPLE 2

[0067] This Example serves to illustrate how various aspects of such above-described methods might be tailored to yield a turbine oil, in accordance with some embodiments of the present invention.

[0068] Turbine oils can be prepared by blending one or more bio-derived diester species (such as described in Section 3) with base oil and ashless additives, which typically include one or more corrosion inhibitors, antioxidants, foam inhibitors, demulsifiers and wear inhibitors. These turbine oils can be engineered to have high oxidative and thermal stability, resulting in longer lubricant life and less equipment down-time. In addition, to avoid water contamination, rapid separation from the oil enables quick settling of water

so it may be drained from the system. Such turbine oils, as described herein, may be used in steam and gas turbines with and without reduction gear sets, as well as in centrifugal, rotary and reciprocating compressors requiring rust and oxidation protection.

EXAMPLE 3

[0069] This Example serves to illustrate how various aspects of such above-described methods might be tailored to yield a metalworking fluid, in accordance with some embodiments of the present invention.

[0070] Metalworking fluids can be prepared by blending the bio-derived diester species (i.e., one or more of those species described in Section 3) with or without base oil (base stock) and ashless and/or ash-containing additives. Typically, additives would include one or more antioxidants, metal deactivators, wear inhibitors, rust inhibitor additives and foam inhibitors. In accordance with some embodiments of the present invention, the metalworking fluids can be engineered to have high thermal and oxidation stability—providing long lubricant life, fewer oil changes, less build up on the parts being machined or moving equipment parts, added lubricity inherent with esters, increased solvency and increased up-time. Additionally, their low volatility results in reduced oil make-up and less oil vapor or mist being created while doing work. This helps to maintain a healthier work environment in machine shops, and it lessens the extent to which oil lands on finished parts and equipment. Finally, their reduced tendency towards sludge and deposit formation results in less filters plugging, less maintenance and increased up-time.

EXAMPLE 4

[0071] This Example serves to illustrate how various aspects of such above-described methods might be tailored to yield a compressor oil, in accordance with some embodiments of the present invention.

[0072] Air compressor oils can be prepared by blending the bio-derived diester species (i.e., one or more of those species described in Section 3) with base oil (base stock) and ashless and/or ash-containing additives. Typically, additives would include one or more antioxidants, metal deactivators, wear inhibitors, rust inhibitor additives and foam

inhibitors. In accordance with some embodiments of the present invention, the compressor oils can be engineered to have high thermal and oxidation stability—providing long lubricant life, fewer oil changes, and increased up-time. Additionally, their low volatility results in reduced oil make-up and less oil downstream of the compressor. Finally, their reduced tendency towards sludge and deposit formation results in less filter plugging, less compressor maintenance and increased up-time. It is contemplated that such compressor oils can be used in reciprocating, rotary and/or vane compressors.

EXAMPLE 5

[0073] This Example serves to illustrate how various aspects of such above-described methods might be tailored to yield a chain oil, in accordance with some embodiments of the present invention.

[0074] The chain oils can be prepared by blending the above-described diester species with base oil (base stock), zinc-based or ashless metal-free anti-wear additives, tackifiers, antioxidants, metal deactivators, foam inhibitors and rust inhibitor additives. Such chain oils can be designed to lubricate chain and bar parts associated with chainsaw and other chain-containing equipment. Such oils are contemplated to have excellent solvency for dissolving rosin in forestry applications. Metal-to-metal contact is kept to a minimum to help extend chain life. These chain oils will typically have a viscosity ranging from 5 cSt to 360 cSt—measured at 40°C, will have viscosity indices ranging from 50 to 250, flash points ranging from 120°C to 400°C, and pour points ranging 0°C to -80°C.

7. Summary

[0075] In summary, the present invention is generally directed to methods of making application-specific finished lubricant compositions comprising bio-derived diester species. In some embodiments, bio-derived fatty acid moieties are reacted with Fischer-Tropsch/gas-to-liquids reaction products/by-products (i.e., α -olefins) to yield bio-derived diester species that can then be selectively blended with base stock (oil) and one or more additive species to yield an application-specific finished lubricant product having a biomass-derived component.

[0076] 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 IS CLAIMED IS:

1. A process for making lubricant compositions, said process comprising the steps of:
 - a) preparing a quantity of epoxidized olefins, wherein said step of preparing comprises the sub-steps of:
 - i) isolating α -olefins made from a gas-to-liquids process to yield isolated α -olefins;
 - ii) isomerizing at least a majority of the isolated α -olefins to yield a quantity of internalized olefins; and
 - iii) epoxidizing at least a majority of the internalized olefins to form a quantity of epoxidized olefins comprising an epoxide ring; and
 - b) obtaining a quantity of esterification agents, the esterification agents being derived from triglyceride-borne fatty acid moieties, whereby said derivation yields esterification agents selected from the group consisting of carboxylic acids, acyl halides, acyl anhydrides, and combinations thereof; wherein the step of obtaining comprises the sub-steps of:
 - i') selecting a biomass source comprising triglycerides, said triglycerides comprising fatty acid moieties of appropriate length;
 - ii') liberating a majority of the fatty acid moieties from the triglyceride molecules of which they are a component so as to yield esterification agents;
 - c) esterifying at least a majority of the epoxidized olefins with the esterification agents so as to yield a quantity of diester species; and
 - d) combining the quantity of diester species with a quantity of base oil and an additive component comprising at least one additive selected from the group consisting of antioxidants, detergents, anti-wear agents, metal deactivators, corrosion inhibitors, rust inhibitors, friction modifiers, anti-foaming agents, viscosity index improvers, demulsifying agents, emulsifying agents, tackifiers, complexing agents, extreme pressure additives, pour point depressants, and combinations thereof;

wherein selection of the at least one additive is directed largely by the end-use of the lubricant composition being made, wherein said lubricant composition can be of a type selected from the group consisting of turbine oils, metalworking fluids, hydraulic fluids, compressor oils, chain oils, farm equipment engine oils, tractor hydraulic fluids, marine oils, paper machine oils, spindle and textile oils, trailer wheel bearing greases, and combinations thereof.

2. The process of Claim 1, wherein the sub-step of isolating the α -olefins comprises their separation from a largely paraffinic GTL product.
3. The process of Claim 1, wherein the sub-step of isomerizing involves use of an olefin isomerization catalyst.
4. The process of Claim 1, wherein the sub-step of epoxidizing is enzymatically-facilitated.
5. The process of Claim 1, wherein the sub-step of liberating triglyceride-borne fatty acid moieties comprises hydrolyzing the triglycerides to yield carboxylic acids as esterification agents.
6. The process of Claim 5, further comprising a sub-step of substantially separating the carboxylic acids on the basis of their degree of unsaturation so that the esterification agents used in the subsequent step of esterifying are substantially homogeneous in terms of their degree of unsaturation.
7. The process of Claim 1, wherein the step of esterifying the epoxidized olefins proceeds through a dihydroxide intermediate.

8. The process of Claim 7, wherein the dihydroxide intermediate is reacted with the esterification agent in the presence of an acid catalyst.
9. The process of Claim 1, wherein the step of esterifying the epoxidized olefins is carried directly via reaction between the epoxidized olefin and the esterification agent.
10. The process of Claim 9, wherein the step of esterifying the epoxidized olefins is carried out in the presence of an acid catalyst.
11. The process of Claim 10, wherein the acid catalyst is selected from the group consisting of H_3PO_4 , H_2SO_4 , sulfonic acid, Lewis acids, silica and alumina-based solid acids, amberlyst, tungsten oxide, and combinations thereof.
12. The process of Claim 1, wherein, in the step of combining, the base oil is selected from the group consisting of GTL base oils, mineral base oils, diester-based base oils, and mixtures thereof.
13. The process of Claim 1, wherein the diester species formed is selected from the group consisting of decanoic acid 2-decanoyloxy-1-hexyl-octyl ester and its isomers, tetradecanoic acid-1-hexyl-2-tetradecanoyloxy-octyl esters and its isomers, dodecanoic acid 2-dodecanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-hexy-octyl ester and its isomers, octanoic acid 2-octanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-pentyl-heptyl ester and isomers, octanoic acid 2-octanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid 2-decanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid-2-cccanoyloxy-1-pentyl-heptyl ester and its isomers, dodecanoic acid-2-dodecanoyloxy-1-pentyl-heptyl ester and isomers, tetradecanoic acid 1-penty-2-tetradecanoyloxy-heptyl ester and isomers, tetradecanoic acid 1-butyl-2-tetradecanoyloxy-hexy ester and isomers, dodecanoic acid-1-butyl-2-dodecanoyloxy-hexyl ester and isomers, decanoic acid 1-butyl-2-decanoyloxy-hexyl ester and isomers, octanoic acid 1-butyl-2-octanoyloxy-hexyl ester and isomers,

hexanoic acid 1-butyl-2-hexanoyloxy-hexyl ester and isomers, tetradecanoic acid 1-propyl-2-tetradecanoyloxy-pentyl ester and isomers, dodecanoic acid 2-dodecanoyloxy-1-propyl-pentyl ester and isomers, decanoic acid 2-decanoyloxy-1-propyl-pentyl ester and isomers, octanoic acid 1-2-octanoyloxy-1-propyl-pentyl ester and isomers, hexanoic acid 2-hexanoyloxy-1-propyl-pentyl ester and isomers, and mixtures thereof.

14. The process of Claim 12, wherein the base oil is a GTL base oil, and wherein the quantity of diester component serves to facilitate dispersion of the additive component in the base oil.

15. The process of Claim 1, wherein the sub-step of selecting a biomass source comprising triglycerides is based on identification and sufficient content of triglyceride molecules bearing fatty acid moieties of length more desirably suitable for use as a particular lubricant composition.

16. The process of Claim 1, wherein the lubricant composition is a hydraulic fluid having a pour point of from about -80°C to about 0°C.

17. The process of Claim 1, wherein the lubricant composition is a turbine oil having a VI of from at least 90 to at most 130, and having an RPVOT oxidative stability of from at least 250 minutes to at most 2300 minutes.

18. The process of Claim 1, wherein the lubricant composition is a metalworking fluid having a pour point of from about -20°C to about 0°C.

19. The process of Claim 1, wherein the lubricant composition is a compressor oil having a VI of from at least 90 to at most 130, and having a pour point of from at least -60°C to at most 0°C.

20. The process of Claim 1, wherein the lubricant composition is a chain oil having a VI in the range of from at least 50 to at most 130, and having an aniline point in the range of from at least 0°C to at most 130°C.