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METHODS OF REFINING AND PRODUCING DIBASIC ESTERS AND ACIDS FROM NATURAL OIL FEEDSTOCKS

CROSS-REFERENCE TO RELATED APPLICATIONS

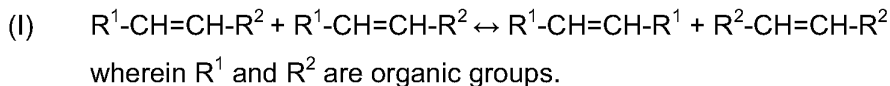
[0001] The present application claims the benefit of priority of United States Patent Application No. 13/647,809, filed October 9, 2012; and United States Patent Application No. 13/647,825, filed October 9, 2012. The disclosures of each of the foregoing applications are hereby incorporated by reference in their entireties as though fully set forth herein.

GOVERNMENT RIGHTS

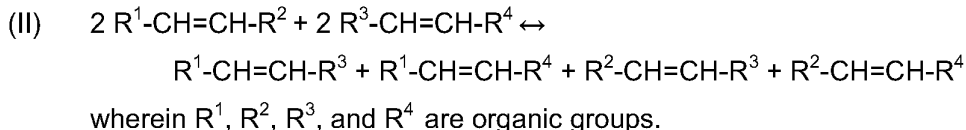
[0002] This invention was made with government support under grant no. DE-EE0002872/001, awarded by the United States Department of Energy. The United States government has certain rights in this invention.

BACKGROUND

[0003] Metathesis is a catalytic reaction that involves the interchange of alkylidene units among compounds containing one or more double bonds (e.g., olefinic compounds) via the formation and cleavage of the carbon-carbon double bonds. Metathesis may occur between two like molecules (often referred to as self-metathesis) and/or it may occur between two different molecules (often referred to as cross-metathesis). Self-metathesis may be represented schematically as shown in Equation I.



[0004] Cross-metathesis may be represented schematically as shown in Equation II.



[0005] In recent years, there has been an increased demand for environmentally friendly techniques for manufacturing materials typically derived from petroleum sources. For example, researchers have been studying the feasibility of manufacturing biofuels, waxes, plastics, and the like, using natural oil

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feedstocks, such as vegetable and seed-based oils. In one non-limiting example, metathesis catalysts are used to manufacture candle wax, as described in WO 2006/076364, which is herein incorporated by reference in its entirety. Metathesis reactions involving natural oil feedstocks offer promising solutions for today and for the future.

[0006] Natural oil feedstocks of interest include non-limiting examples such as natural oils (e.g., vegetable oils, fish oil, animal fats) and derivatives of natural oils, such as fatty acids and fatty acid alkyl (e.g., methyl) esters. These feedstocks may be converted into industrially useful chemicals (e.g., waxes, plastics, cosmetics, biofuels, etc.) by any number of different metathesis reactions. Significant reaction classes include, as non-limiting examples, self-metathesis, cross-metathesis with olefins, and ring-opening metathesis reactions. Representative non-limiting examples of useful metathesis catalysts are provided below. Metathesis catalysts can be expensive and, therefore, it is desirable to improve the efficiency of the metathesis catalyst.

[0007] In certain instances, metathesis of natural oil feedstocks may provide a useful way to make chemical intermediates that may be difficult to make by other means. Or, in some other instances, metathesis of natural oil feedstocks may provide a useful way to make "green" alternatives to existing compounds or materials. Therefore, there is a continuing need to develop processes and systems that employ natural oil metathesis to make commercially and/or technically useful compounds and materials.

SUMMARY

[0008] Methods and systems for making dibasic esters or dibasic acids by olefin metathesis are generally disclosed. In some embodiments, one or more of the compounds used to make such dibasic esters or dibasic acids are derived from refining a natural oil feedstock, for example, through a metathesis reaction of the natural oil feedstock, or a derivative thereof, in the presence of a metathesis catalyst.

[0009] In a first aspect, the disclosure provides methods of making an unsaturated dibasic ester, comprising: providing a reactant composition comprising a terminal olefin ester and an internal olefin ester; and reacting the terminal olefin ester with the internal olefin ester in a reactor in the presence of a first metathesis catalyst

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to form an unsaturated dibasic ester and a first terminal olefin. In some embodiments, at least a portion of the first terminal olefin is removed from the reactor during the reacting. In some embodiments, at least a portion of one or both of the terminal olefin ester and the internal olefin ester are derived from a natural oil feedstock.

[0010] In some embodiments, the weight-to-weight ratio of the terminal olefin ester to the internal olefin ester in the reactor is between 5:1 and 1:5. In other embodiments, the weight-to-weight ratio of the terminal olefin ester to the internal olefin ester is 1:1.

[0011] In some embodiments, the terminal olefin ester is selected from the group consisting of: 4-pentenoic acid ester, 5-hexenoic acid ester, 6-heptenoic acid ester, 7-octenoic acid ester, 8-nonenoic acid ester, 9-decenoic acid ester, 10-undecenoic acid ester, 11-dodecenoic acid ester, 12-tridecenoic acid ester, 13-tetradecenoic acid ester, 14-pentadecenoic acid ester, 15-hexadecenoic acid ester, 16-heptadecenoic acid ester, 17-octadecenoic acid ester, and any mixtures thereof. In some embodiments, the terminal olefin ester is a 9-decenoic acid ester, such as 9-decenoic acid methyl ester. In certain embodiments, the internal olefin ester is selected from the group consisting of: pentenoic acid esters, hexenoic acid esters, heptenoic acid esters, octenoic acid esters, nonenoic acid esters, decenoic acid esters, undecenoic acid esters, dodecenoic acid esters, tridecenoic acid esters, tetradecenoic acid esters, pentadecenoic acid esters, hexadecenoic acid esters, heptadecenoic acid esters, octadecenoic acid esters, and any mixtures thereof. In some embodiments, the internal olefin ester is a 9-dodecenoic acid ester, such as 9-dodecenoic acid methyl ester.

[0012] In some embodiments, at least a portion of the internal olefin ester is formed by reacting a portion of the terminal olefin ester with a low-molecular-weight internal olefin or a mid-weight internal olefin in the presence of a metathesis catalyst. In certain embodiments, the low-molecular-weight internal olefin is selected from the group consisting of: 2-butene, 2-pentene, 2-hexene, 3-hexene, 2-heptene, 3-heptene, 2-octene, 3-octene, 4-octene, 2-nonene, 3-nonene, 4-nonene, and any mixtures thereof. In some embodiments, the low-molecular-weight internal olefin is 3-hexene.

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[0013] In some embodiments, at least a portion of the terminal olefin ester is formed by reacting a portion of the internal olefin ester with a low-molecular-weight terminal olefin or a mid-weight terminal olefin in the presence of a metathesis catalyst. In some embodiments, the low-molecular-weight terminal olefin or a mid-weight terminal olefin is selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, and any mixtures thereof. In some embodiments, it is ethylene.

[0014] In some embodiments, the unsaturated dibasic ester formed is a 9-octadecenedioic acid dibasic ester, such as 9-octadecenedioic acid dimethyl ester.

[0015] In a second aspect, the disclosure provides methods of making a saturated dibasic ester, comprising: making an unsaturated dibasic ester according to any of the embodiments of the first aspect; and hydrogenating the unsaturated dibasic ester to form a saturated dibasic ester. In some embodiments, the saturated dibasic ester is an octadecanedioic acid dibasic ester, such as octadecanedioic acid dimethyl ester.

[0016] In a third aspect, the disclosure provides methods of making a dibasic acid, comprising: making a dibasic ester, wherein the making comprises making an unsaturated dibasic ester according to any methods of the first aspect or making a saturated dibasic ester according to any embodiments of the second aspect; and converting the dibasic ester to a dibasic acid. In embodiments where an unsaturated dibasic acid is formed, the unsaturated dibasic acid can be further hydrogenated to form a saturated dibasic acid. In some embodiments, the converting comprises hydrolyzing the dibasic ester to a dibasic acid, e.g., by reacting the dibasic ester with water in the presence of an acid catalyst. In some other embodiments, the converting comprises saponifying the dibasic ester to form a dibasic acid salt (where "acid salt" refers to a carboxylate anion, whether in solution or in solid-state form), and optionally acidifying the dibasic acid salt to form the dibasic acid. In some embodiments, the resulting dibasic acid is octadecanedioic acid. In some other embodiments, the resulting dibasic acid is 9-octadecenedioic acid.

[0017] In a fourth aspect, the disclosure provides methods of refining a natural oil, comprising: providing a feedstock comprising a natural oil; reacting the feedstock in the presence of a fourth metathesis catalyst to form a metathesized product comprising one or more unsaturated glycerides and one or more olefins; separating

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the unsaturated glycerides in the metathesized product from the olefins in the metathesized product; transesterifying the separated unsaturated glycerides in the presence of an alcohol to form a transesterified product comprising a terminal olefin ester or an internal olefin ester; and using the terminal olefin ester or the internal olefin ester according to the method of any embodiments of the first aspect to form an unsaturated dibasic ester. In some embodiments, the alcohol is methanol. In some embodiments, the unsaturated dibasic ester is a 9-octadecenedioic acid dibasic ester, such as 9-octadecenedioic acid dimethyl ester. In some further embodiments, the resulting unsaturated dibasic ester can be converted to a saturated dibasic ester and/or a saturated dibasic acid according to any of the embodiments of the second and/or third aspects.

[0018] In a fifth aspect, the disclosure provides methods of refining a natural oil, comprising providing a feedstock comprising a natural oil; transesterifying the feedstock in the presence of an alcohol to form a transesterified product comprising one or more unsaturated fatty acid esters; reacting the unsaturated fatty acid esters in the presence of a fifth metathesis catalyst to form a metathesized product comprising one or more metathesized unsaturated esters and one or more olefins; separating the metathesized unsaturated esters in the metathesized product from the olefins in the metathesized product, wherein the separated metathesized esters comprise a terminal olefin ester or an internal olefin ester; and using the terminal olefin ester or the internal olefin ester according to the method of any embodiment of the first aspect to form an unsaturated dibasic ester. In some embodiments, the alcohol is methanol. In some embodiments, the unsaturated dibasic ester is a 9-octadecenedioic acid dibasic ester, such as 9-octadecenedioic acid dimethyl ester. In some further embodiments, the resulting unsaturated dibasic ester can be converted to a saturated dibasic ester and/or a saturated dibasic acid according to any of the embodiments of the second and/or third aspects.

[0019] Further aspects and embodiments are provided in the following drawings, detailed description, and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 shows a schematic diagram of one embodiment of a process to produce a fuel composition and a transesterified product from a natural oil.

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[0021] FIG. 2 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester.

[0022] FIG. 3 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester.

[0023] FIG. 4 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester.

[0024] FIG. 5 shows a flow chart that illustrates certain embodiments for making a saturated dibasic ester.

[0025] FIG. 6 shows a flow chart that illustrates certain embodiments for making a dibasic acid.

[0026] FIG. 7 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester from a feedstock comprising a natural oil.

[0027] FIG. 8 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester from a feedstock comprising a natural oil.

[0028] FIG. 9 shows a graph of 9-DAME and 9-DDAME (wt%) in the reactor verses reaction time (hr) for a process of one embodiment disclosed herein.

DETAILED DESCRIPTION

[0029] The following description recites various aspects and embodiments of the inventions disclosed herein. No particular embodiment is intended to define the scope of the invention. Rather, the embodiments provide non-limiting examples of various compositions, and methods that are included within the scope of the disclosed inventions. The description is to be read from the perspective of one of ordinary skill in the art. Therefore, information that is well known to the ordinarily skilled artisan is not necessarily included.

Definitions

[0030] The following terms and phrases have the meanings indicated below, unless otherwise provided herein. This disclosure may employ other terms and phrases not expressly defined herein. Such other terms and phrases shall have the meanings that they would possess within the context of this disclosure to those of ordinary skill in the art. In some instances, a term or phrase may be defined in the singular or plural. In such instances, it is understood that any term in the singular

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may include its plural counterpart and vice versa, unless expressly indicated to the contrary.

[0031] As used herein, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. For example, reference to “a substituent” encompasses a single substituent as well as two or more substituents, and the like.

[0032] As used herein, the terms “for example,” “for instance,” “such as,” or “including” are meant to introduce examples that further clarify more general subject matter. Unless otherwise specified, these examples are provided only as an aid for understanding the applications illustrated in the present disclosure, and are not meant to be limiting in any fashion.

[0033] As used herein, the term “metathesis catalyst” includes any catalyst or catalyst system that catalyzes a metathesis reaction.

[0034] As used herein, the terms “natural oils,” “natural feedstocks,” or “natural oil feedstocks” may refer to oils derived from plants or animal sources. The term “natural oil” includes natural oil derivatives, unless otherwise indicated. Examples of natural oils include, but are not limited to, vegetable oils, algae oils, fish oils, animal fats, tall oils, derivatives of these oils, combinations of any of these oils, and the like. Representative non-limiting examples of vegetable oils include canola oil, rapeseed oil, coconut oil, corn oil, cottonseed oil, olive oil, palm oil, peanut oil, safflower oil, sesame oil, soybean oil, sunflower oil, linseed oil, palm kernel oil, tung oil, jatropha oil, mustard oil, pennycress oil, camelina oil, and castor oil. Representative non-limiting examples of animal fats include lard, tallow, poultry fat, yellow grease, and fish oil. Tall oils are by-products of wood pulp manufacture.

[0035] As used herein, the term “natural oil derivatives” may refer to the compounds or mixture of compounds derived from the natural oil using any one or combination of methods known in the art. Such methods include but are not limited to saponification, fat splitting, transesterification, esterification, hydrogenation (partial or full), isomerization, oxidation, and reduction. Representative non-limiting examples of natural oil derivatives include gums, phospholipids, soapstock, acidulated soapstock, distillate or distillate sludge, fatty acids and fatty acid alkyl ester (e.g. non-limiting examples such as 2-ethylhexyl ester), hydroxy substituted variations thereof of the natural oil. For example, the natural oil derivative may be a

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fatty acid methyl ester ("FAME") derived from the glyceride of the natural oil. In some embodiments, a feedstock includes canola or soybean oil, as a non-limiting example, refined, bleached, and deodorized soybean oil (i.e., RBD soybean oil). Soybean oil typically comprises about 95% weight or greater (e.g., 99% weight or greater) triglycerides of fatty acids. Major fatty acids in the polyol esters of soybean oil include saturated fatty acids, as a non-limiting example, palmitic acid (hexadecanoic acid) and stearic acid (octadecanoic acid), and unsaturated fatty acids, as a non-limiting example, oleic acid (9-octadecenoic acid), linoleic acid (9,12-octadecadienoic acid), and linolenic acid (9,12,15-octadecatrienoic acid).

[0036] As used herein, the terms "olefin" and "olefins" may refer to hydrocarbon compounds having at least one unsaturated carbon-carbon double bond. In certain embodiments, the term "olefin" or "olefins" may refer to a group of unsaturated carbon-carbon double bond compounds with different carbon lengths. A compound having a terminal carbon-carbon double bond can be referred to as a "terminal olefin," while an olefin having a non-terminal carbon-carbon double bond can be referred to as an "internal olefin."

[0037] As used herein, the term "low-molecular-weight olefin" may refer to any one or combination of unsaturated straight, branched, or cyclic hydrocarbons in the C2 to C14 range. Low-molecular-weight olefins include "alpha-olefins" or "terminal olefins," wherein the unsaturated carbon-carbon bond is present at one end of the compound. Low-molecular-weight olefins may also include dienes or trienes. Low-molecular-weight olefins may also include internal olefins or "low-molecular-weight internal olefins." In certain embodiments, the low-molecular-weight internal olefin is in the C4 to C14 range. Examples of low-molecular-weight olefins in the C2 to C6 range include, but are not limited to: ethylene, propylene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 3-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, cyclopentene, 1,4-pentadiene, 1-hexene, 2-hexene, 3-hexene, 4-hexene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl-2-pentene, 3-methyl-2-pentene, 4-methyl-2-pentene, 2-methyl-3-pentene, and cyclohexene. Non-limiting examples of low-molecular-weight olefins in the C7 to C9 range include 1,4-heptadiene, 1-heptene, 3,6-nonadiene, 3-nonene, 1,4,7-octatriene. Other possible low-molecular-weight olefins include styrene and vinyl cyclohexane. In certain embodiments, it is preferable to use a mixture of olefins, the mixture

comprising linear and branched low-molecular-weight olefins in the C4-C10 range. In one embodiment, it may be preferable to use a mixture of linear and branched C4 olefins (i.e., combinations of: 1-butene, 2-butene, and/or isobutene). In other embodiments, a higher range of C11-C14 may be used.

[0038] As used herein, the term “mid-weight olefin” may refer to any one or combination of unsaturated straight, branched, or cyclic hydrocarbons in the C15 to C24 range. Mid-weight olefins include “alpha-olefins” or “terminal olefins,” wherein the unsaturated carbon-carbon bond is present at one end of the compound. Mid-weight olefins may also include dienes or trienes. Mid-weight olefins may also include internal olefins or “mid-weight internal olefins.” In certain embodiments, it is preferable to use a mixture of olefins.

[0039] As used herein, the terms “ester” and “esters” may refer to compounds having the general formula: $R^a\text{-COO-R}^b$, wherein R^a and R^b denote any organic compound (such as alkyl, aryl, or silyl groups), including those bearing heteroatom containing substituent groups. In certain embodiments, R^a and R^b denote alkyl or aryl groups. In certain embodiments, the term “ester” or “esters” may refer to a group of compounds with the general formula described above, wherein the compounds have different carbon lengths. In certain embodiments, the esters may be esters of glycerol, which is a trihydric alcohol. The term “glyceride” can refer to esters where one, two, or three of the -OH groups of the glycerol have been esterified. Thus, the term “unsaturated glyceride” can refer to monoglycerides, diglycerides, or triglycerides, where one or more of the acid portions of the ester contain unsaturation, e.g., a carbon-carbon double bond.

[0040] It is noted that an olefin may also comprise an ester, and an ester may also comprise an olefin, if the R^a or R^b group in the general formula $R^a\text{-COO-R}^b$ contains an unsaturated carbon-carbon double bond. For example, a “terminal olefin ester” may refer to an ester compound where R^a has an olefin positioned at the end of the chain. An “internal olefin ester” may refer to an ester compound where R has an olefin positioned at an internal location on the chain. Additionally, the term “terminal olefin” may refer to an ester or an acid thereof where R^b denotes hydrogen or any organic compound (such as an alkyl, aryl, or silyl group) and R^a has an olefin positioned at the end of the chain, and the term “internal olefin” may refer to an ester or an acid thereof where R^b denotes hydrogen or any organic compound (such as an

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alkyl, aryl, or silyl group) and R^a has an olefin positioned at an internal location on the chain.

[0041] As used herein, the terms “metathesize” and “metathesizing” may refer to the reacting of a feedstock in the presence of a metathesis catalyst to form a “metathesized product” comprising a new olefinic compound. Metathesizing may refer to cross-metathesis (a.k.a. co-metathesis), self-metathesis, ring-opening metathesis, ring-opening metathesis polymerizations (“ROMP”), ring-closing metathesis (“RCM”), and acyclic diene metathesis (“ADMET”). As a non-limiting example, metathesizing may refer to reacting two triglycerides present in a natural feedstock (self-metathesis) in the presence of a metathesis catalyst, wherein each triglyceride has an unsaturated carbon-carbon double bond, thereby forming a new mixture of olefins and esters which may include a triglyceride dimer. Such triglyceride dimers may have more than one olefinic bond, thus higher oligomers also may form. Additionally, metathesizing may refer to reacting an olefin, such as ethylene, and a triglyceride in a natural feedstock having at least one unsaturated carbon-carbon double bond, thereby forming new olefinic molecules as well as new ester molecules (cross-metathesis).

[0042] As used herein, the term “dibasic ester” may refer to compounds having the general formula $R^a\text{-OOC-Y-COO-R}^b$, wherein Y, R^a , and R^b denote any organic compound (such as alkyl, aryl, or silyl groups), including those bearing heteroatom containing substituent groups. In certain embodiments, Y is a saturated or unsaturated hydrocarbon, and R^a and R^b are alkyl or aryl groups. In instances where Y is a saturated hydrocarbon, the dibasic ester can be referred to as a “saturated dibasic ester.” In instances where Y is an unsaturated hydrocarbon, the dibasic ester can be referred to as an “unsaturated dibasic ester.”

[0043] As used herein, the term “dibasic acid” may refer to compounds having the general formula $R^a\text{-OOC-Y-COO-R}^b$, wherein R^a and R^b are hydrogen, and Y denotes any organic compound (such as an alkyl, aryl, or silyl group), including those bearing heteroatom substituent groups. In certain embodiments, Y is a saturated or unsaturated hydrocarbon. In instances where Y is a saturated hydrocarbon, the dibasic acid can be referred to as a “saturated dibasic acid.” In instances where Y is an unsaturated hydrocarbon, the dibasic acid can be referred to as an “unsaturated dibasic acid.”

[0044] As used herein, “hydrocarbon” refers to an organic group composed of carbon and hydrogen, which can be saturated or unsaturated, and can include aromatic groups. The term “hydrocarbonyl” refers to a monovalent or polyvalent hydrocarbon moiety.

[0045] In some instances, the olefin can be an “alkene,” which refers to a straight- or branched-chain non-aromatic hydrocarbon having 2 to 30 carbon atoms and one or more carbon-carbon double bonds, which may be optionally substituted, as herein further described, with multiple degrees of substitution being allowed. A “monounsaturated alkene” refers to an alkene having one carbon-carbon double bond, while a “polyunsaturated alkene” refers to an alkene having two or more carbon-carbon double bonds. A “lower alkene,” as used herein, refers to an alkene having from 2 to 8 carbon atoms.

[0046] As used herein, “alpha-olefin” refers to an olefin (as defined above) that has a terminal carbon-carbon double bond. In some embodiments, the alpha-olefin is a terminal alkene, which is an alkene (as defined above) having a terminal carbon-carbon double bond. Additional carbon-carbon double bonds can be present.

[0047] As used herein, “alcohol” or “alcohols” refer to compounds having the general formula: $R^a\text{-OH}$, wherein R^a denotes any organic moiety (such as alkyl, aryl, or silyl groups), including those bearing heteroatom-containing substituent groups. In certain embodiments, R^a denotes alkyl, aryl, or alcohol groups. In certain embodiments, the term “alcohol” or “alcohols” may refer to a group of compounds with the general formula described above, wherein the compounds have different carbon lengths. The term “hydroxyl” refers to a -OH moiety.

[0048] As used herein, “alkyl” refers to a straight or branched chain saturated hydrocarbon having 1 to 30 carbon atoms, which may be optionally substituted, as herein further described, with multiple degrees of substitution being allowed. Examples of “alkyl,” as used herein, include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, isobutyl, n-butyl, sec-butyl, tert-butyl, isopentyl, n-pentyl, neopentyl, n-hexyl, and 2-ethylhexyl. The number carbon atoms in an alkyl group is represented by the phrase “ C_{x-y} alkyl,” which refers to an alkyl group, as herein defined, containing from x to y, inclusive, carbon atoms. Thus, “ C_{1-6} alkyl” represents an alkyl chain having from 1 to 6 carbon atoms and, for example, includes, but is not limited to, methyl, ethyl, n-propyl, isopropyl, isobutyl, n-butyl, sec-butyl, tert-butyl,

isopentyl, n-pentyl, neopentyl, and n-hexyl. In some instances, the "alkyl" group can be divalent, in which case the group can alternatively be referred to as an "alkylene" group.

[0049] As used herein, "alkenyl" refers to a straight or branched chain non-aromatic hydrocarbon having 2 to 30 carbon atoms and having one or more carbon-carbon double bonds, which may be optionally substituted, as herein further described, with multiple degrees of substitution being allowed. Examples of "alkenyl," as used herein, include, but are not limited to, ethenyl, 2-propenyl, 2-butenyl, and 3-butenyl. The number carbon atoms in an alkenyl group is represented by the phrase " C_{x-y} alkenyl," which refers to an alkenyl group, as herein defined, containing from x to y, inclusive, carbon atoms. Thus, " C_{2-6} alkenyl" represents an alkenyl chain having from 2 to 6 carbon atoms and, for example, includes, but is not limited to, ethenyl, 2-propenyl, 2-butenyl, and 3-butenyl. In some instances, the "alkenyl" group can be divalent, in which case the group can alternatively be referred to as an "alkenylene" group.

[0050] As used herein, the terms "paraffin" and "paraffins" may refer to hydrocarbon compounds having only single carbon-carbon bonds, having the general formula C_nH_{2n+2} , where, in certain embodiments, n is greater than about 20.

[0051] As used herein, the terms "isomerization," "isomerizes," or "isomerizing" may refer to the reaction and conversion of straight-chain hydrocarbon compounds, such as normal paraffins, into branched hydrocarbon compounds, such as iso-paraffins. In other embodiments, the isomerization of an olefin or an unsaturated ester indicates the shift of the carbon-carbon double bond to another location in the molecule (e.g., conversion from 9-decenoic acid to 8-decenoic acid), or it indicates a change in the geometry of the compound at the carbon-carbon double bond (e.g., cis to trans). As a non-limiting example, n-pentane may be isomerized into a mixture of n-pentane, 2-methylbutane, and 2,2-dimethylpropane. Isomerization of normal paraffins may be used to improve the overall properties of a fuel composition. Additionally, isomerization may refer to the conversion of branched paraffins into further, more branched paraffins.

[0052] As used herein, the term "yield" may refer to the total weight of fuel produced from the metathesis and hydrogenation reactions. It may also refer to the total weight of the fuel following a separation step and/or isomerization reaction. It

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may be defined in terms of a yield %, wherein the total weight of the fuel produced is divided by the total weight of the natural oil feedstock and, in some embodiments, low-molecular-weight olefin and/or mid-weight olefin, combined.

[0053] As used herein, “mix” or “mixed” or “mixture” refers broadly to any combining of two or more compositions. The two or more compositions need not have the same physical state; thus, solids can be “mixed” with liquids, e.g., to form a slurry, suspension, or solution. Further, these terms do not require any degree of homogeneity or uniformity of composition. Thus, such “mixtures” can be homogeneous or heterogeneous, or can be uniform or non-uniform. Further, the terms do not require the use of any particular equipment to carry out the mixing, such as an industrial mixer.

[0054] As used herein, “optionally” means that the subsequently described event(s) may or may not occur. In some embodiments, the optional event does not occur. In some other embodiments, the optional event does occur one or more times.

[0055] As used herein, “comprise” or “comprises” or “comprising” or “comprised of” refer to groups that are open, meaning that the group can include additional members in addition to those expressly recited. For example, the phrase, “comprises A” means that A must be present, but that other members can be present too. The terms “include,” “have,” and “composed of” and their grammatical variants have the same meaning. In contrast, “consist of” or “consists of” or “consisting of” refer to groups that are closed. For example, the phrase “consists of A” means that A and only A is present.

[0056] As used herein, “or” is to be given its broadest reasonable interpretation, and is not to be limited to an either/or construction. Thus, the phrase “comprising A or B” means that A can be present and not B, or that B is present and not A, or that A and B are both present. Further, if A, for example, defines a class that can have multiple members, e.g., A₁ and A₂, then one or more members of the class can be present concurrently.

[0057] As used herein, “providing” is to be construed as having its broadest reasonable scope. For example, providing a composition that comprises a particular compound includes, but is not limited to, adding the compound to the composition,

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generating the compound in the composition via a chemical reaction, or receiving the composition, e.g., as the product of another process.

[0058] As used herein, the various functional groups represented will be understood to have a point of attachment at the functional group having the hyphen or dash (–) or an asterisk (*). In other words, in the case of $-\text{CH}_2\text{CH}_2\text{CH}_3$, it will be understood that the point of attachment is the CH_2 group at the far left. If a group is recited without an asterisk or a dash, then the attachment point is indicated by the plain and ordinary meaning of the recited group.

[0059] As used herein, multi-atom bivalent species are to be read from left to right. For example, if the specification or claims recite A-D-E and D is defined as $-\text{OC}(\text{O})-$, the resulting group with D replaced is: A-OC(O)-E and not A-C(O)O-E.

[0060] As used herein, the terms “fuels” and “fuel compositions” refer to materials meeting required specifications or to blend components that are useful in formulating fuel compositions but, by themselves, do not meet all of the required specifications for a fuel.

[0061] As used herein, the term “jet fuel” or “aviation fuel” may refer to kerosene or naphtha-type fuel cuts, or military-grade jet fuel compositions. “Kerosene-type” jet fuel (including Jet A and Jet A-1) has a carbon number distribution between about 8 and about 16. Jet A and Jet A-1 typically have a flash point of at least approximately 38°C , an auto ignition temperature of approximately 210°C , a freeze point less than or equal to approximately -40°C for Jet A and -47°C for Jet A-1, a density of approximately 0.8 g/cc at 15°C , and an energy density of approximately 42.8–43.2 MJ/kg. “Naphtha-type” or “wide-cut” jet fuel (including Jet B) has a carbon number distribution between about 5 and about 15. Jet B typically comprises a flash point below approximately 0°C , an auto ignition temperature of approximately 250°C , a freeze point of approximately -51°C , a density of approximately 0.78 g/cc, and an energy density of approximately 42.8–43.5 MJ/kg. “Military grade” jet fuel refers to the Jet Propulsion or “JP” numbering system (JP-1, JP-2, JP-3, JP-4, JP-5, JP-6, JP-7, JP-8, etc.). Military grade jet fuels may comprise alternative or additional additives to have higher flash points than Jet A, Jet A-1, or Jet B in order to cope with heat and stress endured during supersonic flight.

[0062] As used herein, the term “diesel fuel” may refer to a hydrocarbon composition having the following property characteristics, including a carbon number

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distribution between about 8 and about 25. Diesel fuels also typically have a specific gravity of approximately 0.82-1.08 at 15.6°C (60°F), based on water having a specific gravity of 1 at 60°F. Diesel fuels typically comprise a distillation range between approximately 180-340°C (356-644°F). Additionally, diesel fuels have a minimum cetane index number of approximately 40.

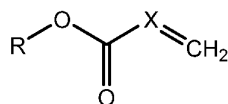
[0063] As used herein, the term “carbon number distribution” may refer to the range of compounds present in a composition, wherein each compound is defined by the number of carbon atoms present. As a non-limiting example, a naphtha-type jet fuel typically comprises a distribution of hydrocarbon compounds wherein a majority of those compounds have between 5 and 15 carbon atoms each. A kerosene-type jet fuel typically comprises a distribution of hydrocarbon compounds wherein a majority of those compounds have between 8 and 16 carbon atoms each. A diesel fuel typically comprises a distribution of hydrocarbon compounds wherein a majority of those compounds have between 8 and 25 carbon atoms each.

[0064] As used herein, the term “energy density” may refer to the amount of energy stored in a given system per unit mass (MJ/kg) or per unit volume (MJ/L), where MJ refer to million Joules. As a non-limiting example, the energy density of kerosene- or naphtha-type jet fuel is typically greater than about 40 MJ/kg.

Methods of Making an Unsaturated Dibasic Ester

[0065] The disclosure provides methods of making an unsaturated dibasic ester, comprising: providing a reactant composition comprising a terminal olefin ester and an internal olefin ester; and reacting the terminal olefin ester with the internal olefin ester in a reactor in the presence of a first metathesis catalyst to form an unsaturated dibasic ester and a first terminal olefin. In some embodiments, the unsaturated dibasic esters can be further converted to dibasic acids, e.g., by methods that include hydrolysis or saponification. In some such embodiments, the converting can occur after hydrogenation.

[0066] In certain embodiments, dibasic acids and/or dibasic esters and olefin byproducts may be formed by reacting terminal olefin esters having the following structure:



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(where X is a C₃-C₁₈ saturated or unsaturated alkyl chain, and R is an alkyl group, which can be optionally unsaturated or contain ether linkages, or hydrogen) with internal olefins (e.g., internal olefin esters) in the presence of a metathesis catalyst. In certain embodiments, the terminal olefin ester is derived from a natural oil feedstock (described in greater detail below). In other embodiments, the terminal olefin is purchased or produced from an external source separate than those derived from the natural oil feedstock.

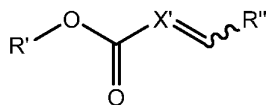
[0067] In some embodiments, X is -(CH₂)₂-CH=, -(CH₂)₃-CH=, -(CH₂)₄-CH=, -(CH₂)₅-CH=, -(CH₂)₆-CH=, -(CH₂)₇-CH=, -(CH₂)₈-CH=, -(CH₂)₉-CH=, -(CH₂)₁₀-CH=, -(CH₂)₁₁-CH=, -(CH₂)₁₂-CH=, -(CH₂)₁₃-CH=, -(CH₂)₁₄-CH=, or -(CH₂)₁₅-CH=. In some such embodiments, X is -(CH₂)₇-CH=. In some embodiments, R is methyl, ethyl, isopropyl, propyl, butyl, isobutyl, sec-butyl, pentyl, isopentyl, neopentyl, hexyl, or 2-ethylhexyl. In some such embodiments, R is methyl, ethyl, or isopropyl. In some such embodiments, R is methyl.

[0068] In certain embodiments, the terminal olefin ester is selected from the group consisting of: a 4-pentenoic acid ester, a 5-hexenoic acid ester, a 6-heptenoic acid ester, a 7-octenoic acid ester, a 8-nonenoic acid ester, a 9-decenoic acid ester, a 10-undecenoic acid ester, a 11-dodecenoic acid ester, a 12-tridecenoic acid ester, a 13-tetradecenoic acid ester, a 14-pentadecenoic acid ester, a 15-hexadecenoic acid ester, a 16-heptadecenoic acid ester, a 17-octadecenoic acid ester, acids thereof, and any mixtures thereof. In some embodiments, the terminal olefin is a 9-decenoic acid ester, such as 9-decenoic acid methyl ester.

[0069] In certain embodiments, the weight-to-weight ratio of terminal olefin ester to internal olefin ester, e.g., in the reactant composition, cross-metathesis reaction is between 1:99 (terminal to internal) and 99:1 (terminal to internal). In some other embodiments, the weight ratio of the terminal and internal olefin is between 1:5 and 5:1. In yet some other embodiments, the weight ratio between the terminal and internal olefin is between 1:2 and 2:1. In some embodiments, the weight ratio between the terminal and internal olefin is approximately 1:1.

[0070] In certain embodiments, dibasic acids and/or dibasic esters and olefin byproducts may be formed by reacting internal olefin esters having the following structure:

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(where X' is a C3-C18 saturated or unsaturated alkyl chain, R' is an alkyl group, which can be optionally unsaturated or contain ether linkages, or hydrogen, and R'' is C1-8 alkyl, which is optionally unsaturated) with terminal olefins (e.g., terminal olefin esters) in the presence of a metathesis catalyst. In certain embodiments, the internal olefin ester is derived from a natural oil feedstock (described in greater detail below). In other embodiments, the internal olefin ester is purchased or produced from an external source separate than those derived from the natural oil feedstock.

[0071] In some embodiments, X' is $-(\text{CH}_2)_2-\text{CH}=\text{}$, $-(\text{CH}_2)_3-\text{CH}=\text{}$, $-(\text{CH}_2)_4-\text{CH}=\text{}$, $-(\text{CH}_2)_5-\text{CH}=\text{}$, $-(\text{CH}_2)_6-\text{CH}=\text{}$, $-(\text{CH}_2)_7-\text{CH}=\text{}$, $-(\text{CH}_2)_8-\text{CH}=\text{}$, $-(\text{CH}_2)_9-\text{CH}=\text{}$, $-(\text{CH}_2)_{10}-\text{CH}=\text{}$, $-(\text{CH}_2)_{11}-\text{CH}=\text{}$, $-(\text{CH}_2)_{12}-\text{CH}=\text{}$, $-(\text{CH}_2)_{13}-\text{CH}=\text{}$, $-(\text{CH}_2)_{14}-\text{CH}=\text{}$, or $-(\text{CH}_2)_{15}-\text{CH}=\text{}$. In some such embodiments, X' is $-(\text{CH}_2)_7-\text{CH}=\text{}$. In some embodiments, R' is methyl, ethyl, isopropyl, propyl, butyl, isobutyl, sec-butyl, pentyl, isopentyl, neopentyl, hexyl, or 2-ethylhexyl. In some such embodiments, R' is methyl, ethyl, or isopropyl. In some such embodiments, R' is methyl. In some embodiments, R'' is C1-6 alkyl. In some such embodiments, R'' is methyl, ethyl, propyl, or butyl. In some such embodiments, R'' is methyl or ethyl. In some such embodiments, R'' is ethyl, and wherein the first terminal olefin is 1-butene.

[0072] In certain embodiments, the internal olefin ester is selected from the group consisting of: pentenoic acid esters, hexenoic acid esters, heptenoic acid esters, octenoic acid esters, nonenoic acid esters, decenoic acid esters, undecenoic acid esters, dodecenoic acid esters, tridecenoic acid esters, tetradecenoic acid esters, pentadecenoic acid esters, hexadecenoic acid esters, heptadecenoic acid esters, octadecenoic acid esters, acids thereof, and mixtures thereof. In one particular embodiment, the internal olefin is 9-undecenoic acid ester. In another particular embodiment, the internal olefin is 9-dodecenoic acid ester.

[0073] In certain embodiments, the methods comprise providing a reactant composition comprising a terminal olefin ester (according to any of the above embodiments) and an internal olefin ester (according to any of the above embodiments). In some such embodiments, the reactant composition can include an amount of a metathesis catalyst (described in more detail below) at suitable

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concentrations. The reactant composition can also include one or more olefins, such as terminal alkenes or internal alkenes. In some embodiments, the terminal olefin ester and the internal olefin ester collectively make up at least 50 percent by weight, or 60 percent by weight, or 70 percent by weight, or 80 percent by weight, of the total weight of compounds in the reactant composition.

[0074] The metathesis reaction can be conducted under any conditions adequate to produce the desired metathesis product. For example, stoichiometry, atmosphere, solvent, temperature, and pressure can be selected by one skilled in the art to produce a desired product and to minimize undesirable byproducts. In some embodiments, the metathesis process may be conducted under an inert atmosphere. Similarly, in embodiments where a reagent is supplied as a gas, an inert gaseous diluent can be used in the gas stream. In such embodiments, the inert atmosphere or inert gaseous diluent typically is an inert gas, meaning that the gas does not interact with the metathesis catalyst to impede catalysis to a substantial degree. For example, non-limiting examples of inert gases include helium, neon, argon, and nitrogen, used individually or in with each other and other inert gases.

[0075] The reactor design for the metathesis reaction can vary depending on a variety of factors, including, but not limited to, the scale of the reaction, the reaction conditions (heat, pressure, etc.), the identity of the catalyst, the identity of the materials being reacted in the reactor, and the nature of the feedstock being employed. Suitable reactors can be designed by those of skill in the art, depending on the relevant factors, and incorporated into processes, such as those disclosed herein.

[0076] The metathesis reactions disclosed herein generally occur in the presence of one or more metathesis catalysts. Such methods can employ any suitable metathesis catalyst. The metathesis catalyst in this reaction may include any catalyst or catalyst system that catalyzes a metathesis reaction. Any known metathesis catalyst may be used, alone or in combination with one or more additional catalysts. Examples of metathesis catalysts and process conditions are described in US 2011/0160472, incorporated by reference herein in its entirety, except that in the event of any inconsistent disclosure or definition from the present specification, the disclosure or definition herein shall be deemed to prevail. A

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number of the metathesis catalysts described in US 2011/0160472 are presently available from Materia, Inc. (Pasadena, Calif.).

[0077] In some embodiments, the metathesis catalyst includes a Grubbs-type olefin metathesis catalyst and/or an entity derived therefrom. In some embodiments, the metathesis catalyst includes a first-generation Grubbs-type olefin metathesis catalyst and/or an entity derived therefrom. In some embodiments, the metathesis catalyst includes a second-generation Grubbs-type olefin metathesis catalyst and/or an entity derived therefrom. In some embodiments, the metathesis catalyst includes a first-generation Hoveda-Grubbs-type olefin metathesis catalyst and/or an entity derived therefrom. In some embodiments, the metathesis catalyst includes a second-generation Hoveda-Grubbs-type olefin metathesis catalyst and/or an entity derived therefrom. In some embodiments, the metathesis catalyst includes one or a plurality of the ruthenium carbene metathesis catalysts sold by Materia, Inc. of Pasadena, California and/or one or more entities derived from such catalysts. Representative metathesis catalysts from Materia, Inc. for use in accordance with the present teachings include but are not limited to those sold under the following product numbers as well as combinations thereof: product no. C823 (CAS no. 172222-30-9), product no. C848 (CAS no. 246047-72-3), product no. C601 (CAS no. 203714-71-0), product no. C627 (CAS no. 301224-40-8), product no. C571 (CAS no. 927429-61-6), product no. C598 (CAS no. 802912-44-3), product no. C793 (CAS no. 927429-60-5), product no. C801 (CAS no. 194659-03-9), product no. C827 (CAS no. 253688-91-4), product no. C884 (CAS no. 900169-53-1), product no. C833 (CAS no. 1020085-61-3), product no. C859 (CAS no. 832146-68-6), product no. C711 (CAS no. 635679-24-2), product no. C933 (CAS no. 373640-75-6).

[0078] In some embodiments, the metathesis catalyst includes a molybdenum and/or tungsten carbene complex and/or an entity derived from such a complex. In some embodiments, the metathesis catalyst includes a Schrock-type olefin metathesis catalyst and/or an entity derived therefrom. In some embodiments, the metathesis catalyst includes a high-oxidation-state alkylidene complex of molybdenum and/or an entity derived therefrom. In some embodiments, the metathesis catalyst includes a high-oxidation-state alkylidene complex of tungsten and/or an entity derived therefrom. In some embodiments, the metathesis catalyst includes molybdenum (VI). In some embodiments, the metathesis catalyst includes

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tungsten (VI). In some embodiments, the metathesis catalyst includes a molybdenum- and/or a tungsten-containing alkylidene complex of a type described in one or more of (a) Angew. Chem. Int. Ed. Engl., 2003, 42, 4592-4633; (b) Chem. Rev., 2002, 102, 145-179; and/or (c) Chem. Rev., 2009, 109, 3211-3226, each of which is incorporated by reference herein in its entirety, except that in the event of any inconsistent disclosure or definition from the present specification, the disclosure or definition herein shall be deemed to prevail.

[0079] In certain embodiments, the metathesis catalyst is dissolved in a solvent prior to conducting the metathesis reaction. In certain such embodiments, the solvent chosen may be selected to be substantially inert with respect to the metathesis catalyst. For example, substantially inert solvents include, without limitation: aromatic hydrocarbons, such as benzene, toluene, xylenes, etc.; halogenated aromatic hydrocarbons, such as chlorobenzene and dichlorobenzene; aliphatic solvents, including pentane, hexane, heptane, cyclohexane, etc.; and chlorinated alkanes, such as dichloromethane, chloroform, dichloroethane, etc. In some embodiments, the solvent comprises toluene.

[0080] In other embodiments, the metathesis catalyst is not dissolved in a solvent prior to conducting the metathesis reaction. The catalyst, instead, for example, can be slurried with the unsaturated ester, where the natural oil or unsaturated ester is in a liquid state. Under these conditions, it is possible to eliminate the solvent (e.g., toluene) from the process and eliminate downstream olefin losses when separating the solvent. In other embodiments, the metathesis catalyst may be added in solid state form (and not slurried) to the unsaturated ester (e.g., as an auger feed).

[0081] The metathesis reaction temperature may, in some instances, be a rate-controlling variable where the temperature is selected to provide a desired product at an acceptable rate. In certain embodiments, the metathesis reaction temperature is greater than -40°C , or greater than -20°C , or greater than 0°C , or greater than 10°C . In certain embodiments, the metathesis reaction temperature is less than 200°C , or less than 150°C , or less than 120°C . In some embodiments, the metathesis reaction temperature is between 0°C and 150°C , or is between 10°C and 120°C .

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[0082] The metathesis reaction can be run under any desired pressure. In some instances, it may be desirable to maintain a total pressure that is high enough to keep the cross-metathesis reagent in solution. Therefore, as the molecular weight of the cross-metathesis reagent increases, the lower pressure range typically decreases since the boiling point of the cross-metathesis reagent increases. The total pressure may be selected to be greater than 0.01 atm, or greater than 0.1 atm (10 kPa), or greater than 0.3 atm (30 kPa), or greater than 1 atm (100 kPa). In some embodiments, the reaction pressure is no more than about 70 atm (7000 kPa), or no more than about 30 atm (3000 kPa). In some embodiments, the pressure for the metathesis reaction ranges from about 1 atm (100 kPa) to about 30 atm (3000 kPa).

[0083] This process of cross-metathesizing a terminal olefin with an internal olefin may have certain advantages over a self-metathesis reactions to create a diacid ester or diacid. In comparison to the self-metathesis of a terminal olefin ester, the cross-metathesis reaction of a terminal olefin ester with an internal olefin ester results in the formation of an alkene byproduct besides ethylene (e.g., a C3+ alkene byproduct). For example, depending on the identity of the internal olefin ester(s) used, the alkene byproduct(s) can include, in some embodiments, a C3-8 terminal alkene, such as propylene, 1-butene, 1-pentene, 1-hexene, and the like. In certain instances, the presence of substantial quantities of ethylene may function as a poison to the metathesis catalyst, thereby reducing the yield and increasing the costs of running the reaction, as increased catalyst concentrations may be required. Further, in some instances, substantial amounts of ethylene may convert some metathesis catalysts into isomerization catalysts, which then requires the addition of isomerization inhibitors to avoid obtaining a disparate array of products. And in comparison to the self-metathesis of an internal olefin ester, the cross-metathesis reaction of a terminal olefin ester with an internal olefin ester results in the formation of an alkene byproduct having fewer carbon atoms (and, thus, a lower boiling point). For example, the self-metathesis of 9-dodecenoic acid methyl ester yields 3-hexene as a byproduct, while the cross-metathesis of 9-dodecenoic acid methyl ester with 9-decenoic acid methyl ester yields 1-butene as a byproduct. Production of a lower-boiling alkene byproduct can, in some embodiments, have certain advantages, such as making it easier to separate the alkene byproduct from the reactor and improve the reaction yield. It also allows for the use of lower temperatures and/or less

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stringent pressure conditions. While self-metathesis reactions of the terminal olefin ester or the internal olefin ester may still occur in the reactor, the availability of the cross-metathesis pathway, along with the option of manipulating conditions to favor the cross-metathesis reaction, provides substantial advantages not as easily obtainable by self-metathesis.

[0084] In certain embodiments, at least 70 wt%, 80 wt%, or 90 wt% dibasic ester and/or dibasic acid is formed from the cross-metathesis reaction of a terminal olefin and an internal olefin in the presence of less than 150 ppm, 100 ppm, 50 ppm, 25 ppm, or 10 ppm catalyst. A comparable self-metathesis reaction with terminal olefins (such as 9-decenoic acid ester) under similar reaction conditions may require more catalyst (e.g., more than 150 ppm, or more than 500 ppm) to achieve similar yields of dibasic esters and/or dibasic acids (potentially due to the formation of the ethylene byproduct).

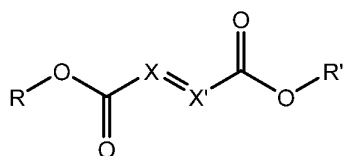
[0085] In certain embodiments, the dibasic ester and/or dibasic acid yield is improved by separating the olefin byproduct (e.g., a terminal olefin, such as propylene, 1-butene, 1-pentene, 1-hexene, etc.) formed in the cross-metathesis reaction from the metathesis product while the reaction between the terminal olefin ester and internal olefin ester is ongoing. For example, in some embodiments, at least a portion of the olefin byproduct is removed from the reactor during the reacting of the terminal olefin ester and the internal olefin ester. In some embodiments, at least 20%, or at least 30%, or at least 40%, or at least 50%, or at least 60%, or at least 70%, or at least 80%, or at least 90%, or at least 95%, or greater than 95%, of the formed terminal olefin byproduct is removed from the reactor during the reacting. The removal of the olefin byproduct can help favor the cross-metathesis reaction at the expense of the self-metathesis reactions, thereby improving the yield of the resulting dibasic ester or acid. The removal can be carried out by any suitable means. For example, in some embodiments, the reactor is equipped with a gas outlet suitable for releasing gases from the reactor. In some such embodiments, the gas outlet may include a pressure regulator. Further, the removal can be carried out during any suitable time or sequence. In some embodiments, the removal is continuous, or at least continuous after a certain stage of the reaction. In other embodiments, however, the removal occurs at certain discontinuous times, such that

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the terminal olefin (as well as other gases) are removed from the reactor for a time, and then the removal stops for a time.

[0086] In other embodiments, the dibasic ester and/or dibasic acid yield is improved by sparging the metathesis products in the metathesis reactor with a chemically inert gas (e.g., nitrogen, argon, or helium) to ventilate dissolved gases/byproducts (e.g., olefin byproducts) in the metathesis product.

[0087] In certain embodiments, the cross-metathesis reaction of the terminal olefin ester and internal olefin ester produces an unsaturated dibasic ester. In some embodiments, the resulting unsaturated dibasic ester is a compound of the following structure:



wherein R, R', X, and X' are as defined in any of the above embodiments. In some embodiments, -X=X'- is $-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-$.

[0088] In some embodiments, at least a portion of the internal olefin ester in the reactant composition is formed by reacting a portion of the terminal olefin ester with a low-molecular-weight internal olefin or mid-weight internal olefin in the presence of a metathesis catalyst. In certain embodiments, the low-molecular-weight internal olefin is selected from the group consisting of: 2-butene, 2-pentene, 2-hexene, 3-hexene, 2-heptene, 3-heptene, 2-octene, 3-octene, 4-octene, 2-nonene, 3-nonene, 4-nonene, and mixtures thereof. In some embodiments, the low-molecular-weight internal olefin is 2-butene. In some other embodiments, the low-molecular-weight internal olefin is 3-hexene. In some embodiments, this reaction to generate internal olefin ester is carried out in the same reactor as the cross-metathesis reaction of the internal olefin ester and the terminal olefin ester, e.g., using the same metathesis catalyst. In some other embodiments, however, this reaction to generate internal olefin ester is carried out separately from the cross-metathesis of the internal olefin ester and the terminal olefin ester. For example, in some embodiments, it is carried out in a separate reactor and/or in the same reactor at an earlier time. In some such embodiments, this metathesis reaction and the cross-metathesis reaction of the olefinic esters use the same metathesis catalyst. In

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some other embodiments, the separate metathesis reactions employ a different metathesis catalyst. This reaction can be beneficially used, for example, in instances where it may be undesirable or inconvenient to obtain certain quantities of the internal olefin ester. Thus, in such embodiments, the internal olefin ester can be generated from the existing supply of the terminal olefin ester.

[0089] In some embodiments, at least a portion of the terminal olefin ester in the reactant composition is formed by reacting a portion of the internal olefin ester with a terminal olefin in the presence of a metathesis catalyst. In certain embodiments, the terminal olefin is ethylene, propylene, 1-butene, or any mixtures thereof. In some embodiments, the terminal olefin is ethylene. In some embodiments, this reaction to generate terminal olefin ester is carried out in the same reactor as the cross-metathesis reaction of the internal olefin ester and the terminal olefin ester, e.g., using the same metathesis catalyst. In some other embodiments, however, this reaction to generate terminal olefin ester is carried out separately from the cross-metathesis of the internal olefin ester and the terminal olefin ester. For example, in some embodiments, it is carried out in a separate reactor and/or in the same reactor at an earlier time. In some such embodiments, this metathesis reaction and the cross-metathesis reaction of the olefinic esters use the same metathesis catalyst. In some other embodiments, the separate metathesis reactions employ a different metathesis catalyst. This reaction can be beneficially used, for example, in instances where it may be undesirable or inconvenient to obtain certain quantities of the terminal olefin ester. Thus, in such embodiments, the terminal olefin ester can be generated from the existing supply of the internal olefin ester.

[0090] FIG. 2 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester. The illustrated method 200 comprises: providing a reactant composition 201, which comprises a terminal olefin ester and an internal olefin ester; and reacting the terminal olefin ester with the internal olefin ester 202, for example, in a reactor in the presence of a metathesis catalyst, to form an unsaturated dibasic ester and a terminal olefin. The terminal olefin ester can be a terminal olefin ester according to any of the embodiments described above. The internal olefin ester can be an internal olefin ester according to any of the embodiments described above. The reacting can be carried out at any suitable

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conditions using any suitable metathesis catalyst, as described above. In some embodiments, at least a portion of the formed terminal olefin can be removed from the reactor during the reacting. In some such embodiments, the removal is continuous. In other such embodiments, however, the removal is discontinuous, e.g., occurring only at certain points during the reaction. The illustrated method can be incorporated into processes that include additional steps, either before or after those illustrated in FIG. 2. In some embodiments, at least a portion of the terminal olefin ester and/or the internal olefin ester is derived from a natural oil feedstock, e.g., by a process that includes metathesis and transesterification (in any order) of a feedstock comprising a natural oil.

[0091] FIG. 3 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester. The illustrated method 300 comprises: reacting a terminal olefin ester with an internal olefin 301 to form an internal olefin ester (and a terminal olefin byproduct), for example, in a reactor in the presence of a metathesis catalyst; and reacting the terminal olefin ester with the internal olefin ester 302, for example, in a reactor in the presence of a metathesis catalyst, to form an unsaturated dibasic ester and a terminal olefin. In some embodiments, the two reactions are carried out in the same reactor at roughly the same time. In some other embodiments, however, the two reactions are carried out at different, and, in some such embodiments, in different reactors and/or using different metathesis catalysts. The terminal olefin ester can be a terminal olefin ester according to any of the embodiments described above. The internal olefin ester can be an internal olefin ester according to any of the embodiments described above. The two reactions can be carried out at any suitable conditions using any suitable metathesis catalyst, as described above. In some embodiments, at least a portion of the formed internal olefin byproduct (from the first reaction) and/or at least a portion of the formed terminal olefin byproduct (from the second reaction) can be removed from the reactor during the reacting. In some such embodiments, the removal is continuous. In other such embodiments, however, the removal is discontinuous, e.g., occurring only at certain points during the reaction. The illustrated method can be incorporated into processes that include additional steps, either before or after those illustrated in FIG. 3. In some embodiments, at least a portion of the terminal olefin ester and/or the internal olefin ester is derived from a natural oil feedstock, e.g., by a process that

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includes metathesis and transesterification (in any order) of a feedstock comprising a natural oil.

[0092] FIG. 4 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester. The illustrated method 400 comprises: reacting an internal olefin ester with a terminal olefin 401 to form a terminal olefin ester (and an internal olefin byproduct), for example, in a reactor in the presence of a metathesis catalyst; and reacting the terminal olefin ester with the internal olefin ester 402, for example, in a reactor in the presence of a metathesis catalyst, to form an unsaturated dibasic ester and a terminal olefin. In some embodiments, the two reactions are carried out in the same reactor at roughly the same time. In some other embodiments, however, the two reactions are carried out at different, and, in some such embodiments, in different reactors and/or using different metathesis catalysts. The terminal olefin ester can be a terminal olefin ester according to any of the embodiments described above. The internal olefin ester can be an internal olefin ester according to any of the embodiments described above. The two reactions can be carried out at any suitable conditions using any suitable metathesis catalyst, as described above. In some embodiments, at least a portion of the formed internal olefin byproduct (from the first reaction) and/or at least a portion of the formed terminal olefin byproduct (from the second reaction) can be removed from the reactor during the reacting. In some such embodiments, the removal is continuous. In other such embodiments, however, the removal is discontinuous, e.g., occurring only at certain points during the reaction. The illustrated method can be incorporated into processes that include additional steps, either before or after those illustrated in FIG. 4. In some embodiments, at least a portion of the terminal olefin ester and/or the internal olefin ester is derived from a natural oil feedstock, e.g., by a process that includes metathesis and transesterification (in any order) of a feedstock comprising a natural oil.

Reactions of Unsaturated Dibasic Esters

[0093] In certain other aspects, the unsaturated dibasic esters can be further reacted in various ways. Such further reactions include, but are not limited to, any combination of hydrogenation, isomerization, and reactions to convert the dibasic ester to a dibasic acid (e.g., by methods that include hydrolysis or saponification).

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[0094] In certain aspects, the methods disclosed herein comprise: making a dibasic ester (e.g., wherein the making comprises making an unsaturated dibasic ester according to any methods described above, which can be optionally hydrogenated); and converting the dibasic ester to a dibasic acid. In some embodiments, the converting comprises hydrolyzing the dibasic ester to a dibasic acid, e.g., by reacting the dibasic ester with water in the presence of an acid catalyst. Any suitable hydrolysis method can be used. In some other embodiments, the converting comprises saponifying the dibasic ester to form a dibasic acid salt (where "acid salt" refers to a carboxylate anion, whether in solution or in solid-state form), and optionally acidifying the dibasic acid salt to form the dibasic acid. Any suitable method of saponification can be used. In some embodiments, the resulting dibasic acid is octadecanedioic acid. In some other embodiments, the resulting dibasic acid is 9-octadecenedioic acid.

[0095] In other embodiments, the dibasic acid and/or dibasic ester is isomerized to form an isomerized dibasic acid and/or isomerized dibasic ester. The isomerization of the dibasic acid and/or dibasic ester may be conducted at an elevated temperature (i.e., greater than 25°C). In certain embodiments, the temperature of the heat treatment for the isomerization reaction is greater than 100°C, greater than 150°C, or greater than 200°C. In other embodiments, the temperature is between 100°C-300°C, between 150-250°C, or about 200°C. In some embodiments, the heat treatment step is conducted in the presence of an isomerization catalyst. In one particular embodiment, the isomerization catalyst is $(PCy_3)_2(Cl)(H)Ru(CO)$, where "Cy" represents a cyclohexyl group.

[0096] In certain embodiments, the isomerized dibasic acid and/or isomerized dibasic ester comprises compounds selected from the group consisting of: isomerized dimethyl 9-octadecenedioate or isomerized 9-octadecene dioic acid.

[0097] In certain embodiments, the isomerized dibasic acid and/or isomerized dibasic ester is self-metathesized or cross-metathesized with a low-molecular-weight olefin or mid-weight olefin. Typical metathesis reaction conditions and catalysts are discussed in greater detail below. In one embodiment, the isomerized dibasic acid and/or isomerized dibasic ester is self-metathesized in the presence of approximately 10 ppm, 20 ppm, 40 ppm, 50 ppm, 80 ppm, 100 ppm, 120 ppm, or greater than 150 ppm metathesis catalyst.

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[0098] In certain embodiments, the dibasic acid, dibasic ester, isomerized dibasic acid, and/or isomerized dibasic ester is hydrogenated. Typical hydrogenation reaction conditions and catalysts are discussed in greater detail below. In one particular example, the hydrogenation reaction is conducted in the presence of a nickel based catalyst at approximately 150°C and 150 psig.

[0099] In certain embodiments, the dibasic acids, dibasic esters, isomerized dibasic acids, and/or isomerized dibasic esters may be used in a variety of different commercial applications, including, but not limited to: lubricants, waxes, films, paints, paint strippers, coatings, plasticizers, resins, binders, solvents, polyols, soil stabilization, chemical grouting, oilfield drilling fluids, crop protection products, surfactants, intermediates, and adhesives.

[00100] FIG. 5 shows a flow chart that illustrates certain embodiments for making a saturated dibasic ester. The illustrated method 500 comprises: making an unsaturated dibasic ester 501, for example, according to any of the embodiments disclosed above; and hydrogenating the unsaturated dibasic ester. Any suitable hydrogenation conditions can be used, as described above.

[00101] FIG. 6 shows a flow chart that illustrates certain embodiments for making a dibasic acid. The illustrated method 600 comprises: making a dibasic ester 601, e.g., according to any of the embodiments described above; and converting the dibasic ester to a dibasic acid 602. In some embodiments, the dibasic ester is an unsaturated dibasic ester, which can be made, for example, according to any of the methods described above. In some other embodiments, the dibasic ester is a saturated dibasic ester, which, for example, can be made by making an unsaturated dibasic ester (according to any of the embodiments described above) and then hydrogenating the unsaturated dibasic ester to form a saturated dibasic ester. Any suitable method can be used to convert the ester groups to acid groups. For example, in some embodiments, the converting comprises hydrolyzing the dibasic ester, e.g., by reacting it with water, and, in some embodiments, in the presence of an acid catalyst. In some other embodiments, the converting comprises saponifying the dibasic ester, followed by acidification.

Unsaturated Esters Derived from Natural Oil Feedstocks

[00102] As mentioned above, the terminal olefin ester and/or the internal olefin ester may be derived from a natural oil feedstock, in addition to other valuable compositions. For example, a number of valuable compositions may be targeted through the self-metathesis reaction of a natural oil feedstock, or the cross-metathesis reaction of the natural oil feedstock with a low-molecular-weight olefin or mid-weight olefin, in the presence of a metathesis catalyst. Such valuable compositions may include fuel compositions, detergents, surfactants, and other specialty chemicals. Non-limiting examples of fuel compositions include jet, kerosene, and diesel fuel. Additionally, transesterified products (i.e., the products formed from transesterifying an ester in the presence of an alcohol) may also be targeted, non-limiting examples of which include: fatty acid methyl esters; biodiesel; 9-decenoic acid ("9DA") esters, 9-undecenoic acid ("9UDA") esters, and/or 9-dodecenoic acid ("9DDA") esters; 9DA, 9UDA, and/or 9DDA; alkali metal salts and alkaline earth metal salts of 9DA, 9UDA, and/or 9DDA; dimers of the transesterified products; and mixtures thereof. Any suitable method of deriving the internal unsaturated ester and/or the terminal unsaturated ester from a natural oil feedstock can be used.

[00103] In certain embodiments, prior to a metathesis reaction, a natural oil feedstock may be treated to render the natural oil more suitable for the subsequent metathesis reaction. In certain embodiments, the natural oil preferably is a vegetable oil or vegetable oil derivative, such as soybean oil, palm oil, or rapeseed (canola) oil.

[00104] In one embodiment, the treatment of the natural oil involves the removal of catalyst poisons, such as peroxides, which may potentially diminish the activity of the metathesis catalyst. Non-limiting examples of natural oil feedstock treatment methods to diminish catalyst poisons include those described in WO 2009/020665, WO 2009/020667, and U.S. Patent Application Publication Nos. 2011/0160472 and 2011/0313180, herein incorporated by reference in their entireties. In certain embodiments, the natural oil feedstock is thermally treated by heating the feedstock to a temperature greater than 100°C in the absence of oxygen and held at the temperature for a time sufficient to diminish catalyst poisons in the feedstock. In other embodiments, the temperature is between approximately 100°C

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and 300°C, between approximately 120°C and 250°C, between approximately 150°C and 210°C, or approximately between 190 and 200°C. In one embodiment, the absence of oxygen is achieved by sparging the natural oil feedstock with nitrogen, wherein the nitrogen gas is pumped into the feedstock treatment vessel at a pressure of approximately 10 atm (150 psig).

[00105] In certain embodiments, the natural oil feedstock is chemically treated under conditions sufficient to diminish the catalyst poisons in the feedstock through a chemical reaction of the catalyst poisons. In certain embodiments, the feedstock is treated with a reducing agent or a cation-inorganic base composition. Non-limiting examples of reducing agents include bisulfite, borohydride, phosphine, thiosulfate, individually or combinations thereof.

[00106] In certain embodiments, the natural oil feedstock is treated with an adsorbent to remove catalyst poisons. In one embodiment, the feedstock is treated with a combination of thermal and adsorbent methods. In another embodiment, the feedstock is treated with a combination of chemical and adsorbent methods. In another embodiment, the treatment involves a partial hydrogenation treatment to modify the natural oil feedstock's reactivity with the metathesis catalyst. Additional non-limiting examples of feedstock treatment are also described below when discussing the various metathesis catalysts.

[00107] Additionally, in certain embodiments, the low-molecular-weight olefin or mid-weight olefin may also be treated prior to the metathesis reaction with the natural oil. Like the natural oil treatment, the low-molecular-weight olefin or mid-weight olefin may be treated to remove poisons that may impact or diminish catalyst activity.

[00108] In certain embodiments, the low-molecular-weight olefin or mid-weight olefin may be self-metathesized to form a metathesized low-molecular-weight olefin or metathesized mid-weight olefin in order to adjust the properties of the olefin and the potential products following metathesis with the natural oil. In some embodiments, the low-molecular-weight olefin or mid-weight olefin is self-metathesized in the presence of a rhenium oxide catalyst (e.g., rhenium oxide supported on alumina) or tungsten oxide catalyst (e.g., tungsten oxide supported on silica). This reaction may be conducted in a fixed bed reactor. In one embodiment, the low-molecular-weight olefin is 1-butene. The low-molecular-weight olefin may be

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self-metathesized over rhenium oxide catalyst in a fixed bed reactor to produce mainly 3-hexene and ethylene. Ethylene may be separated from the reactor effluent for further processing, such as being sent to an ethylene purification system or ethylene oxide system. Unreacted low-molecular-weight olefin (e.g., 1-butene) may be recycled to the fixed bed reactor and the metathesized low-weight-olefin (e.g., 3-hexene) may be sent to the metathesis reactor for metathesis with the natural oil.

[00109] In other embodiments, the low-molecular-weight olefin or mid-weight olefin is isomerized prior to being metathesized with the natural oil. Adjusting the composition and properties of the low-molecular-weight olefin or mid-weight olefin through isomerization may allow for different products or different ratios of products to be formed following metathesis of the low-molecular-weight olefin or mid-weight olefin with a natural oil. In some embodiments, the isomerized or branched low-molecular-weight olefin is in the C4 to C10 range. In one embodiment, hexene is isomerized to form a branched low-molecular-weight olefin. Non-limiting examples of branched low-molecular-weight olefins include isobutene, 3-methyl-1-butene, 2-methyl-3-pentene, and 2,2-dimethyl-3-pentene.

[00110] By using branched low-molecular-weight olefins or branched mid-weight olefins in the metathesis reaction, the metathesized product will include branched olefins, which can be subsequently hydrogenated to iso-paraffins. In certain embodiments, the branched low-molecular-weight olefins or branched mid-weight olefins may help achieve the desired performance properties for a fuel composition, such as jet, kerosene, or diesel fuel. In certain embodiments, C11-C14 olefins may be targeted following metathesis and separation steps through isomerization of the low-molecular-weight olefin. In other embodiments, the branched low-molecular-weight olefins or branched mid-weight olefins may help target longer chain esters for use as detergents or cleaning compositions. In some embodiments, C10-C15 or C11-C14 methyl esters may be targeted following metathesis, separation, and transesterification steps (discussed in detail below). Isomerization reactions are well-known in the art, as described in U.S. Patent Nos. 3,150,205; 4,210,771; 5,095,169; and 6,214,764, herein incorporated by reference in their entireties.

[00111] After any optional pre-treatment, the natural oil can be refined in any suitable manner to form an internal unsaturated ester and/or a terminal unsaturated

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ester. In some embodiments, the disclosure provides methods of refining a natural oil, comprising: providing a feedstock comprising a natural oil; reacting the feedstock in the presence of a fourth metathesis catalyst to form a metathesized product comprising one or more unsaturated glycerides and one or more olefins; separating the unsaturated glycerides in the metathesized product from the olefins in the metathesized product; and transesterifying the separated unsaturated glycerides in the presence of an alcohol to form a transesterified product comprising a terminal olefin ester or an internal olefin ester. In some embodiments, the terminal olefin ester and/or the internal olefin ester can be used according to the method of any of the above embodiments, e.g., to form an unsaturated dibasic ester. In some embodiments, the alcohol is methanol. In some embodiments, the unsaturated dibasic ester is a 9-octadecenedioic acid dibasic ester, such as 9-octadecenedioic acid dimethyl ester. In some further embodiments, the resulting unsaturated dibasic ester can be converted to a saturated dibasic ester and/or a saturated dibasic acid according to any of the embodiments of the second and/or third aspects.

[00112] FIG. 1 provides an illustration of one embodiment for carrying out such a refining process. As shown in FIG. 1, after this optional treatment of the natural oil feedstock, low-molecular-weight olefin, and/or mid-weight olefin, the natural oil 12 is reacted with itself, or combined with a low-molecular-weight olefin 14 or mid-weight olefin 15 in a metathesis reactor 20 in the presence of a metathesis catalyst.

Metathesis catalysts and metathesis reaction conditions are discussed in greater detail below. In certain embodiments, in the presence of a metathesis catalyst, the natural oil 12 undergoes a self-metathesis reaction with itself. In other embodiments, in the presence of the metathesis catalyst, the natural oil 12 undergoes a cross-metathesis reaction with the low-molecular-weight olefin 14 or mid-weight olefin 15. In certain embodiments, the natural oil 12 undergoes both self- and cross-metathesis reactions in parallel metathesis reactors. The self-metathesis and/or cross-metathesis reaction form a metathesized product 22 wherein the metathesized product 22 comprises olefins 32 and esters 34.

[00113] In certain embodiments, the low-molecular-weight olefin 14 is in the C2 to C6 range. As a non-limiting example, in one embodiment, the low-molecular-weight olefin 14 may comprise at least one of the following: ethylene, propylene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 3-pentene, 2-methyl-1-butene,

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2-methyl-2-butene, 3-methyl-1-butene, cyclopentene, 1,4-pentadiene, 1-hexene, 2-hexene, 3-hexene, 4-hexene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl-2-pentene, 3-methyl-2-pentene, 4-methyl-2-pentene, 2-methyl-3-pentene, and cyclohexene. Non-limiting examples of low-molecular-weight olefins in the C7 to C9 range include 1,4-heptadiene, 1-heptene, 3,6-nonadiene, 3-nonene, 1,4,7-octatriene. In another embodiment, the low-molecular-weight olefin 14 comprises at least one of styrene and vinyl cyclohexane. In another embodiment, the low-molecular-weight olefin 14 may comprise at least one of ethylene, propylene, 1-butene, 2-butene, and isobutene. In another embodiment, the low-molecular-weight olefin 14 comprises at least one alpha-olefin or terminal olefin in the C2 to C10 range.

[00114] In another embodiment, the low-molecular-weight olefin 14 comprises at least one branched low-molecular-weight olefin in the C4 to C10 range. Non-limiting examples of branched low-molecular-weight olefins include isobutene, 3-methyl-1-butene, 2-methyl-3-pentene, and 2,2-dimethyl-3-pentene.

[00115] In certain embodiments, the mid-weight olefin 15 comprises unsaturated straight, branched, or cyclic hydrocarbons in the C15 to C24 range. In some embodiments, the mid-weight olefin is an alpha-olefin or terminal olefin.

[00116] As noted, it is possible to use a mixture of various linear or branched low-molecular-weight olefins and linear or branched mid-weight olefins in the reaction to achieve the desired metathesis product distribution. In certain embodiments, the mixture comprises linear and/or branched low-molecular-weight olefins. In other embodiments, the mixture comprises linear and/or branched mid-weight olefins. In one embodiment, a mixture of butenes (1-butene, 2-butenes, and, optionally, isobutene) may be employed as the low-molecular-weight olefin, offering a low cost, commercially available feedstock instead a purified source of one particular butene. Such low cost mixed butene feedstocks are typically diluted with n-butane and/or isobutane.

[00117] In certain embodiments, recycled streams from downstream separation units may be introduced to the metathesis reactor 20 in addition to the natural oil 12 and, in some embodiments, the low-molecular-weight olefin 14 and/or mid-weight olefin 15. For instance, in some embodiments, a C2-C6 recycle olefin stream or a C3-C4 bottoms stream from an overhead separation unit may be returned to the

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metathesis reactor. In one embodiment, as shown in FIG. 1, a light weight olefin stream 44 from an olefin separation unit 40 may be returned to the metathesis reactor 20. In another embodiment, the C3-C4 bottoms stream and the light weight olefin stream 44 are combined together and returned to the metathesis reactor 20. In another embodiment, a C15+ bottoms stream 46 from the olefin separation unit 40 is returned to the metathesis reactor 20. In another embodiment, all of the aforementioned recycle streams are returned to the metathesis reactor 20.

[00118] In other embodiments, various ester streams downstream of the transesterification unit (discussed below) may also be recycled or returned to the metathesis reactor 20. In certain embodiments, a glycerolysis reaction may be conducted on the recycled ester stream to prevent or limit the amount of free glycerol entering the metathesis reactor 20. In some embodiments, the recycled ester stream will undergo a purification step to limit the amount of methanol being recycled to the metathesis reactor 20. In some embodiments, the recycled ester stream is combined with the low-molecular-weight olefin 14 and/or mid-weight olefin 15 prior to conducting the glycerolysis reaction and entering the metathesis reactor 20. The glycerolysis reaction may also limit or prevent free fatty acid methyl esters from entering the metathesis reaction and subsequently exiting the metathesis reactor as free fatty acid methyl esters that may boil close to various high-valued olefin products. In such cases, these methyl ester components may be separated with the olefins during the separation of the olefins and esters. Such methyl ester components may be difficult to separate from the olefins by distillation.

[00119] The metathesis reaction in the metathesis reactor 20 produces a metathesized product 22. In one embodiment, the metathesized product 22 enters a flash vessel operated under temperature and pressure conditions which target C2 or C2-C3 compounds to flash off and be removed overhead. The C2 or C2-C3 light ends are comprised of a majority of hydrocarbon compounds having a carbon number of 2 or 3. In certain embodiments, the C2 or C2-C3 light ends are then sent to an overhead separation unit, wherein the C2 or C2-C3 compounds are further separated overhead from the heavier compounds that flashed off with the C2-C3 compounds. These heavier compounds are typically C3-C5 compounds carried overhead with the C2 or C2-C3 compounds. After separation in the overhead separation unit, the overhead C2 or C2-C3 stream may then be used as a fuel

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source. These hydrocarbons have their own value outside the scope of a fuel composition, and may be used or separated at this stage for other valued compositions and applications. In certain embodiments, the bottoms stream from the overhead separation unit containing mostly C3-C5 compounds is returned as a recycle stream to the metathesis reactor. In the flash vessel, the metathesized product 22 that does not flash overhead is sent downstream for separation in a separation unit 30, such as a distillation column.

[00120] Prior to the separation unit 30, in certain embodiments, the metathesized product 22 may be contacted with a reactant or reagent to deactivate or to extract the catalyst. In certain embodiments, the metathesized product 22 is introduced to an adsorbent or complexing agent to facilitate the separation of the metathesized product 22 from the metathesis catalyst. In one embodiment, the adsorbent or complexing agent is a clay bed. The clay bed will adsorb the metathesis catalyst, and after a filtration step, the metathesized product 22 can be sent to the separation unit 30 for further processing. In another embodiment, the adsorbent or complexing agent is a water soluble phosphine reagent such as tris hydroxymethyl phosphine (THMP). Catalyst may be separated with a water soluble phosphine through known liquid-liquid extraction mechanisms by decanting the aqueous phase from the organic phase.

[00121] In some embodiments, the metathesized product 22 may be sent to a catalyst kill drum where the reagent (e.g., THMP aqueous solution) is added to deactivate the metathesis catalyst. THMP may be added at a rate equivalent to at least 1:1, 5:1, 10:1, 25:1, or 50:1 molar ratio relative to the catalyst pumped into the catalyst kill drum.

[00122] In certain embodiments, the reagent (e.g., THMP) can be left in the metathesized product 22 and carried along, either in whole or in part, into a subsequent chemical reaction or processing step. In other embodiments, the reagent can be separated and removed from the mixture, either partially or completely, prior to any subsequent reaction or processing step. In some embodiments, passivation and extraction can be coupled into one step (e.g., by providing the reagent in the extracting material).

[00123] In one embodiment, the catalyst separation occurs by sending the effluent from the catalyst kill drum to a catalyst decanter drum. The decanter drum

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may function as a horizontal vessel with a vertical baffle and a boot to collect the water phase containing the metathesis catalyst. In some embodiments, the decanter drum operates at a temperature between approximately 60-90°C and a pressure between 1-1.5 atm, or approximately 53°C (127°F) and 1.1 atm (16 psia).

[00124] In other embodiments, the catalyst separation comprises washing or extracting the mixture with a polar solvent (e.g., particularly, though not exclusively, for embodiments in which the reagent is at least partially soluble in the polar solvent). In some embodiments, the polar solvent is added in a subsequent step following catalyst deactivation. In other embodiments, the polar solvent (e.g., water) is added to the metathesized product 22 at approximately the same time as the deactivation reagent (e.g., THMP). Near simultaneous addition of the deactivation reagent and polar solvent to the metathesized product can eliminate the need for an additional reaction/separation vessel, which may simplify the process and potentially save capital.

[00125] In some embodiments, the polar solvent is at least partially non-miscible with the mixture, such that a separation of layers can occur. In some embodiments, at least a portion of the reagent is partitioned into the polar solvent layer, which can then be separated from the non-miscible remaining layer and removed. Representative polar solvents for use in accordance with the present teachings include but are not limited to water, alcohols (e.g., methanol, ethanol, etc.), ethylene glycol, glycerol, DMF, multifunctional polar compounds including but not limited to polyethylene glycols and/or glymes, ionic liquids, and the like, and combinations thereof. In some embodiments, the mixture is extracted with water. In some embodiments, when a phosphite ester that is at least partially hydrolyzable (e.g., in some embodiments, a phosphite ester having a low molecular weight, including but not limited to trimethyl phosphite, triethyl phosphite, and a combination thereof) is used as a reagent, washing the mixture with water may convert the phosphite ester into a corresponding acid. While neither desiring to be bound by any particular theory nor intending to limit in any measure the scope of the appended claims or their equivalents, it is presently believed that such a hydrolysis may occur more rapidly with lower molecular weight esters.

[00126] In some embodiments, when extraction with a polar solvent is desired, the extracting may comprise high shear mixing (e.g., mixing of a type sufficient to

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disperse and/or transport at least a portion of a first phase and/or chemical species into a second phase with which the first phase and/or a chemical species would normally be at least partly immiscible) although such mixing, in some embodiments, may contribute to undesirable emulsion formation. In some embodiments, the extracting comprises low-intensity mixing (e.g., stirring that is not high shear). The present teachings are in no way restricted to any particular type or duration of mixing. However, for purposes of illustration, in some embodiments, the extracting comprises mixing the polar solvent and the mixture together for at least about 1 second, 10 seconds, 30 seconds, 1 minute, 2 minutes, 5 minutes, 10 minutes, 15 minutes, 20 minutes, 25 minutes, 30 minutes, 35 minutes, 40 minutes, 45 minutes, 50 minutes, 55 minutes, or 60 minutes. While neither desiring to be bound by any particular theory nor intending to limit in any measure the scope of the appended claims or their equivalents, it is presently believed that shorter mixing times (e.g., on the order of a second or seconds) are achievable when inline shear mixing is used for mixing.

[00127] When extraction with a polar solvent is desired, the present teachings are in no way restricted to any particular amount of polar solvent added to the mixture for the extracting. However, for purposes of illustration, in some embodiments, the amount by weight of polar solvent (e.g., water) added to the mixture for the extracting is more than the weight of the mixture. In some embodiments, the amount by weight of polar solvent (e.g., water) added to the mixture for the extracting is less than the weight of the mixture. In some embodiments, the weight ratio of the mixture to the water added to the mixture is at least about 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 20:1, 40:1, or 100:1. For higher oil to water ratios, extraction and separation using a centrifuge and/or coalescer may be desirable.

[00128] In some embodiments, when extraction with a polar solvent is desired, methods for suppressing dehydrogenation in accordance with the present teachings further comprise allowing a settling period following the polar solvent wash to promote phase separation. The present teachings are in no way restricted to any particular duration of settling period. However, for purposes of illustration, in some embodiments, the settling period is at least about 1 minute, 2 minutes, 5 minutes, 10 minutes, 15 minutes, 30 minutes, 60 minutes, or 120 minutes.

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[00129] In addition to or as an alternative to washing the mixture with a polar solvent to remove the reagent (e.g., THMP)—a method in accordance with the present teachings can optionally further comprise removing at least a portion of the reagent by adsorbing it onto an adsorbent, which optionally can then be physically separated from the mixture (e.g., via filtration, centrifugation, crystallization, or the like). In some embodiments, the adsorbent is polar. Representative adsorbents for use in accordance with the present teachings include but are not limited to carbon, silica, silica-alumina, alumina, clay, magnesium silicates (e.g., Magnesols), the synthetic silica adsorbent sold under the tradename TRISYL by W. R. Grace & Co., diatomaceous earth, polystyrene, macroporous (MP) resins, and the like, and combinations thereof.

[00130] Additionally, in certain embodiments, prior to the separation unit 30 (and after catalyst separation, in some instances), the metathesis product 22 may be sent to a hydrogenation unit, wherein the carbon-carbon double bonds in the olefins and esters are partially to fully saturated with hydrogen gas. Hydrogenation may be conducted according to any known method in the art for hydrogenating double bond-containing compounds such as the olefins and esters present in the metathesis product 22. In certain embodiments, in the hydrogenation unit, hydrogen gas is reacted with the metathesis product 22 in the presence of a hydrogenation catalyst to produce a hydrogenated product comprising partially to fully hydrogenated paraffins/olefins and partially to fully hydrogenated esters.

[00131] In some embodiments, the metathesis product 22 is hydrogenated in the presence of a hydrogenation catalyst comprising nickel, copper, palladium, platinum, molybdenum, iron, ruthenium, osmium, rhodium, or iridium, individually or in combinations thereof. Useful catalyst may be heterogeneous or homogeneous. In some embodiments, the catalysts are supported nickel or sponge nickel type catalysts.

[00132] In some embodiments, the hydrogenation catalyst comprises nickel that has been chemically reduced with hydrogen to an active state (i.e., reduced nickel) provided on a support. The support may comprise porous silica (e.g., kieselguhr, infusorial, diatomaceous, or siliceous earth) or alumina. The catalysts are characterized by a high nickel surface area per gram of nickel.

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[00133] Commercial examples of supported nickel hydrogenation catalysts include those available under the trade designations "NYSOFACT", "NYSOSEL", and "NI 5248 D" (from BASF Catalysts LLC, Iselin, NJ). Additional supported nickel hydrogenation catalysts include those commercially available under the trade designations "PRICAT 9910", "PRICAT 9920", "PRICAT 9908", "PRICAT 9936" (from Johnson Matthey Catalysts, Ward Hill, MA).

[00134] The supported nickel catalysts may be of the type described in U.S. Patent No. 3,351,566, US Patent No. 6,846,772, EP 0168091, and EP 0167201, incorporated by reference herein in their entireties. Hydrogenation may be carried out in a batch or in a continuous process and may be partial hydrogenation or complete hydrogenation. In certain embodiments, the temperature ranges from about 50°C to about 350°C, about 100°C to about 300°C, about 150°C to about 250°C, or about 100°C to about 150°C. The desired temperature may vary, for example, with hydrogen gas pressure. Typically, a higher gas pressure will require a lower temperature. Hydrogen gas is pumped into the reaction vessel to achieve a desired pressure of H₂ gas. In certain embodiments, the H₂ gas pressure ranges from about 15 psig (1 atm) to about 3000 psig (204.1 atm), about 15 psig (1 atm) to about 90 psig (6.1 atm), or about 100 psig (6.8 atm) to about 500 psig (34 atm). As the gas pressure increases, more specialized high-pressure processing equipment may be required. In certain embodiments, the reaction conditions are "mild," wherein the temperature is approximately between approximately 50°C and approximately 100°C and the H₂ gas pressure is less than approximately 100 psig. In other embodiments, the temperature is between about 100°C and about 150°C, and the pressure is between about 100 psig (6.8 atm) and about 500 psig (34 atm). When the desired degree of hydrogenation is reached, the reaction mass is cooled to the desired filtration temperature.

[00135] The amount of hydrogenation catalyst is typically selected in view of a number of factors including, for example, the type of hydrogenation catalyst used, the amount of hydrogenation catalyst used, the degree of unsaturation in the material to be hydrogenated, the desired rate of hydrogenation, the desired degree of hydrogenation (e.g., as measure by iodine value (IV)), the purity of the reagent, and the H₂ gas pressure. In some embodiments, the hydrogenation catalyst is used

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in an amount of about 10 weight% or less, for example, about 5 weight% or less or about 1 weight% or less.

[00136] When the desired degree of hydrogenation is reached, the reaction mass is cooled to the desired filtration temperature. During hydrogenation, the carbon-carbon double bonds are partially to fully saturated by the hydrogen gas. In one embodiment, the olefins in the metathesis product 22 are reacted with hydrogen to form a fuel composition comprising only or mostly paraffins. Additionally, the esters from the metathesis product are fully or nearly fully saturated in the hydrogenation unit. In another embodiment, the resulting hydrogenated product includes only partially saturated paraffins/olefins and partially saturated esters.

[00137] In the separation unit 30, in certain embodiments, the metathesized product 22 (from a hydrogenation unit, metathesis reactor 20, or catalyst separation unit) is separated into at least two product streams. In one embodiment, the metathesized product 22 is sent to the separation unit 30, or distillation column, to separate the olefins 32 from the esters 34. In another embodiment, a byproduct stream comprising C₇'s and cyclohexadienes (e.g., 1,4-cyclohexadiene) may be removed in a side-stream from the separation unit 30. In certain embodiments, the separated olefins 32 may comprise hydrocarbons with carbon numbers up to 24. In certain embodiments, the esters 34 may comprise metathesized glycerides. In other words, the lighter end olefins 32 are preferably separated or distilled overhead for processing into olefin compositions, while the esters 34, comprised mostly of compounds having carboxylic acid/ester functionality, are drawn into a bottoms stream. Based on the quality of the separation, it is possible for some ester compounds to be carried into the overhead olefin stream 32, and it is also possible for some heavier olefin hydrocarbons to be carried into the ester stream 34. Additionally, the separated cyclohexadienes (e.g., 1,4-cyclohexadiene) may be further processed in a dehydrogenation step to form benzene. Examples of catalytic dehydrogenation catalysts include platinum supported on alumina. Examples of oxidative dehydrogenation catalysts include mixed metal oxides consisting of molybdenum, vanadium, niobium, tellurium, magnesium, and/or aluminum. Other dehydrogenation catalysts examples include cerium/zirconium, alkaline earth/nickel, calcium-nickel-phosphate, chromium, iron-chromium oxide, bismuth/molybdenum, tin/antimony, silver, copper.

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[00138] In one embodiment, the olefins 32 may be collected and sold for any number of known uses. In other embodiments, the olefins 32 are further processed in an olefin separation unit 40 and/or hydrogenation unit 50 (where the olefinic bonds are saturated with hydrogen gas 48, as described below). In other embodiments, esters 34 comprising heavier end glycerides and free fatty acids are separated or distilled as a bottoms product for further processing into various products. In certain embodiments, further processing may target the production of the following non-limiting examples: fatty acid methyl esters; biodiesel; 9DA esters, 9UDA esters, and/or 9DDA esters; 9DA, 9UDA, and/or 9DDA; alkali metal salts and alkaline earth metal salts of 9DA, 9UDA, and/or 9DDA; diacids, and/or diesters of the transesterified products; and mixtures thereof. In certain embodiments, further processing may target the production of C₁₅-C₁₈ fatty acids and/or esters. In other embodiments, further processing may target the production of diacids and/or diesters. In yet other embodiments, further processing may target the production of compounds having molecular weights greater than the molecular weights of stearic acid and/or linolenic acid.

[00139] As shown in FIG. 1, regarding the overhead olefins 32 from the separation unit 30, the olefins 32 may be further separated or distilled in the olefin separation unit 40 to separate the various compositions. The olefin separation unit 40 may comprise a number of distillation towers. In some embodiments, the various composition streams are separated using at least four distillation towers. In other embodiments, three towers or less are used to separate the olefin compositions.

[00140] In one embodiment, light end olefins 44 consisting of mainly C₂-C₉ compounds may be distilled into an overhead stream from the olefin separation unit 40. In certain embodiments, the light end olefins 44 are comprised of a majority of C₃-C₈ hydrocarbon compounds. In other embodiments, heavier olefins having higher carbon numbers may be separated overhead into the light end olefin stream 44 to assist in targeting a specific fuel composition. The light end olefins 44 may be recycled to the metathesis reactor 20, purged from the system for further processing and sold, or a combination of the two. In one embodiment, the light end olefins 44 may be partially purged from the system and partially recycled to the metathesis reactor 20. With regards to the other streams in the olefin separation unit 40, a heavier C₁₆+, C₁₈+, C₂₀+, C₂₂+, or C₂₄+ compound stream may be separated out

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as an olefin bottoms stream 46. This olefin bottoms stream 46 may be purged or recycled to the metathesis reactor 20 for further processing, or a combination of the two. In another embodiment, a center-cut olefin stream 42 may be separated out of the olefin distillation unit for further processing. The center-cut olefins 42 may be designed to target a selected carbon number range for a specific fuel composition. As a non-limiting example, a C5-C15 distribution may be targeted for further processing into a naphtha-type jet fuel. Alternatively, a C8-C16 distribution may be targeted for further processing into a kerosene-type jet fuel. In another embodiment, a C8-C25 distribution may be targeted for further processing into a diesel fuel.

[00141] In some embodiments, processing steps may be conducted to maximize alpha olefin purity. In other embodiments, processing steps may be conducted to maximize C10 olefin purity. For example, C10+ olefins from the separation unit 30 or a particular olefin stream may be reacted with ethylene in the presence of a metathesis catalyst in a secondary metathesis reactor to improve the C10 olefin purity. In one embodiment, the metathesis catalyst is a rhenium oxide catalyst (e.g., rhenium oxide supported on alumina). In another embodiment, the metathesis is a tungsten oxide catalyst (e.g., tungsten oxide supported on silica). This metathesis reaction may be conducted in a fixed bed reactor. In some embodiments, the ethylene reagent can be recycled back to the secondary metathesis reactor. Lighter olefins (C4-C9) from the secondary metathesis reactor may be mixed with the main metathesis reactor olefins from the separation unit 30 for further processing.

[00142] In certain embodiments, the olefins 32 may be oligomerized to form poly-alpha-olefins (PAOs) or poly-interval-olefins (PIOs), mineral oil substitutes, and/or biodiesel fuel. The oligomerization reaction may take place after the distillation unit 30 or after the overhead olefin separation unit 40. In certain embodiments, byproducts from the oligomerization reactions may be recycled back to the metathesis reactor 20 for further processing.

[00143] In other embodiments, the olefins 32, light end olefins 44, or center-cut olefins 42 may be self-metathesized in the presence of a metathesis catalyst in a secondary metathesis reactor in order to produce heavier weight C14+, C16+, or C18+ olefin products. In one embodiment, the metathesis catalyst is a rhenium oxide catalyst (e.g., rhenium oxide supported on alumina). In another embodiment,

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the metathesis is a tungsten oxide catalyst (e.g., tungsten oxide supported on silica). This metathesis reaction may be conducted in a fixed bed reactor. The heavier weight C14+, C16+, or C18+ olefins may be used as surfactants or oil lubes. In some embodiments, the lighter olefin byproducts from the self-metathesis reaction may be recycled back to the secondary metathesis reactor or primary metathesis reactor 20 for further processing.

[00144] As mentioned, in one embodiment, the olefins 32 from the separation unit 30 may be sent directly to the hydrogenation unit 50. In another embodiment, the center-cut olefins 42 from the overhead olefin separation unit 40 may be sent to the hydrogenation unit 50. Hydrogenation may be conducted according to any known method in the art for hydrogenating double bond-containing compounds such as the olefins 32 or center-cut olefins 42. In certain embodiments, in the hydrogenation unit 50, hydrogen gas 48 is reacted with the olefins 32 or center-cut olefins 42 in the presence of a hydrogenation catalyst to produce a hydrogenated product 52.

[00145] Typical hydrogenation catalysts and reaction conditions are discussed above. During hydrogenation, the carbon-carbon double bond containing compounds in the olefins are partially to fully saturated by the hydrogen gas 48. In one embodiment, the resulting hydrogenated product 52 includes hydrocarbons with a distribution centered between approximately C10 and C12 hydrocarbons for naphtha- and kerosene-type jet fuel compositions. In another embodiment, the distribution is centered between approximately C16 and C18 for a diesel fuel composition.

[00146] In certain embodiments, after hydrogenation, the hydrogenation catalyst may be removed from the hydrogenated product 52 using known techniques in the art, for example, by filtration. In some embodiments, the hydrogenation catalyst is removed using a plate and frame filter such as those commercially available from Sparkler Filters, Inc., Conroe TX. In some embodiments, the filtration is performed with the assistance of pressure or a vacuum. In order to improve filtering performance, a filter aid may be used. A filter aid may be added to the product directly or it may be applied to the filter. Representative non-limiting examples of filtering aids include diatomaceous earth, silica, alumina, and carbon. Typically, the filtering aid is used in an amount of about 10 weight % or less, for

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example, about 5 weight % or less or about 1 weight % or less. Other filtering techniques and filtering aids also may be employed to remove the used hydrogenation catalyst. In other embodiments the hydrogenation catalyst is removed using centrifugation followed by decantation of the product.

[00147] In certain embodiments, based upon the quality of the hydrogenated product 52 produced in the hydrogenation unit 50, it may be preferable to isomerize the olefin hydrogenated product 52 to assist in targeting of desired fuel properties such as flash point, freeze point, energy density, cetane number, or end point distillation temperature, among other parameters. Isomerization reactions are well-known in the art, as described in U.S. Patent Nos. 3,150,205; 4,210,771; 5,095,169; and 6,214,764, herein incorporated by reference in their entireties. In one embodiment, the isomerization reaction at this stage may also crack some of the C₁₅₊ compounds remaining, which may further assist in producing a fuel composition having compounds within the desired carbon number range, such as 5 to 16 for a jet fuel composition.

[00148] In certain embodiments, the isomerization may occur concurrently with the hydrogenation step in the hydrogenation unit 50, thereby targeting a desired fuel product. In other embodiments, the isomerization step may occur before the hydrogenation step (i.e., the olefins 32 or center-cut olefins 42 may be isomerized before the hydrogenation unit 50). In yet other embodiments, it is possible that the isomerization step may be avoided or reduced in scope based upon the selection of low-molecular-weight olefin(s) 14 and/or mid-weight olefin(s) 15 used in the metathesis reaction.

[00149] In certain embodiments, the hydrogenated product 52 comprises approximately 15-25 weight % C7, approximately <5 weight % C8, approximately 20-40 weight % C9, approximately 20-40 weight % C10, approximately <5 weight % C11, approximately 15-25 weight % C12, approximately <5 weight % C13, approximately <5 weight % C14, approximately <5 weight % C15, approximately <1 weight % C16, approximately <1 weight % C17, and approximately <1 weight % C18+. In certain embodiments, the hydrogenated product 52 comprises a heat of combustion of at least approximately 40, 41, 42, 43 or 44 MJ/kg (as measured by ASTM D3338). In certain embodiments, the hydrogenated product 52 contains less than approximately 1 mg sulfur per kg hydrogenated product (as measured by ASTM

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D5453). In other embodiments, the hydrogenated product 52 comprises a density of approximately 0.70-0.75 (as measured by ASTM D4052). In other embodiments, the hydrogenated product has a final boiling point of approximately 220-240°C (as measured by ASTM D86).

[00150] The hydrogenated product 52 produced from the hydrogenation unit 50 may be used as a fuel composition, non-limiting examples of which include jet, kerosene, or diesel fuel. In certain embodiments, the hydrogenated product 52 may contain byproducts from the hydrogenation, isomerization, and/or metathesis reactions. As shown in FIG. 1, the hydrogenated product 52 may be further processed in a fuel composition separation unit 60, removing any remaining byproducts from the hydrogenated product 52, such as hydrogen gas, water, C2-C9 hydrocarbons, or C15+ hydrocarbons, thereby producing a targeted fuel composition. The fuel composition separation unit 60 may comprise a number of distillation towers. In some embodiments, the various composition streams are separated using at least four distillation towers. In other embodiments, three towers or less are used to separate the fuel compositions.

[00151] In one embodiment, the hydrogenated product 52 may be separated into the desired fuel C9-C15 product 64, and a light-ends C2-C9 fraction 62 and/or a C15+ heavy-ends fraction 66. Distillation may be used to separate the fractions. Alternatively, in other embodiments, such as for a naphtha- or kerosene-type jet fuel composition, the heavy ends fraction 66 can be separated from the desired fuel product 64 by cooling the hydrogenated product 52 to approximately -40°C, -47°C, or -65°C and then removing the solid, heavy ends fraction 66 by techniques known in the art such as filtration, decantation, or centrifugation.

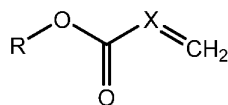
[00152] With regard to the esters 34 from the distillation unit 30, in certain embodiments, the esters 34 may be entirely withdrawn as an ester product stream 36 and processed further or sold for its own value, as shown in FIG. 1. As a non-limiting example, the esters 34 may comprise various triglycerides that could be used as a lubricant. Based upon the quality of separation between olefins and esters, the esters 34 may comprise some heavier olefin components carried with the triglycerides. In other embodiments, the esters 34 may be further processed in a biorefinery or another chemical or fuel processing unit known in the art, thereby producing various products such as biodiesel or specialty chemicals that have higher

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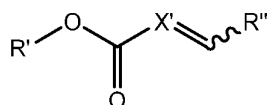
value than that of the triglycerides, for example. Alternatively, in certain embodiments, the esters 34 may be partially withdrawn from the system and sold, with the remainder further processed in the biorefinery or another chemical or fuel processing unit known in the art.

[00153] In certain embodiments, the ester stream 34 is sent to a transesterification unit 70. Within the transesterification unit 70, the esters 34 are reacted with at least one alcohol 38 in the presence of a transesterification catalyst. In certain embodiments, the alcohol comprises methanol and/or ethanol. In another embodiment, the alcohol 38 comprises glycerol (and the transesterification reaction is a glycerolysis reaction). In one embodiment, the transesterification reaction is conducted at approximately 60-70°C and approximately 1 atm. In certain embodiments, the transesterification catalyst is a homogeneous sodium methoxide catalyst. Varying amounts of catalyst may be used in the reaction, and, in certain embodiments, the transesterification catalyst is present in the amount of approximately 0.5-1.0 weight % of the esters 34.

[00154] In certain embodiments, the transesterification reaction may produce a transesterified product 72 comprising terminal olefin esters, such as terminal olefin esters having the following structure:



where X is a C₃-C₁₈ saturated or unsaturated alkyl chain, and R is an alkyl group, which can be optionally unsaturated or contain ether linkages. In some embodiments, R is an alkyl group. In some embodiments, R is methyl and X is -(CH₂)₇CH=. In certain embodiments, the transesterification reaction may produce a transesterified product 72 comprising internal olefin esters, such as internal olefin esters having the following structure:



where X' is a C₃-C₁₈ saturated or unsaturated alkyl chain, R' is an alkyl group, which can be optionally unsaturated or contain ether linkages, or hydrogen, and R'' is C₁₋₈ alkyl, which is optionally unsaturated. In some embodiments, R' is an alkyl group

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and R'' is C₁₋₈ alkyl. In some embodiments, R' is methyl, R'' is ethyl, and X' is - (CH₂)₇CH=.

[00155] The transesterification reaction may produce transesterified products 72 including saturated and/or unsaturated fatty acid methyl esters ("FAME"), glycerin, methanol, and/or free fatty acids. In certain embodiments, the transesterified products 72, or a fraction thereof, may comprise a source for biodiesel. In certain embodiments, the transesterified products 72 comprise C₁₀-C₁₅ or C₁₁-C₁₄ esters. In certain embodiments, the transesterified products 72 comprise 9DA esters, 9UDA esters, and/or 9DDA esters. Non-limiting examples of 9DA esters, 9UDA esters and 9DDA esters include methyl 9-decenoate ("9-DAME"), methyl 9-undecenoate ("9-UDAME"), and methyl 9-dodecenoate ("9-DDAME"), respectively. As a non-limiting example, in a transesterification reaction, a 9DA moiety of a metathesized glyceride is removed from the glycerol backbone to form a 9DA ester.

[00156] As discussed above, the types of transesterified products formed are based upon the reactants entering the metathesis reactor 20. In one particular embodiment, C₁₂ methyl esters (9-DDAME) are produced downstream of the metathesis reaction between 3-hexene and a natural oil.

[00157] In another embodiment, a glycerin alcohol may be used in the reaction with a glyceride stream. This reaction may produce monoglycerides and/or diglycerides.

[00158] In certain embodiments, the transesterified products 72 from the transesterification unit 70 can be sent to a liquid-liquid separation unit, wherein the transesterified products 72 (i.e., FAME, free fatty acids, and/or alcohols) are separated from glycerin. Additionally, in certain embodiments, the glycerin byproduct stream may be further processed in a secondary separation unit, wherein the glycerin is removed and any remaining alcohols are recycled back to the transesterification unit 70 for further processing.

[00159] In one embodiment, the transesterified products 72 are further processed in a water-washing unit. In this unit, the transesterified products undergo a liquid-liquid extraction when washed with water. Excess alcohol, water, and glycerin are removed from the transesterified products 72. In another embodiment, the water-washing step is followed by a drying unit in which excess water is further

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removed from the desired mixture of esters (*i.e.*, specialty chemicals). Such specialty chemicals include non-limiting examples such as 9DA, 9UDA, and/or 9DDA, alkali metal salts and alkaline earth metal salts of the preceding, individually or in combinations thereof.

[00160] In one embodiment, the monomer specialty chemical (e.g., 9DA) may be further processed in an oligomerization reaction to form a lactone, which may serve as a precursor to a surfactant.

[00161] In certain embodiments, the transesterified products 72 from the transesterification unit 70 or specialty chemicals from the water-washing unit or drying unit are sent to an ester distillation column 80 for further separation of various individual or groups of compounds, as shown in FIG. 1. This separation may include, but is not limited to, the separation of 9DA esters, 9UDA esters, and/or 9DDA esters. In one embodiment, the 9DA ester 82 may be distilled or individually separated from the remaining mixture 84 of transesterified products or specialty chemicals. In certain process conditions, the 9DA ester 82 should be the lightest component in the transesterified product or specialty chemical stream, and come out at the top of the ester distillation column 80. In another embodiment, the remaining mixture 84, or heavier components, of the transesterified products or specialty chemicals may be separated off the bottom end of the column. In certain embodiments, this bottoms stream 84 may potentially be sold as biodiesel.

[00162] The 9DA esters, 9UDA esters, and/or 9DDA esters may be further processed after the distillation step in the ester distillation column. In one embodiment, under known operating conditions, the 9DA ester, 9UDA ester, and/or 9DDA ester may then undergo a hydrolysis reaction with water to form 9DA, 9UDA, and/or 9DDA, alkali metal salts and alkaline earth metal salts of the preceding, individually or in combinations thereof.

[00163] In certain embodiments, the monomer fatty acid esters from the transesterified products 72 may be reacted with each other to form other specialty chemicals such as dimers.

[00164] In other embodiments, specific ester products, such as 9DDA methyl ester, may be enriched through subsequent processing and reaction steps of the transesterified products. In one embodiment, a C₁₀ methyl ester stream may be separated from heavier C₁₂₊ methyl esters. The C₁₀ methyl ester stream may then

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be reacted with 1-butene in the presence of a metathesis catalyst to form C₁₂ methyl esters and ethylene. The ethylene may be separated from the methyl esters and the C10 and C12 methyl esters may be removed or returned to an ester distillation column for further processing.

[00165] In certain embodiments, the monomer fatty acids and/or monomer fatty acid esters from the transesterified products 72 are isomerized to form isomerized monomer fatty acids and/or isomerized monomer fatty acid esters. The isomerization of the fatty acids and/or fatty acid esters from the transesterified products 72 may be conducted at an elevated temperature (i.e., greater than 25°C). In certain embodiments, the temperature of the heat treatment for the isomerization reaction is greater than 100°C, greater than 150°C, or greater than 200°C. In other embodiments, the temperature is between 100°C-300°C, between 150-250°C, or about 200°C. In some embodiments, the heat treatment step is conducted in the presence of an isomerization catalyst. In one particular embodiment, the isomerization catalyst is (PCy₃)₂(Cl)(H)Ru(CO), where "Cy" represents a cyclohexyl group.

[00166] In certain embodiments, the monomer fatty acids and/or monomer fatty acid esters that undergo the isomerization reaction are selected from the group consisting of: 9DA, 9DA esters, 9UDA, 9UDA esters, 9DDA, and 9DDA esters. The isomerization of the fatty acids and/or fatty acid esters may produce isomerized monomer fatty acids and/or isomerized monomer fatty acid esters selected from the group consisting of isomerized 9DA, isomerized 9DA esters, isomerized 9UDA, isomerized 9UDA esters, isomerized 9DDA, and isomerized 9DDA esters.

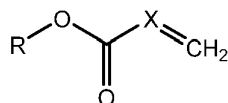
[00167] Isomerizing the monomer fatty acids and/or monomer fatty acid esters may improve various performance properties. For example, the isomerized product composition may have an observed broadening of the freezing and melting points, which may allow for transportation of the isomerized fatty acid/ester product composition at higher concentrations of the monomer fatty acids and/or monomer fatty acid esters without incurring shipping problems.

[00168] Isomerized monomer fatty acids and/or isomerized monomer fatty acid esters may be used in a variety of different commercial applications, including, but not limited to: lubricants, waxes, films, paints, paint strippers, coatings, plasticizers,

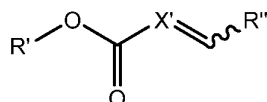
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resins, binders, solvents, polyols, soil stabilization, chemical grouting, oilfield drilling fluids, crop protection products, surfactants, intermediates, and adhesives.

[00169] In certain embodiments, the transesterification reaction may produce a transesterified product 72 comprising terminal olefin esters, such as terminal olefin esters having the following structure:



where X is a C₃-C₁₈ saturated or unsaturated alkyl chain, and R is an alkyl group, which can be optionally unsaturated or contain ether linkages. In some embodiments, R is alkyl. In some embodiments, R is methyl and X is -(CH₂)₇CH=. In certain embodiments, the transesterification reaction may produce a transesterified product 72 comprising internal olefin esters, such as internal olefin esters having the following structure:



where X' is a C₃-C₁₈ saturated or unsaturated alkyl chain, R' is an alkyl group, which can be optionally unsaturated or contain ether linkages, or hydrogen, and R'' is C₁₋₈ alkyl, which is optionally unsaturated. In some embodiments, R'' is C₁₋₈ alkyl. In some embodiments, R' is methyl, R'' is ethyl, and X' is -(CH₂)₇CH=.

[00170] In certain embodiments, the terminal olefin-internal olefin cross-metathesis reaction is conducted at a weight ratio between 1:99 (terminal to internal) and 99:1 (terminal to internal). In other embodiments, the weight ratio of the terminal and internal olefin is between 1:5 and 5:1. In yet other embodiments, the weight ratio between the terminal and internal olefin is between 1:2 and 2:1. In one particular embodiment, the weight ratio between the terminal and internal olefin is approximately 1:1.

[00171] In certain embodiments, the terminal olefin is selected from the group consisting of: 4-pentenoic acid ester, 5-hexenoic acid ester, 6-heptenoic acid ester, 7-octenoic acid ester, 8-nonenoic acid ester, 9-decenoic acid ester, 10-undecenoic acid ester, 11-dodecenoic acid ester, 12-tridecenoic acid ester, 13-tetradecenoic acid ester, 14-pentadecenoic acid ester, 15-hexadecenoic acid ester, 16-

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heptadecenoic acid ester, 17-octadecenoic acid ester, acids thereof, and mixtures thereof. In one particular embodiment, the terminal olefin is 9-decenoic acid ester.

[00172] In certain embodiments, the terminal olefin is cross-metathesized with an internal olefin selected from the group consisting of: pentenoic acid esters, hexenoic acid esters, heptenoic acid esters, octenoic acid esters, nonenoic acid esters, decenoic acid esters, undecenoic acid esters, dodecenoic acid esters, tridecenoic acid esters, tetradecenoic acid esters, pentadecenoic acid esters, hexadecenoic acid esters, heptadecenoic acid esters, octadecenoic acid esters, acids thereof, and mixtures thereof. In one particular embodiment, the internal olefin is 9-undecenoic acid ester. In another particular embodiment, the internal olefin is 9-dodecenoic acid ester.

[00173] In some embodiments, the internal olefin is formed by reacting a portion of the terminal olefin ester derived from the transesterified product 72 with a low-molecular-weight internal olefin or mid-weight internal olefin in the presence of a metathesis catalyst. In certain embodiments, the low-molecular-weight internal olefin is selected from the group consisting of: 2-butene, 2-pentene, 2-hexene, 3-hexene, 2-heptene, 3-heptene, 2-octene, 3-octene, 4-octene, 2-nonene, 3-nonene, 4-nonene, and mixtures thereof. In one particular embodiment, the low-molecular-weight internal olefin is 2-butene. In another particular embodiment, the low-molecular-weight internal olefin is 3-hexene.

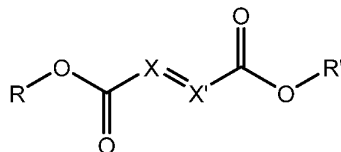
[00174] In certain embodiments, at least 70 wt%, 80 wt%, or 90 wt% dibasic ester and/or dibasic acid is formed from the cross-metathesis reaction of a terminal olefin and an internal olefin in the presence of less than 150 ppm, 100 ppm, 50 ppm, 25 ppm, or 10 ppm catalyst. A comparable self-metathesis reaction with terminal olefins (such as 9-decenoic acid ester) under similar reaction conditions may require more catalyst (e.g., more than 150 ppm, or more than 500 ppm) to achieve similar yields of dibasic esters and/or dibasic acids (potentially due to the formation of the ethylene byproduct).

[00175] In certain embodiments, the dibasic ester and/or dibasic acid yield is improved by separating the olefin byproduct formed in the cross-metathesis reaction from the metathesis product while the reaction between the terminal olefin and internal olefin is ongoing. In other embodiments, the dibasic ester and/or dibasic acid yield is improved by sparging the metathesis products in the metathesis reactor

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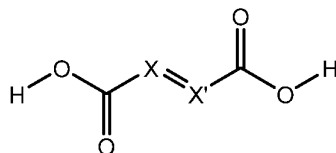
with a chemically inert gas (e.g., nitrogen, argon, or helium) to ventilate dissolved gases/byproducts (e.g., olefin byproducts) in the metathesis product.

[00176] In certain embodiments, the cross-metathesis reaction of the terminal olefin ester and internal olefin ester produces an unsaturated dibasic ester. In some embodiments, the resulting unsaturated dibasic ester is a compound of the following structure:



wherein R, R', X, and X' are as defined in any of the above embodiments. In some embodiments, -X=X'- is $-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-$.

[00177] In some embodiments, the dibasic ester derived from the transesterified product 72 may further undergo a hydrolysis reaction with water to form a dibasic acid having the following structure:



wherein X and X' are as defined above. In some embodiments, -X=X'- is $-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-$. In some other embodiments, saponification can be used to obtain a dibasic acid salt (where "acid salt" refers to a carboxylate anion, whether in solution or in solid-state form), which can be optionally acidified to form the dibasic acid.

[00178] Following conversion to a dibasic acid, in some embodiments, the product stream may be sent to a flash column or decanter to remove methanol and water, or other substances from the dibasic acid.

[00179] In other embodiments, the dibasic acid and/or dibasic ester is isomerized to form an isomerized dibasic acid and/or isomerized dibasic ester. The isomerization of the dibasic acid and/or dibasic ester may be conducted at an elevated temperature (i.e., greater than 25°C). In certain embodiments, the temperature of the heat treatment for the isomerization reaction is greater than 100°C, greater than 150°C, or greater than 200°C. In other embodiments, the temperature is between 100°C-300°C, between 150-250°C, or about 200°C. In some embodiments, the heat treatment step is conducted in the presence of an

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isomerization catalyst. In one particular embodiment, the isomerization catalyst is $(\text{PCy}_3)_2(\text{Cl})(\text{H})\text{Ru}(\text{CO})$, where "Cy" represents a cyclohexyl group.

[00180] In certain embodiments, the isomerized dibasic acid and/or isomerized dibasic ester comprises compounds selected from the group consisting of: isomerized dimethyl 9-octadecenedioate or isomerized 9-octadecene dioic acid.

[00181] In certain embodiments, the isomerized dibasic acid and/or isomerized dibasic ester is self-metathesized or cross-metathesized with a low-molecular-weight olefin or mid-weight olefin. Typical metathesis reaction conditions and catalysts are discussed in greater detail below. In one embodiment, the isomerized dibasic acid and/or isomerized dibasic ester is self-metathesized in the presence of approximately 10 ppm, 20 ppm, 40 ppm, 50 ppm, 80 ppm, 100 ppm, 120 ppm, or greater than 150 ppm metathesis catalyst.

[00182] In certain embodiments, the isomerized fatty acid, isomerized fatty acid ester, dibasic acid, dibasic ester, isomerized dibasic acid, and/or isomerized dibasic ester is hydrogenated. Typical hydrogenation reaction conditions and catalysts are discussed above. In one particular example, the hydrogenation reaction is conducted in the presence of a nickel based catalyst at approximately 150°C and 150 psig.

[00183] As noted, the self-metathesis of the natural oil, cross-metathesis between the natural oil and low-molecular-weight olefin or mid-weight olefin, or cross-metathesis between a terminal olefin and internal olefin occurs in the presence of a metathesis catalyst. As stated previously, the term "metathesis catalyst" includes any catalyst or catalyst system that catalyzes a metathesis reaction. Any known or future-developed metathesis catalyst may be used, individually or in combination with one or more additional catalysts. Non-limiting exemplary metathesis catalysts and process conditions are described in WO 2009/020667, incorporated by reference herein. A number of the metathesis catalysts as shown are manufactured by Materia, Inc. (Pasadena, CA).

[00184] The metathesis process can be conducted under any conditions adequate to produce the desired metathesis products. For example, stoichiometry, atmosphere, solvent, temperature, and pressure can be selected by one skilled in the art to produce a desired product and to minimize undesirable byproducts. The metathesis process may be conducted under an inert atmosphere. Similarly, if a

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reagent is supplied as a gas, an inert gaseous diluent can be used. The inert atmosphere or inert gaseous diluent typically is an inert gas, meaning that the gas does not interact with the metathesis catalyst to substantially impede catalysis. For example, particular inert gases are selected from the group consisting of helium, neon, argon, nitrogen, individually or in combinations thereof.

[00185] In certain embodiments, the metathesis catalyst is dissolved in a solvent prior to conducting the metathesis reaction. In certain embodiments, the solvent chosen may be selected to be substantially inert with respect to the metathesis catalyst. For example, substantially inert solvents include, without limitation, aromatic hydrocarbons, such as benzene, toluene, xylenes, etc.; halogenated aromatic hydrocarbons, such as chlorobenzene and dichlorobenzene; aliphatic solvents, including pentane, hexane, heptane, cyclohexane, etc.; and chlorinated alkanes, such as dichloromethane, chloroform, dichloroethane, etc. In one particular embodiment, the solvent comprises toluene.

[00186] In other embodiments, the metathesis catalyst is not dissolved in a solvent prior to conducting the metathesis reaction. The catalyst, instead, may be slurried with the natural oil 12, where the natural oil 12 is in a liquid state. Under these conditions, it is possible to eliminate the solvent (e.g., toluene) from the process and eliminate downstream olefin losses when separating the solvent. In other embodiments, the metathesis catalyst may be added in solid state form (and not slurried) to the natural oil 12 (e.g., as an auger feed).

[00187] The metathesis reaction temperature may be a rate-controlling variable where the temperature is selected to provide a desired product at an acceptable rate. In certain embodiments, the metathesis reaction temperature is greater than about -40°C, greater than about -20°C, greater than about 0°C, or greater than about 10°C. In certain embodiments, the metathesis reaction temperature is less than about 150°C, or less than about 120°C. In one embodiment, the metathesis reaction temperature is between about 10°C and about 120°C.

[00188] The metathesis reaction can be run under any desired pressure. Typically, it will be desirable to maintain a total pressure that is high enough to keep the cross-metathesis reagent in solution. Therefore, as the molecular weight of the cross-metathesis reagent increases, the lower pressure range typically decreases since the boiling point of the cross-metathesis reagent increases. The total pressure

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may be selected to be greater than about 0.1 atm (10 kPa), in some embodiments greater than about 0.3 atm (30 kPa), or greater than about 1 atm (100 kPa). Typically, the reaction pressure is no more than about 70 atm (7000 kPa), in some embodiments no more than about 30 atm (3000 kPa). A non-limiting exemplary pressure range for the metathesis reaction is from about 1 atm (100 kPa) to about 30 atm (3000 kPa).

[00189] The above description provides certain ways of making a dibasic acid and/or dibasic ester from a feedstock comprising a natural oil. Other methods can be used as well. For example, in another aspect, the disclosure provides methods of refining a natural oil, comprising providing a feedstock comprising a natural oil; transesterifying the feedstock in the presence of an alcohol to form a transesterified product comprising one or more unsaturated fatty acid esters; reacting the unsaturated fatty acid esters in the presence of a metathesis catalyst to form a metathesized product comprising one or more metathesized unsaturated esters and one or more olefins; separating the metathesized unsaturated esters in the metathesized product from the olefins in the metathesized product, wherein the separated metathesized esters comprise a terminal olefin ester or an internal olefin ester. The resulting terminal olefin ester and/or internal olefin ester can be used to form an unsaturated dibasic ester, for example, according to any of the embodiments described above. In some embodiments, the alcohol is methanol. In some embodiments, the unsaturated dibasic ester is a 9-octadecenedioic acid dibasic ester, such as 9-octadecenedioic acid dimethyl ester. In some further embodiments, the resulting unsaturated dibasic ester can be converted to a saturated dibasic ester and/or a saturated dibasic acid using any suitable combination of hydrogenation, hydrolysis, and/or saponification/acidification.

[00190] FIG. 7 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester from a feedstock comprising a natural oil. The illustrated method 700 comprises: providing a feedstock comprising a natural oil 701; reacting the feedstock in the presence of a metathesis catalyst 702 to form a metathesized product that comprises esters, e.g., unsaturated glycerides, and olefins; separating (at least a portion of) the esters from the olefins 703 in the metathesized product; transesterifying the separated esters 704, e.g., in the presence of an alcohol (e.g., methanol) to form a terminal olefin ester and/or an

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internal olefin ester; and reacting the internal olefin ester and/or the terminal olefin ester (according to any of the aspects and embodiments described above) 705 to form an unsaturated dibasic ester. The unsaturated dibasic ester can, for example, be further reacted according to any of the above aspects and embodiments to form a saturated dibasic acid, such as octadecanedioic acid.

[00191] FIG. 8 shows a flow chart that illustrates certain embodiments for making an unsaturated dibasic ester from a feedstock comprising a natural oil. The illustrated method 800 comprises: providing a feedstock comprising a natural oil 801; transesterifying the feedstock 802, e.g., in the presence of an alcohol (e.g., methanol) to form a transesterified product comprising one or more unsaturated fatty acid esters; reacting the unsaturated fatty acid esters 803, e.g., in the presence of a metathesis catalyst to form a metathesized product comprising one or more metathesized unsaturated esters and one or more olefins; separating (at least a portion of) the metathesized unsaturated esters from the olefins 804, e.g., in the metathesized product, wherein the separated metathesized product comprises a terminal olefin ester and/or an internal olefin ester; and reacting the internal olefin ester and/or the terminal olefin ester (according to any of the aspects and embodiments described above) 805 to form an unsaturated dibasic ester. The unsaturated dibasic ester can, for example, be further reacted according to any of the above aspects and embodiments to form a saturated dibasic acid, such as octadecanedioic acid.

[00192] While the invention as described may have modifications and alternative forms, various embodiments thereof have been described in detail. It should be understood, however, that the description herein of these various embodiments is not intended to limit the invention, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the claims. Further, while the invention will also be described with reference to the following non-limiting examples, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art, particularly in light of the foregoing teachings.

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EXAMPLES**Example 1**

[00193] A clean, dry, stainless steel jacketed 5-gal. Parr reactor vessel equipped with a dip tube, overhead stirrer, internal cooling/heated coils, temperature probe, sampling valve, and headspace gas release valve was purged with argon to 15 psig. Soybean oil (SBO, 2.5 kg, 2.9 mol, Costco, MWn = 864.4 g/mol, 85 weight % unsaturation as determined by gas chromatographic analysis ("by gc"), 1 hour argon sparged in 5-gal container) was added into the Parr reactor. The Parr reactor was sealed and the SBO was purged with argon for 2 hours while cooling to 10°C. After 2 hours, the reactor was vented until the internal pressure reached 10 psig. The dip tube valve on the reactor was connected to a 1-butene cylinder (Airgas, CP grade, 33 psig headspace pressure, >99 weight %) and re-pressurized to 15 psig of 1-butene. The reactor was vented again to 10 psig to remove residual argon in the headspace. The SBO was stirred at 350 rpm and 9-15°C under 18-28 psig 1-butene until 3 mol 1-butene per SBO olefin bond was transferred into the reactor (approximately 2.2 kg 1-butene over approximately 4-5 hours). A toluene solution of [1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichlororuthenium(3-methyl-2-butenylidene)(tricyclohexylphosphine) (C827, Materia) was prepared in Fischer-Porter pressure vessel by dissolving 130 mg catalyst in 30 grams of toluene as a catalyst carrier (10 mol ppm per olefin bond of SBO) and was added to the reactor via the reactor dip tube by pressurizing the headspace inside the Fischer-Porter vessel to 50-60 psig with argon. The Fischer-Porter vessel and dip tube were rinsed with an additional 30 g toluene. The reaction mixture was stirred for 2.0 hours at 60°C. The reaction mixture was allowed to cool to ambient temperature while the gases in the headspace were vented. After the pressure was released, the reaction mixture was transferred to a 3-neck round bottom flask containing 58 g bleaching clay (2 % w/w SBO, Pure Flow B80 CG) and a magnetic stir bar. The reaction mixture was treated by stirring at 85°C under argon. After 2 hours, during which time any remaining 1-butene was allowed to vent, the reaction mixture was allowed to cool to 40°C and filtered through a fritted glass filter. An aliquot of the product mixture was found by gas chromatographic analysis (following transesterification with 1 % w/w NaOMe in methanol at 60°C) to contain approximately 22 weight % methyl 9-decenoate, approximately 16 weight % methyl 9-dodecenoate,

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approximately 3 weight % dimethyl 9-octadecenedioate, and approximately 3 weight % methyl 9-octadecenoate (by gc). These results compare favorably with the calculated yields at equilibrium of 23.4 wt% methyl 9-decenoate, 17.9 wt% methyl 9-dodecenoate, 3.7 wt% dimethyl 9-octadecenedioate, and 1.8 wt% methyl 9-octadecenoate.

Example 2

[00194] By the general procedures described in example 1, a reaction was performed using 1.73 kg SBO and 3 mol 1-butene/SBO double bond. An aliquot of the product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 24 weight % methyl 9-decenoate, approximately 18 weight % methyl 9-dodecenoate, approximately 2 weight % dimethyl 9-octadecenedioate, and approximately 2 weight % methyl 9-octadecenoate (as determined by gc).

Example 3

[00195] By the general procedures described in example 1, a reaction was performed using 1.75 kg SBO and 3 mol 1-butene/SBO double bond. An aliquot of the product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 24 weight % methyl 9-decenoate, approximately 17 weight % methyl 9-dodecenoate, approximately 3 weight % dimethyl 9-octadecenedioate, and approximately 2 weight % methyl 9-octadecenoate (as determined by gc).

Example 4

[00196] By the general procedures described in example 1, a reaction was performed using 2.2 kg SBO, 3 mol 1-butene/SBO double bond, and the 60 g of toluene used to transfer the catalyst was replaced with SBO. An aliquot of the product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 25 weight % methyl 9-decenoate, approximately 18 weight % methyl 9-dodecenoate, approximately 3 weight % dimethyl 9-octadecenedioate, and approximately 1 weight % methyl 9-octadecenoate (as determined by gc).

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Example 5

[00197] A 12-liter, 3-neck, glass round bottom flask that was equipped with a magnetic stir bar, heating mantle, and temperature controller was charged with 8.42 kg of the combined reaction products from examples 1-4. A cooling condenser with a vacuum inlet was attached to the middle neck of the flask and a receiving flask was connected to the condenser. Hydrocarbon olefins were removed from the reaction product by vacuum distillation over the follow range of conditions: 22-130°C pot temperature, 19-70°C distillation head temperature, and 2000-160 μ torr pressure. The weight of material remaining after the volatile hydrocarbons were removed was 5.34 kg. An aliquot of the non-volatile product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 32 weight % methyl 9-decenoate, approximately 23 weight % methyl 9-dodecenoate, approximately 4 weight % dimethyl 9-octadecenedioate, and approximately 5 weight % methyl 9-octadecenoate (as determined by gc).

Example 6

[00198] A 12-liter, 3-neck round bottom flask that was fitted with a magnetic stir bar, condenser, heating mantle, temperature probe, and gas adapter was charged with 4 liters of 1% w/w NaOMe in MeOH and 5.34 kg of the non-volatile product mixture produced in example 5. The resulting light yellow heterogeneous mixture was stirred at 60°C. After about an hour, the mixture turned a homogeneous orange color (detected pH = 11.) After a total reaction time of 2 hours, the mixture was cooled to ambient temperature and two layers were observed. The organic phase was washed twice with 3 L of 50 % (v/v) aqueous MeOH, separated, and neutralized by washing with glacial HOAc in MeOH (1 mol HOAc/mol NaOMe) to a detected pH of 6.5, yielding 5.03 kg.

Example 7

[00199] A glass, 12 L, 3-neck round bottom flask fitted with a magnetic stirrer, packed column, and temperature controller was charged with the methyl ester mixture (5.03 kg) produced in example 6 and placed in the heating mantle. The column attached to the flask was a 2-inch x 36-inch glass column containing 0.16"

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Pro-Pak™ stainless steel saddles. The distillation column was attached to a fractional distillation head to which a 1 L pre-weighed round bottom flask was fitted for collecting the distillation fractions. The distillation was carried out under vacuum at 100-120 μ torr. A reflux ratio of 1:3 was used for isolating both methyl 9-decenoate (9-DAME) and methyl 9-dodecenoate (9-DDAME). A reflux ratio of 1:3 referred to 1 drop collected for every 3 drops sent back to the distillation column. The samples collected during the distillation, the vacuum distillation conditions, and the 9-DAME and 9-DDAME content of the fractions, as determined by gc, are shown in **Table 1**. Combining fractions 2-7 yielded 1.46 kg methyl 9-decenoate with 99.7 % purity. After collecting fraction 16, 2.50 kg of material remained in the distillation pot: it was found by gc to contain approximately 14 weight % 9-DDAME, approximately 42 weight % methyl palmitate, and approximately 12 weight % methyl stearate.

TABLE 1

Distillation Fractions #	Head temp. (°C)	Pot temp. (°C)	Vacuum (μ torr)	Weight (g)	9-DAME (wt %)	9-DDAME (wt %)
1	40-47	104-106	110	6.8	80	0
2	45-46	106	110	32.4	99	0
3	47-48	105-110	120	223.6	99	0
4	49-50	110-112	120	283	99	0
5	50	106	110	555	99	0
6	50	108	110	264	99	0
7	50	112	110	171	99	0
8	51	114	110	76	97	1
9	65-70	126-128	110	87	47	23
10	74	130-131	110	64	0	75
11	75	133	110	52.3	0	74
12	76	135-136	110	38	0	79
13	76	136-138	100	52.4	0	90
14	76	138-139	100	25.5	0	85
15	76-77	140	110	123	0	98
16	78	140	100	426	0	100

Example 8

[00200] A reaction was performed by the general procedures described in example 1 with the following changes: 2.2 kg SBO, 7 mol propene/mol SBO double bond, and 200 mg [1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichlororuthenium(benzylidene)(tricyclohexyl-phosphine) [C848 catalyst, Materia Inc., Pasadena, California, USA, 90 ppm (w/w) vs. SBO] at a reaction temperature of

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40°C were used. The catalyst removal step using bleaching clay also was replaced by the following: after venting excess propene, the reaction mixture was transferred into a 3-neck round bottom flask to which 50 mol of tris(hydroxymethyl)phosphine (THMP)/mol C848 catalyst was added. The THMP was formed as a 1.0 M solution in isopropanol, where phosphonium salt, inorganic salt, formaldehyde, THMPO, and THMP were mixed together. The resulting hazy yellow mixture was stirred for 20 hours at 60°C, transferred to a 6-L separatory funnel and extracted with 2 × 2.5 L deionized H₂O. The organic layer was separated and dried over anhydrous Na₂SO₄ for 4 hours, then filtered through a fritted glass filter containing a bed of silica gel.

Example 9

[00201] A reaction was performed by the general procedures described in example 8, except that 3.6 kg SBO and 320 mg C848 catalyst were used. Following catalyst removal, the reaction product from example 9 was combined with that from example 8, yielding 5.12 kg of material. An aliquot of the combined product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 34 weight % methyl 9-decenoate, approximately 13 weight % methyl 9-undecenoate, < 1 weight % dimethyl 9-octadecenedioate, and < 1 weight % methyl 9-octadecenoate (as determined by gc).

[00202] Hydrocarbon olefins were removed from the 5.12 kg of combined reaction product described above by vacuum distillation by the general procedure described in example 5. The weight of material remaining after the volatile olefins were removed was 4.0 kg. An aliquot of the non-volatile product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 46 weight % methyl 9-decenoate, approximately 18 weight % methyl 9-undecenoate, approximately 2 weight % dimethyl 9-octadecenedioate, and approximately 1 weight % methyl 9-octadecenoate (as determined by gc).

Example 10

[00203] Two reactions were performed by the general procedures described in example 8, except that for each reaction, 3.1 kg SBO and 280 mg C848 catalyst

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were used. Following catalyst removal, the reaction products from the two preparations were combined, yielding 5.28 kg of material. An aliquot of the combined product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 40 weight % methyl 9-decenoate, approximately 13 weight % methyl 9-undecenoate, approximately 2 weight % dimethyl 9-octadecenedioate, and approximately 1 weight % methyl 9-octadecenoate (as determined by gc).

[00204] Hydrocarbon olefins were removed from the 5.28 kg of combined reaction product by vacuum distillation by the general procedure described in example 5. The weight of material remaining after the volatile olefins were removed was 4.02 kg. An aliquot of the non-volatile product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 49 weight % methyl 9-decenoate, approximately 16 weight % methyl 9-undecenoate, approximately 2 weight % dimethyl 9-octadecenedioate, and approximately 3 weight % methyl 9-octadecenoate (as determined by gc).

Example 11

[00205] By the general procedures described in example 10, two metathesis reactions were performed using SBO, 7 mol cis-2-butene/mol SBO double bond, and 220 mg C848 catalyst/kg SBO. Following catalyst removal, the reaction products from the two preparations were combined, yielding 12.2 kg of material. An aliquot of the combined product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 49 weight % methyl 9-undecenoate, approximately 2 weight % dimethyl 9-octadecenedioate, and approximately 1 weight % methyl 9-octadecenoate (as determined by gc).

[00206] Hydrocarbon olefins were removed from the 12.2 kg of combined reaction product by vacuum distillation by the general procedure described in example 5. The weight of material remaining after the volatile olefins were removed was 7.0 kg. An aliquot of the non-volatile product mixture was found by gas chromatographic analysis following transesterification with 1 % w/w NaOMe in methanol at 60°C to contain approximately 57 weight % methyl 9-undecenoate,

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approximately 4 weight % dimethyl 9-octadecenedioate, and approximately 2 weight % methyl 9-octadecenoate (as determined by gc).

Example 12

[00207] By the general procedures described in example 1, approximately 7 kg of cross metathesis product was produced by reacting SBO with 3 mol 1-butene/mol SBO double bond using 43 mg C827 catalyst/kg SBO, following catalyst removal with THMP. An initial 2.09 kg portion of the metathesis product was hydrogenated at 136°C and 400 psig H₂ until hydrogen uptake ceased in a one gallon batch autoclave using 105 g of Johnson-Matthey A-7000 Sponge Metal™ catalyst. The resulting mixture was filtered warm (22-55°C), yielding 1.40 kg filtrate and 350 g of a mixture consisting of the catalyst and the hydrogenated product. The entirety of the catalyst-containing mixture was returned to the one gallon reactor along with a second 2.18 kg portion of the metathesis product and a second hydrogenation reaction was similarly carried out until hydrogen uptake ceased. The catalyst was allowed to settle and the majority of the organic product was decanted and filtered, yielding 1.99 kg filtrate and 380 g catalyst-hydrogenated product mixture. The remaining approximately 3 kg of metathesis product was hydrogenated in two additional batch reactions that in like manner were carried out using the catalyst from the previous reaction, yielding 1.65 kg and 1.28 kg of hydrogenated product, respectively. The total weight of hydrogenated product that was isolated after filtration was 6.32 kg. Aliquots of the hydrogenated product were found by gas chromatographic analysis to contain approximately 30 weight % C₆-C₁₈ n-paraffins and approximately 70 weight % triglycerides. The relative distribution of the C₈-C₁₈ n-paraffins contained in the hydrogenated product compares well with the calculated distribution of olefins by carbon number: observed (calculated) 2.3 (0.6) weight % C₈, 35.6 (36.2) weight % C₉, 30.0 (27.6) weight % C₁₀, 0.6 (0.1) weight % C₁₁, 22.2 (23.6) weight % C₁₂, 3.4 (3.7) weight % C₁₃, 0.1 (0.0) weight % C₁₄, 4.4 (6.3) weight % C₁₅, 0.4 (0.4) weight % C₁₆, 0.1 (0.0) weight % C₁₇, and 1.0 (1.6) weight % C₁₈.

The paraffin components were separated by wiped film evaporation from a 4.84 kg aliquot of the hydrogenated paraffin/triglyceride product. An initial wiped film evaporation was carried out at 75°C, 100 torr, 300 rpm, and condensation temperature of 15°C using a feed rate of 300 g/h and yielded a condensate that was

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subjected to a second wiped film evaporation at 125°C, 90 torr, 300 rpm, and condensation temperature of 10°C to remove the lighter alkanes. The resultant residual liquid was found by gas chromatography to contain the following distribution of n-alkanes: 17.5 weight % C₇, 1.7 weight % C₈, 31.0 weight % C₉, 28.3 weight % C₁₀, 0.6 weight % C₁₁, 17.4 weight % C₁₂, 2.1 weight % C₁₃, 0.1 weight % C₁₄, 1.2 weight % C₁₅, 0.1 weight % C₁₆, 0.0 weight % C₁₇, and 0.1 weight % C₁₈. The material was found to have a heat of combustion of 43.86 MJ/kg (ASTM D3338), less than 1 mg/kg sulfur (ASTM D5453), density of 0.7247 (ASTM D4052), and a final boiling point of 232.3 °C (ASTM D86), indicating the majority of this material would be suitable as a blend stock in a fuel application such as diesel or jet fuel.

Example 13

[00208] An oligomerization reaction of 1-olefin/1,4-diene (92 wt% 1-decene, 4.5 wt% 1,4-decadiene, 2 wt% 1,4-undecadiene) that was produced from the cross metathesis of palm oil with 1-octene was performed on a 550 g scale using 1.1 mol% ethyl aluminum dichloride (1M solution in hexane)/1.1 mol% tert-butyl chloride for 3 hours at 10 °C. The reaction mixture was quenched with water and 1M sodium hydroxide solution and stirred until it became colorless. Hexane (300 ml) was added and mixture was transferred to a separatory funnel. The organic layer was washed with water and brine, and then concentrated on a rotary evaporator to remove the hexane. The oligomeric mixture was devolatilized via short path vacuum distillation (100°C and 5 Torr) and the product distribution was determined to be 97% mixture oligomers by GC/MS. The dynamic viscosity (Brookfield, #34 spindle, 100 rpm, 22°C) of the sample is 540 cps. The kinematic viscosity for the sample at 40°C is 232 cSt.

Example 14

[00209] An Aspen model was developed to simulate the process of maximizing the purity of an alpha olefin (i.e., 1-decene) based on the metathesis process of using a soybean oil feed and 1-butene feed at molar ratio of 3:1. A C10-C18+ olefin stream (Stream A) was created and separated downstream from the cross-metathesis reaction of the soybean oil feed and 1-butene feed. The C10-C18+ olefin stream was then cross-metathesized with ethylene in a fixed bed ethylene

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metathesis reactor to create an olefin product. The ethylene product was separated from the olefin product and recycled back to the ethylene metathesis reactor. A heavier olefin product stream (i.e., C16-C18+) was also separated from the olefin product to form a final olefin product (Stream B) and the heavier olefin product stream was recycled back to the ethylene metathesis reactor. The C10-C18+ olefin input stream (Stream A) and final olefin product stream (Stream B) have the following olefin product distributions, shown in **Table 2** below:

TABLE 2

	Stream A	Stream B
Olefin Distribution	wt%	wt%
C10:1	36.1	86.8
C10 isomers	52.7	3.0
C11	0.0	0.0
C12	0.0	1.8
C13	0.0	4.1
C14-18	11.2	4.3
Total	100.0	100

Example 15

[00210] An Aspen model was developed to simulate the process of maximizing heavier weight olefins (i.e., C18+ olefins) based on the metathesis process of using a soybean oil feed and a hexene isomer feed at molar ratio of 3:1. A C11-C18+ olefin stream (Stream A) was created and separated downstream from the cross-metathesis reaction of the soybean oil feed and hexene isomer feed. The C11-C18+ olefin stream was then self-metathesized in a fixed bed reactor to create an olefin product. A C11-C16 olefin stream was separated from the olefin product recycled back to the self-metathesis reactor. The C10 olefin can also be separated as a product to form a final olefin product stream (B). The olefin input stream (Stream A) and final product stream (Stream B) have the following olefin product distributions, shown in **Table 3** below:

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TABLE 3

Stream A	Stream A	Stream B
Olefin Distribution	wt%	wt%
< C10	0.0	2.5
C10	0.0	21.3
C11	24.7	0.0
C12	36.2	0.0
C13	16.8	0.0
C14	4.5	0.0
C15	12.1	0.0
C16	2.4	0.0
C17	0.4	4.1
C18	2.4	46.7
C18+	0.5	25.4
Total	100.0	100

Example 16

[00211] An Aspen model was developed to simulate the process of maximizing the purity of C11-C15 methyl esters based on the metathesis process of using a soybean oil feed and a hexene isomer feed at molar ratio of 3:1. A mixed triglyceride and ester stream is formed from the cross-metathesis reaction of the soybean oil and hexene isomer feeds. The mixed triglyceride and ester stream undergoes glycerolysis after metathesis, followed by olefin separation and transesterification. A C10 and lighter olefin stream is separated from the mixed triglyceride and ester stream and recycled back to the metathesis reactor. A C10 methyl ester (ME) stream is also recycled to the metathesis reactor. A C16 ME stream is purged. A fraction (e.g., 10%) of the C17-C20 ME stream is purged and the remaining fraction, mixed with the heavier esters, is recycled back to the metathesis reactor. The final ester product stream (comprising primarily C11-C15 ME) downstream of the olefin separation, transesterification, and ester recycle streams has the following ester distribution, shown in **Table 4**:

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TABLE 4

	Ester Product Stream
FAME Distribution	wt%
< C10ME	0.0
C10ME	0.0
C11ME	17.3
C12ME	21.7
C13ME	17.7
C14ME	4.6
C15ME	16.8
C16ME	15.6
C17ME	0.1
C18ME	6.2
C18+ME	0.0
Total	100.0

Example 17 – 9-DAME/9-DDAME on a 10 g scale

[00212] In this example, methyl 9-decenoate (distillation cut from butenolyzed, stripped, trans-esterified palm oil), and methyl 9-dodecenoate (distillation cut from butenolyzed, stripped, trans-esterified palm oil) were prepared and cross-metathesized. Their compositions are shown in **Tables 5 and 6** below. PV was undetected (AOCS method AOCS Method Cd 8b-90 Peroxide Value Acetic Acid – Isooctane Method (Revised 2003)).

[00213]

Table 5. 9-DAME Feed composition

Component	Wt%
1,4-tridecadiene	0.18
Methyl 8-nonenoate	0.08
Methyl decanoate	0.16
Methyl 9-decenoate	98.51
Methyl 8-decenoate	0.76
Other	0.29
TOTAL	100.00

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Table 6. 9-DDAME feed composition

Component	Wt%
6-pentadecene	0.18
3,6-pentadecadiene	0.21
7-hexadecene	0.25
Methyl decanoate	0.01
Methyl 9-decenoate	0.76
Methyl decanoate	3.01
Methyl 9-dodecenoate*	95.46
Other	0.12
TOTAL	100.00

*contaminated with 11-isomer dodecenoic acid, methyl ester

[00214] Clean, dry, 20 CC scintillation vials outfitted with a magnetic stir bar and septum top were charged with 9-DAME or a mixture of 9-DAME/9-DDAME according to the experiment design **Table 7** below.

TABLE 7

Example	9-DAME	9-DDAME	C-827 (ppm wt)	Headspace Treatment
17a (comparative)	10.02 g	0 g	80	Vent only
17b (comparative)	10.00 g	0 g	80	Nitrogen purge
17c (comparative)	10.00 g	0 g	500	Vent only
17d (comparative)	10.00 g	0 g	500	Nitrogen purge
17e	4.42 g	5.60 g	80	Vent only
17f	4.41 g	5.61g	80	Nitrogen purge

[00215] In Example 17e, about 50% by weight of the formed olefins (e.g., 1-butene and 3-hexene) were removed during the reaction. In Example 17f, greater than 95% by weight of the formed olefins (e.g., 1-butene and 3-hexene) were removed during the reaction. In Examples 17a-17d, no olefin were removed during the reaction.

[00216] The vials were placed in an eight-cell aluminum block on top of a heater/stirrer. The aluminum block was heated to 60°C. While the aluminum block was heating (~15 min.), the vial headspace was degassed by providing a nitrogen inlet (~65 mL/min) and an exhaust needle. Meanwhile, a metathesis catalyst solution (0.01 mg/μL) was prepared by first placing C-827 (21.10 mg) in a 2 mL volumetric flask, second capping the flask with a rubber septum, third purging with nitrogen, and fourth adding toluene to the 2.00 mL mark. Metathesis catalyst

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solution was added to each reaction mixture (time=0). According to the experimental design, the nitrogen inlet (65 mL/min) was left in place to sweep by-product olefins away from the reaction or it was removed. In both cases the vent needle was left in place to avoid over-pressuring the scintillation vial. In the latter case, the oxygen free headspace was provided by olefin formed by metathesis. After 2 hours, the composition (normalized wt %, exclusive of light olefins) was determined by GC FID2, Table 8.

TABLE 8

	17a	17b	17c	17d	17e	17f
Methyl 8-nonenoate	1.39	1.67	3.58	3.65	0.00	0.00
Methyl 9-decenoate	80.51	77.53	41.12	28.66	28.41	17.48
Methyl 8-decenoate	0.00	0.00	4.41	4.86	0.00	0.00
Methyl undecenoate	0.00	0.00	3.87	3.41	0.00	0.00
Methyl 9-dodecenoate	0.00	0.00	0.00	0.00	29.44	12.59
Methyl 9-octadecenoate	0.09	0.10	0.18	0.19	0.35	0.58
Dimethyl hexadecenedioate	0.12	0.17	0.41	0.96	0.00	0.00
Dimethyl heptadecenedioate	0.45	0.65	5.14	8.63	0.62	1.04
Dimethyl 9-octadecenedioate	16.25	18.80	39.08	46.37	36.28	62.68
Dimethyl nonadecenedioate	0.00	0.00	0.50	1.09	0.00	0.00
Dimethyl eicosenedioate	0.00	0.00	0.00	0.00	0.89	1.54
Other	1.20	1.08	1.73	2.19	4.00	4.11
Total	100	100	100	100	100	100

Example 18 - 9-DAME/9-DDAME on a 330 g scale

[00217] A dibasic ester composition was produced by conducting a cross-metathesis reaction between methyl 9-decenoate (9-decenoic acid methyl ester, 9-DAME) and methyl 9-dodecenoate (9-dodecenoic acid methyl ester, 9-DDAME). A 1.0:1.0 mole ratio mixture of 9-DAME and 9-DDAME (332 g) was charged to a 1 L round bottom flask and heated to 60°C. Pressure was adjusted to 100 mg Hg with ChemGlass diaphragm vacuum pump model CG-4812-30 / and J-Kem Scientific Digital Vacuum Regulator Model 200 and stirring was initiated with a magnetic stir bar. The feed composition (distillation cut from butenolyzed, stripped, trans-esterified palm oil) is shown below in **Table 9**.

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TABLE 9

Component	wt%
Methyl decanoate	0.04
Methyl 9-decenoate	44.81
Methyl 8-decenoate	0.07
Methyl undecenoate	0.19
Methyl decanoate	0.76
Methyl 9-dodecenoate*	52.87
Methyl 9,12-tridecadienoate	0.86
Methyl tetradecenoate	0.20
Methyl 9-pentadecenoate	0.03
Methyl 9,12-pentadienoate	0.02
Methyl hexadecanoate	0.15
Total	100

*contaminated with methyl 11-dodecenoate

[00218] After the system stabilized at desired conditions, 80 ppm of C-827 (as toluene solution) was added (t=0 min). At approximately 15-20 min, the reaction started bubbling vigorously and the pressure rose to approximately 500 mm Hg. Pressure re-stabilized at 100 mm Hg after approximately 5-10 more minutes. Samples were taken at 30, 60, 90, 120, 150, 180, 240, and 300 minutes. At 180 min, an additional 40 ppm of C-827 (as toluene solution) was added. The graph in FIG. 9 shows 9-DAME & 9-DDAME (wt%) verses reaction time (hr).

[00219] The crude product composition ((normalized wt %, exclusive of light olefins)) at five hours is shown in **Table 10** below:

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TABLE 10

FAME	wt%
Methyl decanoate	0.05
Methyl 9-decenoate	6.79
Methyl 8-decenoate	0.56
Methyl undecenoate	0.37
Methyl dodecanoate	0.84
Methyl 9-dodecenoate*	6.53
Methyl 9,12-tridecadienoate	0.05
Methyl tetradecenoate	0.20
Methyl hexadecanoate	0.14
Dimethyl hexadecenedioate	0.07
Dimethyl heptadecenedioate	1.11
Dimethyl 9-octadecenedioate	78.92
Dimethyl nonadecenedioate	0.45
Dimethyl eicosenedioate	2.85
Dimethyl 9,12-heneicosadienedioate	0.53
	99.46

*contaminated with methyl 11-dodecenoate

[00220] Subsequently, the catalyst was deactivated with 25 equivalents THMP to C-827 at 80°C for 120 min, THMP being prepared by the general procedure of example 8. The catalyst was then removed by water extraction (5:1 oil to water). The composition was dried with MgSO₄. Then, light FAME stripping was conducted at 1 mm Hg and approximately 100°C. The wt% concentration of the various products included a large fraction of 18:1 dibasic ester, see **Table 11**.

TABLE 11

Component	Content (wt%)
Methyl Hexadecenoate	0.17
Dimethyl 8-hexadecenedioate	0.06
Dimethyl 8-heptadecenedioate	1.34
Dimethyl 9-octadecenedioate	92.95
Dimethyl nonadecenedioate	0.58
Dimethyl eicosenedioate	3.41
Dimethyl 9,12-heneicosadienedioate	0.92
Heavies	0.57

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Example 19 - 9-DAME/9-DDAME on a 3 kg scale

[00221] A 12 L glass round bottom flask fitted with 1) a reflux condenser (5 C) to which a vacuum gauge and ChemGlass diaphragm vacuum pump model CG-4812-30 were attached, 2) a rubber septum through which nitrogen and catalyst were introduced, magnetic stir bar, and thermo-couple and alternate vent (in case vacuum pump failed to maintain sub-atmospheric pressure). No vacuum regulator was used for this example. Heating was provided by heating mantle.

[00222] To the nitrogen-purged 12 L reaction-flask was added low PV 9-DAME (1.34 kg) and 9-DDAME (1.68 kg). The condenser was chilled to 5 C with glycol. Under continued flow of nitrogen, the mixture was heated to ~70 C and then placed under full vacuum. The first catalyst solution (C-827 in toluene) addition marked the beginning of the reaction (t = 0 min). Temperature and pressure were recorded, see **Table 12**.

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TABLE 12

Time (min)	Temperature (deg C)	Pressure (mm Hg)
0	73.4	35.0
5	74.2	30.5
10	74.0	30.7
15	72.8	28.7
20	71.5	28.3
25	70.3	28.4
30	69.9	28.3
35	72.2	28.4
40	72.3	30.9
45	71.4	65.9
50	71.1	233.0
55	70.0	237.5
60	69.0	196.0
65	68.4	218.6
70	69.1	215.8
75	68.5	188.5
80	68.2	194.2
85	70.1	207.9
90	70.0	185.9
95	68.8	175.6
100	68.6	172.8
105	70.2	172.1
110	72.2	169.5
115	71.6	170.1
120	71.1	147.0
125	69.3	140.5
140	70.4	92.1
150	69.8	74.1
155	71.0	68.6
160	71.1	64.9
165	70.8	57.5
175	69.6	57.5
185	70.9	56.6
195	67.3	54.7
210	63.6	56.4
239	56.0	64.5

[00223] In Example 19, greater than 95% by weight of the formed olefins (e.g., 1-butene and 3-hexene) were removed during the reaction.

[00224] Catalyst solution was added in 30 mg increments at 0, 10, 22, 32, 40, 60, 76, 97, 110, 120, and 121 minutes. Total catalyst added was 0.33 g (110 ppm).

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The reaction initiated about 5 minutes after the fifth increment of catalyst. With each addition of catalyst with exception of the last two, an increased rate of bubbling was observed. After 239 minutes, heat was turned off and the reaction cooled to ambient. Vacuum was turned off and the system was backfilled with nitrogen. A total of 2.66 kg of liquid product were collected. Its composition, analyzed by liquid sample analysis (normalized wt %) is shown in **Table 13**.

TABLE 13

	Initial (wt %)	Final (wt %)
Butenes	0.00	0.12
3-hexene	0.00	0.32
1,4-tridecadiene	0.03	0.00
Pentadecene	0.09	0.00
pentadecadiene	0.15	0.00
Methyl 8-nonenoate	0.00	0.13
Methyl 9-decenoate	43.59	8.65
Methyl 8-decenoate	0.10	0.00
Methyl undecenoate	0.07	0.74
Methyl 9-dodecenoate*	55.78	11.50
Methyl 9,12-tridecadienoate	0.06	0.00
Methyl tetradecenoate	0.00	0.19
Methyl 9-pentadecenoate	0.00	0.19
Methyl 9,12-pentadienoate	0.00	0.08
Methyl 9-octadecenoate	0.00	0.28
Dimethyl hexadecenedioate	0.00	0.16
Dimethyl heptadecenedioate	0.00	2.19
Dimethyl 9-octadecenedioate	0.13	72.41
Dimethyl nonadecenedioate	0.00	0.23
Dimethyl eicosenedioate	0.00	2.74
other	0.00	0.09
TOTAL	100.00	100.00

* contaminated with methyl 11-dodecenoate

[00225] Samples of the pump exhaust at were collected at 54 minutes (highest off-gas rate) and at 239 minutes (end of experiment) and then analyzed on GASPRO column (see **Table 14** below). Formation of ethylene is evidence of 9-DAME self-metathesis. Formation of propylene and 2-butene is evidence of isomerization (for instance 9-DAME to 8-DAME).

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TABLE 14

Gas sample analysis (area %, known components)

	At 54 minutes	At 239 minutes
Ethylene	1.67	0.57
Propylene	1.07	1.84
1-butene	92.17	46.46
<i>trans</i> -2-butene	0.08	0.09
<i>cis</i> -2-butene	0.03	0.03
<i>trans</i> -3-hexene	2.95	14.99
<i>cis</i> -3-hexene	1.02	2.69
Toluene	0.62	30.15

Example 20 – 9-DAME/9-DDAME on a 10 kg scale

[00226] A clean, dry, stainless steel jacketed 20 liter Parr reactor vessel equipped with a dip tube, overhead stirrer, internal cooling/heated coils, temperature probe, sampling valve, and headspace gas release valve was purged with nitrogen. Premixed 9-DAME/9-DDAME feedstock (10.08 kg, PV $\sim$ 13) was charged to the reactor; see **Table 15** for composition. The reaction was purged with nitrogen through the dip tube at 14.2 L/min (0.5 scfm) for 30 minutes while gently stirring the mixture. The reactor was heated to 200°C and held for 30 minutes while maintaining a nitrogen purge of 14.2 L/min (0.5 scfm) through the dip tube and a gentle stir rate. The mixture was cooled to 60°C and nitrogen flow was reduced to 5.7 L/min (0.2 scfm) with continued stirring. The stirrer was turned off and a sample was removed through the sample port. PV was measured and no peroxide detected. GC analysis shown in **Table 15**. While maintaining gentle stirring and a reactor temperature of 60°C, the reactor pressure was reduced to 100 mm Hg. Catalyst solution (0.33 g of C827 in 40 g of toluene) was added through the sample port (T=0) (9:26). Pressure was maintained at 100 mm Hg with gentle stirring. The first sample (1st metathesis sample) was collected at 1 hr. Another charge of catalyst solution (0.33 g of C827 in 40 g of toluene) was added at 1.5 hr. A second sample (2nd metathesis sample) was collected at 2.25 hr.

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TABLE 15

	Feed	Heat treated	1 hr sample	2.25 hr sample	Final Product
Methyl 9-decenoate	43.68	42.78	10.92	8.00	6.32
Methyl 9-dodecenoate*	55.50	56.10	10.95	8.56	7.93
Methyl 9,12-tridecadienoate	0.00	0.00	0.00	0.01	0.01
Dimethyl hexadecenedioate	0.00	0.00	0.05	0.08	0.11
Dimethyl heptadecenedioate	0.00	0.00	0.54	1.17	1.79
Dimethyl 9-octadecenedioate	0.00	0.00	69.64	73.43	74.76
Dimethyl nonadecenedioate	0.00	0.00	0.11	0.25	0.38
Dimethyl eicosenedioate	0.00	0.00	4.95	5.33	5.33
Dimethyl 9,12-heneicosadienedioate	0.00	0.00	0.34	0.24	0.25
Other	0.82	1.12	2.26	2.93	3.12
Total	100.00	100.00	100.00	100.00	100.00

* contaminated with methyl 11-dodecenoate

[00227] The reaction was stopped. A total of 2.9 kg of olefins was collected in cold-traps. Liquid contents of the 20-liter Parr reactor were transferred at 60°C to a 20-liter nitrogen purged glass reactor and then heated to 80°C. With 567 L/min (20 scfm) of nitrogen flowing through the headspace, a 1 M THMP solution (433 g) was added to the reactor and vigorous stirring was provided. After 2 h, the mixture was cooled to 35°C and the stirrer was turned off. The reactor was allowed to set overnight. The next day, the mixture was reheated and the temperature was maintained between 50°C and 55°C. Deionized water (1.8 kg) was added and the two-phase system was vigorously stirred for 30 minutes. The stirrer was turned off to let phases separate. The bottom aqueous phase was removed. Another portion of deionized water (1.8 kg) was added to the reactor. The mixture was stirred well mixed. The stirrer was then turned off to let phases separate. The bottom aqueous phase was removed. The final product (6.29 kg) was removed from the reactor and analyzed by GC.

Example 21 – 9-DAME/3-hexene on 10 g scale

[00228] 9-DAME composition (distillation cut from butenolyzed, stripped, transesterified palm oil) is given in **Table 5**. Clean, dry, 20 cc scintillation vials outfitted with a magnetic stir bar and septum top was charged with 9-DAME (PV<1) and 3-hexene (distillation cut of olefins stripped from butenolyzed palm oil) according to the experiment design, **Table 16**. Each vial was placed in an eight-cell aluminum

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block on top of a heater/stirrer. The aluminum block was heated to 60°C. While the aluminum block was heating (~15 min), the each vial's headspace was degassed by providing a nitrogen inlet (~65 mL/min) and an exhaust needle. Meanwhile, a 0.01 mg/μL metathesis catalyst solution was prepared by first placing C827 (21.10 mg) in a 2 mL volumetric flask, second capping the flask with a rubber septum, third purging with nitrogen, and fourth adding toluene to the 2.00 mL mark. Metathesis catalyst was added to the reaction mixture (time=0). According to the experimental design, the nitrogen inlet (65 mL/min) was left in place to sweep by-product olefins away from the reaction or it was removed. In both cases the vent needle was left in place. In the latter case, olefin formed by metathesis provided the oxygen-free environment needed by the catalyst. After 2 hours, an aliquot was analyzed by GC. Composition ((normalized wt %, exclusive of light olefins) is shown in **Table 17**.

TABLE 16

Example	9-DAME	3-Hexene	C-827 (ppm wt)	Headspace treatment
21a	6.42 g	3.61 g	80	Vent only
21b	6.43 g	3.66 g	80	Nitrogen purge
21c	6.42 g	3.60 g	120	Vent only
21d	6.44 g	3.58 g	120	Nitrogen purge

TABLE 17

Example	21a	21b	21c	21d
Methyl 8-nonenoate	0.00	0.00	0.00	0.00
Methyl 9-decenoate	72.85	0.44	10.91	0.46
Methyl 8-decenoate	0.90	0.00	0.00	0.00
Methyl undecenoate	0.00	0.00	2.17	0.00
Methyl 9-dodecenoate	23.24	19.45	58.87	19.34
Methyl tridecenoate	0.00	0.00	0.00	0.00
Methyl tetradecenoate	0.00	0.00	0.00	0.00
Methyl 9-octadecenoate	0.00	0.00	0.14	0.40
Dimethyl hexadecenedioate	0.00	0.00	0.00	0.00
Dimethyl heptadecenedioate	0.10	1.75	0.79	1.95
Dimethyl 9-octadecenedioate	1.68	74.27	24.48	73.96
Other	1.23	4.09	2.64	3.88
Total	100.00	100.00	100.00	100.00

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Example 22 – 9-DAME/*trans*-2-butene on 40 g scale

[00229] 9-DAME (40.16 g) was charged to a 100 mL 3-neck round bottom flask fitted with a coil-type reflux condenser (exhausted to an oil bubbler), a magnetic stir bar, and septum caps. The reaction system was purged, for 30 minutes, with nitrogen by a needle inserted into one of the septum caps and allowing the exhaust out the bubbler. The reaction flask was immersed in an oil bath which was heated to 55°C. The condenser was cooled by means of 15°C glycol fluid. Nitrogen purge was replaced by a flow of *trans*-2-butene through the liquid. After a consistent reflux of *trans*-2-butene was observed, 80 ppm catalyst was added (T=0). The flow of *trans*-2-butene was continued for the duration of the reaction except as follows. The reaction was monitored by interrupting *trans*-2-butene flow and observing bubble rate in the bubbler. In addition to the initial 80 ppm charge of catalyst, three additional 20 ppm increments of catalyst were added at T=30, 81, 125 minutes. Final product weight was 31.25 g. Conversion to diesters was 85% and selectivity to 9-ODDAME was 81%.

Example 23 – 9-DAME/*trans*-2-butene in Fisher-Porter tube

[00230] Using a 3 ounce Fisher-Porter tube equipped with an addition ports for catalyst and *trans*-2-butene. In a glove box, 40.0 mg C827 was dissolved in 1 mL of toluene. Sixty microliters of catalyst solution were loaded into the catalyst addition manifold using a 250 uL syringe, removed from glove box, and attached to the pressure vessel manifold. Twenty grams of 9-DAME charged to the pressure tube which was subsequently degassed for 30 minutes with nitrogen. Meanwhile *trans*-2-butene was condensed/transferred into a second 3-ounce Fisher-Porter tube. The pressure vessel containing *trans*-2-butene was pressured with nitrogen to 4 psig. The pressure vessel containing the ester was heated to 60°C in a silicone oil bath. The catalyst solution was transferred to the ester under nitrogen. Immediately, about 7.6 mL (4.57 g) of *trans*-2-butene (target for 0.75:1 ratio) was transferred to the pressure vessel containing the 9-DAME, which washed any residual catalyst solution into the reaction vessel.

[00231] The volume was measured using mm graduation marks on the vessel and the measured cross sectional area of the tube. The targeted volume was based on converting the targeted mass to a targeted volume assuming a *trans*-2-butene

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density of 0.6 g/mL. The pressure tube containing the reaction mixture was then pressurized to 36 psig with nitrogen. Samples were taken at 10 minutes and 60 minutes using a sampling tube apparatus. The vessel was depressurized slowly to atmospheric pressure and sparged with nitrogen. After 60 minutes of sparging, the vessel was disassembled, and the sample was collected. The pressure, bath temperature, and liquid level were monitored as a function of time and summarized in **Table 18**. GC analysis (normalized wt %, exclusive of light olefins) is summarized in **Table 19**.

TABLE 18

Time (min)	Pressure (psig)	Temperature (°C)	Liquid level (mm)	Comments
0	36	58.9	60.5	Closed system
5	76	59.2	55.0	Closed system
10	83	59.3	55.0	Closed system, Sample #1
10	84	59.2	53.5	Closed system
15	84	59.1	53.5	Closed system
20	88	59.1	54.0	Closed system
30	91	58.9	53.5	Closed system
40	92	58.9	53.5	Closed system
50	92	58.9	53.5	Closed system
60	92	58.9	53.5	Closed system, Sample #2
60	96	58.9	43.5	Nitrogen sparge
120	0			Reaction End, Sample #3

TABLE 19

	Sample 1 (10 min)	Sample 2 (60 min)	Sample 3 (120 min)
Methyl 9-decenoate	36.2	36.9	35.3
Methyl undecenoate	31.9	39.0	39.1
Methyl 8-decenoate	2.5	4.3	5.6
Methyl 8-nonenoate	1.3	1.4	1.3
Dimethyl hexadecenedioate	0.2	0.1	0.2
Dimethyl heptadecenedioate	2.4	1.8	1.9
Dimethyl 9-octadecenedioate	25.4	16.4	16.6
Dimethyl nonadecenedioate	0.1	0.1	0.1

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Example 24 – 9-DAME/*trans*-2-butene on 8 kg scale

[00232] A two-stage cross-metathesis strategy using 9-DAME and purchased *trans*-2-butene was employed. In the first stage, 9-DAME was partially converted *in situ* to 9-UDAME. In the second stage, the mixture of 9-DAME and 9-UDAME was converted to 9-ODDAME. The 9-DAME feedstock (from octenolyzed palm oil) for this example was contaminated with significant concentrations of 8-DAME and 7-tetradecene, **Table 20**.

TABLE 20

	Lot A (wt%)	Lot B (wt%)
Methyl 9-decenoate	81.4	88.6
Methyl 8-decenoate	8.9	5.7
7-tetradecene	8.0	4.6

[00233] The two-stage synthesis was performed eight times and was found to scale-up without difficulties. The first batch was performed using an initial 4 kg charge of an 81% pure 9-DAME and 1.2 mol *trans*-2-butene/mol 9-DAME, yielding a crude product containing 57 wt% 9-ODDAME. The second preparation used a 6 kg charge of the 81% pure 9-DAME and only 0.75 mol *trans*-2-butene/mol 9-DAME, yielding a crude product containing 53 wt% 9-ODDAME. The remaining preparations used 8 kg initial charges of 89% pure 9-DAME and 0.75 mol *trans*-2-butene/mol 9-DAME, yielding crude products containing from 60 to 69 wt% 9-ODDAME. **Table 21** summarizes key reaction measures for the eight batches. Composition is in normalized wt %, exclusive of light olefins.

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TABLE 21

Run #	24a	24b	24c	24d	24e	24f	24g	24h
9-DAME lot	A	A	B	B	B	B	B	B
Run size (kg 9-DAME)	4	6	8	8	8	8	8	8
(kg trans-2-butene)	1.4	1.4	1.9	1.9	1.9	1.9	1.9	1.9
Molar ratio (2-butene : 9-DAME)	1.2	0.75	0.75	0.75	0.75	0.75	0.75	0.75
C-827 charge (ppmwt) stage 1	93	68	68	68	68	68	68	68
stage 2	93	68	68	68	68	68	68	68
Stage 1 wt ratio 9-UDAME : 9-DAME	4.93	2.43	2.21	2.37	1.88	1.92	1.98	NA
Stage 2 composition (wt %)								
1-octene	0.00	0.00	0.31	0.18	0.31	0.00	0.00	0.00
2-nonene	0.00	2.62	1.09	0.48	0.68	1.17	0.58	0.46
7-tetradecene	0.75	0.75	0.20	0.18	0.25	0.27	0.11	0.22
Methyl decanoate	0.35	0.43	0.42	0.41	0.55	0.65	0.69	0.00
Methyl 9-decenoate	0.23	1.02	2.08	1.90	2.84	2.20	1.69	1.70
Methyl 8-decenoate	0.38	1.71	0.86	0.65	0.91	1.14	0.89	1.04
Methyl undecenoate	2.13	13.64	10.38	8.47	11.57	14.00	11.66	11.43
Methyl pentadecenoate	1.39	0.08	0.50	0.58	0.68	0.77	0.65	0.66
Methyl hexadecenoate	10.30	9.64	5.14	5.83	6.46	6.96	6.46	6.68
Methyl heptadecenoate	2.08	0.28	0.00	0.00	0.19	0.22	0.19	0.20
Dimethyl hexadecenedioate	1.19	1.18	0.96	1.11	1.11	1.15	1.12	1.08
Dimethyl heptadecenedioate	13.02	12.24	9.26	9.91	9.54	9.42	9.64	9.40
Dimethyl 9-octadecenedioate	57.05	53.15	66.79	68.68	64.20	60.34	65.06	65.24
Total	97.06	96.74	97.99	98.39	99.28	98.29	98.74	98.10

[00234] Purification was accomplished in approximately 2 kg batches by crystallizing trans-ODDAME from crude product using four volumes of cold methanol, vacuum filtration including a wash with additional cold methanol, and then vacuum drying. Typical yield was about 50% and typical purity is shown in Table 22.

TABLE 22

	From lot A feed	From lot B feed
Dimethyl 9-octadecenedioate	96.9	97.6

Example 30

[00235] Time of trishydroxymethyl phosphine (THMP) treatment and water treatment, as well as type of water, were varied to study the effects on ruthenium removal from a natural oil/metathesis catalyst solution.

[00236] In the experiments described, THMP was supplied from a stock solution by the following method: 10.20 g of 75 wt % tetrakis(hydroxymethyl) phosphonium sulfate in water (Bricorr 75, Rhodia) was diluted with 37.69 deionized water (Type II) under an nitrogen-inerted atmosphere 4.02 g of 50 wt% sodium hydroxide (Aldrich) was then added to the diluted solution, followed by the addition of

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4.08 g of 75 wt % tetrakis(hydroxymethyl) phosphonium sulfate to the mixture, to adjust the pH to 8. The pH of the solution was measured using a pH probe. The solution was transferred to a plastic container and stored until use. The molar concentration of THMP in the solution was based on the total amount of the limiting reagent sodium hydroxide (1 mole of tris(hydroxymethyl) phosphine = 1 mole of sodium hydroxide in excess tetrakis(hydroxymethyl) phosphonium sulfate). In a 500 mL kettle flask (4 inch inner diameter), equipped with an overhead stirrer (4-pitch blades, 45°, 2 inch diameter), overhead condenser (set at 5°C), and baffles, a water stream containing extracted ruthenium and tris(hydroxymethyl) phosphine (derived from tetrakis(hydroxymethyl) phosphonium sulfate) was generated by the following procedure.

[00237] In a 500 mL kettle flask (4 inch inner diameter), equipped with an overhead stirrer (4-pitch blades, 45°, 2 inch diameter), overhead condenser (set at 5°C), and baffles, a water stream containing extracted ruthenium and tris(hydroxymethyl) phosphine (derived from tetrakis(hydroxymethyl) phosphonium sulfate) was generated by the following procedure: 1-octene (Aldrich, 98%) was reacted with palm oil (Wilmar, refined, bleached, deodorized, pretreated at 200 °C for 2 hours batch under nitrogen sparging) at a 1.5:1 molar double bond ratio of 1-octene: palm oil in the presence of 800 ppmw catalyst (C827, Materia, based on mass of oil), 60 minute batch contact time, 60°C reaction temperature, atmospheric pressure, and under a nitrogen-blanketed headspace. After generating the metathesized mixture, the mixture was heated to 90°C and 19:1 molar equivalents of tris(hydroxymethyl) phosphine to catalyst (target) was added to the metathesized mixture. The metathesized mixture containing tris(hydroxymethyl) phosphine was stirred for 60 minutes batch. Then, deionized water (Type II) was added to the metathesized mixture at 1 g of water to 5 g of metathesized oil and stirred for 1 hour, batch at 72 to 90°C. After 1 hour of water mixing, the mixture was allowed to gravity settle for 1 hour while heating at 90°C. The bottom layer was removed from the mixture and stored. This bottom layer was assumed to simulate a 20:1 recycle ratio of water in a continuous extraction process (based on a typical 40 ppmw catalyst concentration, based on mass of oil), and referred to as "Simulated Recycled Water Stream" herein.

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[00238] Additional metathesized mixtures of oil were generated by reacting 1-octene with palm oil (1.5:1 molar double bond ratio of 1-octene: palm oil) in the presence of 40 ppmw catalyst (based on mass of oil), 60 minute batch contact time, 60°C reaction temperature, atmospheric pressure, and under a nitrogen-blanketed headspace. A sample was removed after 60 minutes to analyze for ruthenium concentration. Samples generated from the method described are referred to as “Before THMP Treatment” herein.

[00239] After generating the additional metathesized mixture, the mixture was heated to 90°C, and 19:1 molar equivalents of trishydroxymethyl phosphine to catalyst (target) was added to the metathesized mixture. The metathesized mixture containing trishydroxymethyl phosphine was stirred for 60 minutes batch. Samples generated from the method described are referred to as “After THMP Treatment” herein.

[00240] Then, the simulated recycled water was added to the metathesized mixture at 1g of water to 5 g of metathesized oil and stirred for various times (15 minutes, 30 minutes, 60 minutes) batch at 72 to 90°C. After water mixing, the mixture was allowed to gravity settle for 1 hour at 90°C. The top layer and bottom layers were sampled for ruthenium concentration and the top layer was sampled for isomerization testing. Samples generated from the method described are referred to as “After Water Extraction” herein.

[00241] Ruthenium analysis was performed using ICP-MS at STAT Analysis Corporation, Chicago, Illinois. Ruthenium efficiency (%), assuming mass is conserved, is defined by the following equation:

$$\text{Ruthenium Removal Efficiency (\%)} = 100 \frac{C_{\text{Ru Before Extraction}} - C_{\text{Ru After Extraction}}}{C_{\text{Ru Before Extraction}}}$$

[00242] Isomerization tests were performed on the samples to determine the effectiveness of the trishydroxymethyl phosphine reaction with the ruthenium-containing catalyst. The isomerization test included heating the sample to 250°C for 1 hour under an open-system nitrogen headspace, maintained at 1 psig.

[00243] Standard sample analysis was performed on the isomerized samples. About 6 drops (~100-200 mg) of the sample were transferred to a 20 mL borosilicate scintillation vial. 1 mL of 1 mass % sodium methoxide in methanol (Aldrich) was added to the vial using an autopipette. The vial was sealed and was heated to 60 C

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while shaken at 240 rpm for at least 40 minutes until one liquid phase was visually observed. 5 mL of saturated brine solution was added to the vial using an autopipette. 5 mL of ethyl acetate was then added to the vial using an autopipette. The mixture was further shaken and allowed to settle into two distinct phases. Approximately 1.5-2 mL of the top layer (ethyl acetate) was transferred to a 2 mL gas chromatography vial.

[00244] The vial was analyzed for 9-decenoic acid ester isomerization using an Agilent 7890 gas chromatograph, equipped with a split/splitless injection port, an RTX-65TG column (Restek 17008, 30 m length x 0.25 mm inner diameter x 0.1 mm film thickness), quadrupole mass spectrometer detector. Helium was used as the carrier gas.

[00245] The 9-decenoic acid ester and isomers were quantified using ion extraction of the ester fragments with the MS Chem software; the integrated areas were assumed to be proportional to the relative mass concentration of the esters.

[00246] The percent isomerization was defined by the following equation:

$$\text{Isomerization (\%)} = 100 \frac{A_{\text{Isomer 1}} + A_{\text{Isomer 2}} + A_{\text{Isomer 3}}}{A_{\text{Isomer 1}} + A_{\text{Isomer 2}} + A_{\text{Isomer 3}} + A_{\text{9-Decenoic Acid Ester}}}$$

where $A_{\text{Isomer 1}}$ is the integrated area of isomer 1 of 9-decenoic acid ester, $A_{\text{Isomer 2}}$ is the integrated area of isomer 2 of 9-decenoic acid ester, $A_{\text{Isomer 3}}$ is the integrated area of isomer 3 of 9-decenoic acid ester, $A_{\text{9-Decenoic Acid Ester}}$ is the integrated area of 9-decenoic acid ester. Isomer 1 and 2 are the cis- and trans- 8-decenoic acid methyl esters. Isomer 3 is a 7-decenoic acid methyl ester. Other isomers can form, but are not chromatographically resolved from the peaks observed.

[00247] Testing was performed within 24 hours of sampling from reactor vessel. For most cases, the testing was within an hour of sampling. Sample analysis was run in duplicate, and an average of two runs is reported. For reference, the result of the isomerization test on a sample not treated with THMP was typically 20-40% isomerization (average of two samples) at the catalyst loadings studied. Results are shown in **Table 23**.

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TABLE 23

Water Type	Process	Conditions	Isom %	Water content (ppmw)	Ru (ppmw)	Ru removal eff (%)
Type II DI	60 min THMP treatment, 60 min water extraction, and 60 min settling	Before THMP treatment	44.41	93	3.8	80
		After THMP treatment	0.08	88	--	
		After water extraction	0.18	1524	0.75	
Simulated recycled, 20 recycles, ~360 ppmw Ru	60 min THMP treatment, 60 min water extraction, and 60 min settling	Before THMP treatment	31.10	51	3.4	47
		After THMP treatment	0.60	51	--	
		After water extraction	0.69	1162	1.8	
Simulated recycled, 20 recycles, ~360 ppmw Ru	60 min THMP treatment, 30 min Water Extraction, and 60 min settling	Before THMP treatment	34.70	50	5	48
		After THMP treatment	0.06	57	--	
		After water extraction	0.28	1657	2.6	
Simulated recycled, 20 recycles, ~360 ppmw Ru	60 min THMP treatment, 15 min water extraction, and 60 min settling	Before THMP treatment	43.25	28	9.3	63
		After THMP treatment	1.06	37	--	
		After water extraction	0.21	1733	3.4	
Simulated recycled, 20 recycles, ~360 ppmw Ru	0 min THMP treatment, 60 min water extraction, and 60 min settling	Before THMP treatment	31.65	43	6.2	42
		---	--	--	--	
		After water extraction	0.57	1750	3.6	
Simulated recycled, 20 recycles, ~320 ppmw Ru	15 min THMP treatment, 15 min water extraction, and 60 min settling	Before THMP treatment	33.5	125.1	3.5	46
		After THMP treatment	0.50	1854	--	
		After water extraction	0.31	974	1.9	

[00248] Unless otherwise described, the aforementioned examples utilized the following analytical methods described below:

[00249] Volatile products were analyzed by gas chromatography and flame ionization detector (FID). Alkene analyses were performed using an Agilent 6890 instrument and the following conditions:

Column: Restek Rtx-5, 30m x 0.25mm (ID) x 0.25µm film thickness

Injector temperature: 250°C

Detector temperature: 280°C

Oven temperature: 35°C starting temperature, 4 minute hold time, ramp rate 12°C/min to 260°C, 8 minute hold time

Carrier gas: Helium

Mean gas velocity: 31.3 ± 3.5% cm/sec (calculated)

Split ratio: ~50:1

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[00250] The products were characterized by comparing peaks with known standards, in conjunction with supporting data from mass spectrum analysis (GCMS-Agilent 5973N). GCMS analysis was accomplished with a second Rtx-5, 30m x 0.25mm (ID) x 0.25µm film thickness GC column, using the same method as above.

[00251] Alkane analyses were performed using an Agilent 6850 instrument and the following conditions:

Column: Restek Rtx-65, 30m x 0.32mm (ID) x 0.1µm film thickness
Injector temperature: 250°C
Detector temperature: 350°C
Oven temperature: 55°C starting temperature, 5 minute hold time, ramp rate 20°C/min to 350°C, 10 minute hold time
Carrier gas: Hydrogen
Flow rate: 1.0 mL/min
Split ratio: 40:1

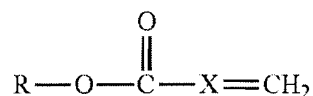
[00252] The products were characterized by comparing peaks with known standards. Fatty acid methyl ester (FAME) analyses were performed using an Agilent 6850 instrument and the following conditions:

Column: J&W Scientific, DB-Wax, 30m x 0.32mm (ID) x 0.5µm film thickness
Injector temperature: 250°C
Detector temperature: 300°C
Oven temperature: 70°C starting temperature, 1 minute hold time, ramp rate 20°C/min to 180°C, ramp rate 3°C/min to 220°C, 10 minute hold time
Carrier gas: Hydrogen
Flow rate: 1.0 mL/min

[00253] The examples above collectively demonstrate the major steps described in the process schemes, showing the production of olefins, paraffins, metathesized triglycerides, unsaturated fatty acid esters and acids, and diacid compounds from natural oils that are useful as chemicals, solvents and fuels blending stocks.

Claims:

1. A method of refining a natural oil, comprising:
providing a feedstock comprising a natural oil;
reacting the feedstock in a metathesis reactor in the presence of a first metathesis catalyst to form a metathesized product comprising olefins and esters;
separating the olefins in the metathesized product from the esters in the metathesized product;
transesterifying the esters in the presence of an alcohol to form a transesterified product comprising a terminal olefin ester having the following structure:



wherein X is a C₃-C₁₈ saturated or unsaturated alkyl chain, and R is an alkyl group;
and

reacting the terminal olefin ester with an internal olefin ester in the presence of a second metathesis catalyst to form a dibasic ester.

2. The method of claim 1, wherein R is methyl.

3. The method of claim 1, wherein the weight ratio of the terminal olefin ester to the internal olefin ester is between 5:1 and 1:5.

4. The method of claim 1, wherein the weight ratio of the terminal olefin ester to the internal olefin ester is 1:1.

5. The method of claim 1, wherein the terminal olefin ester is selected from the group consisting of: 4-pentenoic acid ester, 5-hexenoic acid ester, 6-heptenoic acid ester, 7-octenoic acid ester, 8-nonenoic acid ester, 9-decenoic acid ester, 10-undecenoic acid ester, 11-dodecenoic acid ester, 12-tridecenoic acid ester, 13-tetradecenoic acid ester, 14-pentadecenoic acid ester, 15-hexadecenoic acid ester, 16-heptadecenoic acid ester, 17-octadecenoic acid ester, and mixtures thereof.

6. The method of claim 1, wherein the terminal olefin ester is 9-decenoic acid ester.

7. The method of claim 1, wherein the internal olefin ester is selected from the group consisting of: pentenoic acid esters, hexenoic acid esters, heptenoic acid esters, octenoic acid esters, nonenoic acid esters, decenoic acid esters, undecenoic acid esters, dodecenoic acid esters, tridecenoic acid esters, tetradecenoic acid esters, pentadecenoic acid esters, hexadecenoic acid esters, heptadecenoic acid esters, octadecenoic acid esters, and mixtures thereof.

8. The method of claim 1, wherein the internal olefin ester is 9-dodecenoic acid ester.

9. The method of claim 1, further comprising providing a low-molecular-weight olefin or a mid-weight olefin, wherein the reacting step comprises a cross-metathesis reaction between the feedstock and the low-molecular-weight olefin or mid-weight olefin.

10. The method of claim 9, wherein the low-molecular-weight olefin comprises at least one low-molecular-weight olefin selected from the group consisting of propylene, 1-butene, 2-butene, 3-hexene, and mixtures thereof.

11. The method of claim 1, wherein the internal olefin ester is formed by reacting a portion of the terminal olefin ester with a low-molecular-weight internal olefin in the presence of a third metathesis catalyst.

12. The method of claim 11, wherein the low-molecular-weight internal olefin is selected from the group consisting of: 2-butene, 2-pentene, 2-hexene, 3-hexene, 2-heptene, 3-heptene, 2-octene, 3-octene, 2-nonene, 3-nonene, and mixtures thereof.

13. The method of claim 11, wherein the low-molecular-weight internal olefin is 3-hexene.

14. The method of claim 1, wherein the dibasic ester is 9-octadecene dioic acid dimethyl ester.

15. The method of claim 1, further comprising hydrolyzing the dibasic ester.

16. The method of claim 1, wherein the olefin byproduct is removed from the metathesis product during the reaction of the terminal olefin and internal olefin, improving the yield of the dibasic ester and/or dibasic acid.

17. The method of claim 1, wherein at least 70 wt % dibasic ester and/or dibasic acid is formed in the presence of less than 150 ppm.

18. A method of refining a natural oil, comprising:
providing a feedstock comprising a natural oil;
reacting the feedstock in a metathesis reactor in the presence of a first metathesis catalyst to form a metathesized product comprising olefins and esters;
separating the olefins in the metathesized product from the esters in the metathesized product;
transesterifying the esters in the presence of an alcohol to form a transesterified product comprising 9-decenoic acid ester; and
reacting the 9-decenoic acid ester with 9-dodecenoic acid ester in the presence of a second metathesis catalyst to form 9-octadecene dioic acid ester.

19. The method of claim 18, wherein the 9-dodecenoic acid ester is formed by reacting a portion of the 9-decenoic acid ester with a low-molecular-weight internal olefin or a mid-weight internal olefin in the presence of a third metathesis catalyst.

20. The method of claim 19, wherein the low-molecular-weight internal olefin is 3-hexene.

21. The method of claim 18, further comprising hydrolyzing the 9-octadecene dioic acid ester to form 9-octadecene dioic acid.