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(54) **PROCESS FOR THE PRODUCTION OF JET-RANGE HYDROCARBONS**

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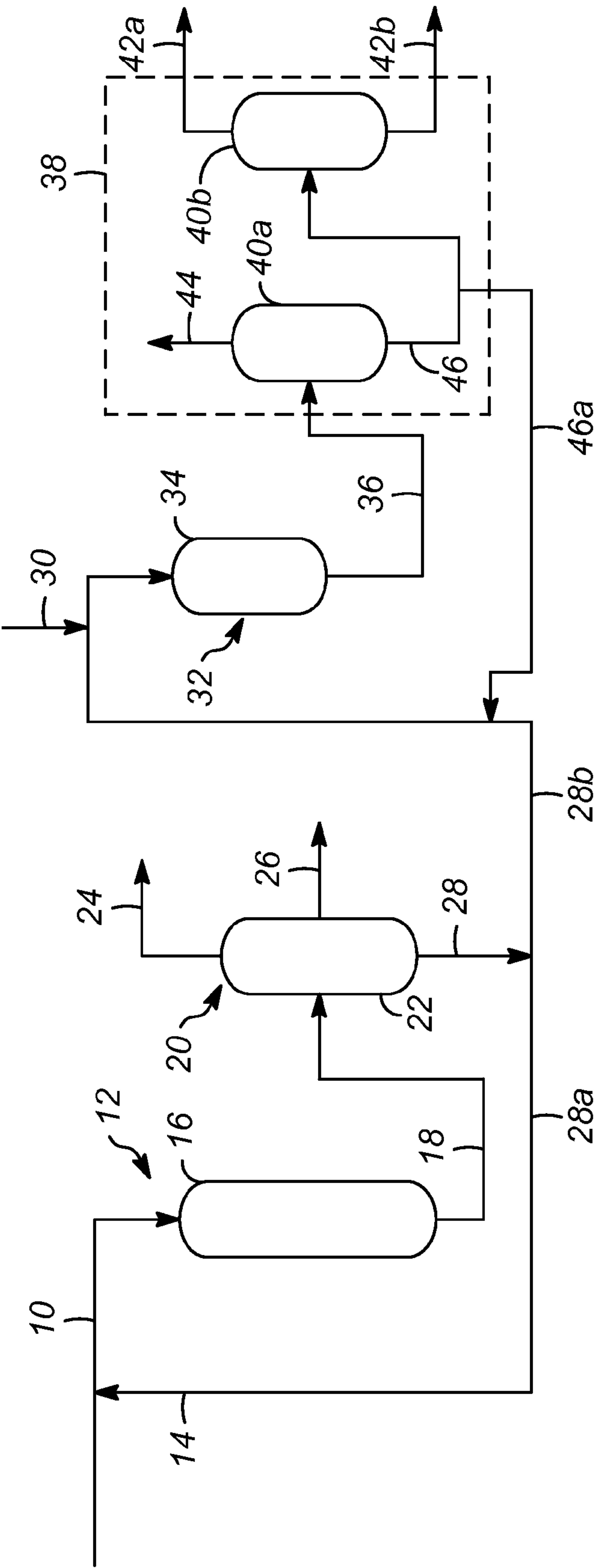
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(57) **ABSTRACT**

A method for producing jet-range hydrocarbons includes passing a renewable olefin feedstock comprising C₃ to C₈ olefins to an oligomerization reactor containing a zeolite catalyst to produce an oligomerized effluent, separating the oligomerized effluent into at least a light stream, and a heavy olefin stream. At least a first portion of the heavy olefin stream is recycled to the oligomerization reactor to dilute the renewable olefin feedstock. portion of heavy olefin stream may be hydrogenated and separated to provide a jet range hydrocarbon product.



PROCESS FOR THE PRODUCTION OF JET-RANGE HYDROCARBONS

FIELD OF THE INVENTION

[0001] The present disclosure generally relates to methods for producing renewable fuels and chemicals from biorenewable sources and the renewable fuels and chemicals produced thereby, and more particularly relates to methods for producing jet-range hydrocarbons from alkanols, including for example isobutanol, and the jet-range hydrocarbons produced thereby.

BACKGROUND OF THE INVENTION

[0002] As the worldwide demand for fuel increases, interest in sources other than crude oil from which to produce transportation fuels, including aviation fuels, is ever increasing. For example, due to the growing environmental concerns over fossil fuel extraction and economic concerns over exhausting fossil fuel deposits, there is a demand for using an alternate or “green” feed source for producing hydrocarbons for use as transportation fuels and for use in other industries. Such sources of interest include, for example, biorenewable sources, such as vegetable and seed oils, animal fats, and algae byproducts, among others as are well-known to those skilled in the art. conventional catalytic hydro-processing technique is known for converting a biorenewable feedstock into green diesel fuel that may be used as a substitute for the diesel fuel produced from crude oil. As used herein, the terms “green diesel fuel” and “green jet fuel” refer to fuel produced from biorenewable sources, in contrast to those produced from crude oil. The process also supports the possible co-production of propane and other light hydrocarbons, as well as naphtha or green jet fuel.

[0003] Biomass fermentation products typically include lower isoalkanols such as, for example, C_3 to C_8 isoalkanols obtained by contacting biomass with biocatalysts that facilitate conversion (by fermentation) of the biomass to isoalkanols of interest. The biomass feedstock for such fermentation processes can be any suitable fermentable feedstock known in the art, such as fermentable sugars derived from agricultural crops including sugarcane, corn, etc. Suitable fermentable biomass feedstock can also be prepared by the hydrolysis of biomass, for example lignocellulosic biomass (e.g. wood, corn stover, switchgrass, herbiage plants, ocean biomass, etc.), to form fermentable sugars.

[0004] Jet-range fuels are an important product for the aerospace industry and the military. The specific characteristics of various grades and types of jet-range fuels vary slightly according to the particular application and environment in which they are used. Generally, jet-range fuels comprise a mixture of primarily C_8 to C_{16} hydrocarbons and typically have a freezing point of about -40 or -47°C . (-40 or -52.6°F). In order to produce jet-range fuels from isoalkanols derived from fermented biomass, in one example known in the art, isobutanol is first dehydrated to form butenes. The butenes are then oligomerized, in the presence of an oligomerization catalyst, in one or more reactors to form heavier olefins, such as C_5 to C_{20} , or even higher, olefinic oligomers. Finally, the resulting olefinic oligomers are hydrogenated in a saturation reactor to form the corresponding C_5 to C_{20} , or even higher, paraffins in a mixture which can then be subjected to separation to obtain C_9 to C_{20+} paraffins suitable for use as biorenewable jet fuel.

[0005] Since the oligomerization reaction is highly exothermic, the butene fed to the oligomerization reactors may be cooled before entering the oligomerization reactors. Another measure taken to control the temperature increase in the oligomerization reactors is to limit the proportion of olefins contained in the feedstream provided to each reactor to no more than about 15 percent by weight (wt %). This is accomplished, at least in part, by adding non-reactive diluent material to the reactors which also provides a heat sink to control the temperature rise in the reactors.

[0006] Typically, this dilution may be done by recycling saturated distillate product from a stripped effluent of a hydrogenation section back to the oligomerization and hydrogenation reactors. Hydrogen transfer from the saturated diluent to the light olefinic feed to the oligomerization reactor can cause yield loss by saturating the light olefin feeds into paraffins. Paraffins, however, will not participate in the oligomerization reactions and will be recovered as saturated liquefied petroleum gas, instead of olefinic distillate range material. Since the desired product is a distillate range material, conversion of the olefins into saturated liquefied petroleum gas amounts to a loss of potential distillate yield, and thus is considered undesirable. Therefore, it would be desirable to have one or more processes in which the dilution of the feedstock to the oligomerization reactor is less likely to result in yield loss.

SUMMARY OF THE INVENTION

[0007] One or more processes have been invented in which a portion of an olefin effluent from an oligomerization reaction is used to dilute the feedstock to the oligomerization reaction.

[0008] In a first aspect of the invention, the present invention may be broadly characterized as a providing a process for producing jet range hydrocarbons by oligomerizing a renewable olefin feedstock comprising C_3 to C_8 olefins in an oligomerization reactor containing a catalyst and being operated under conditions to produce an oligomerized effluent; separating the oligomerized effluent to produce a light hydrocarbon stream, a naphtha hydrocarbon stream, and a heavy stream comprising C_8+ olefins; splitting the heavy stream into a first portion and a second portion; and, diluting the renewable C_4 olefin feedstock with the first portion of the heavy stream.

[0009] In one or more embodiments of the present invention, the process further comprises controlling a flow rate of the first portion of the heavy stream. It is contemplated that the flow rate of the first portion of the heavy stream is controlled to obtain a desired ΔT in the oligomerization reactor of at least 25°C . and no more than 60°C .

[0010] In various embodiments of the present invention, the process further comprises hydrogenating the second portion of the heavy stream in a hydrogenation zone having a hydrogenation reactor to provide a hydrogenated effluent. It is contemplated that the process includes separating the hydrogenated effluent into a vent gas stream and a saturated hydrocarbons stream. It is further contemplated that the process includes separating the saturated hydrocarbons stream into a saturated jet range stream and a saturated diesel range hydrocarbons stream. It is still further contemplated that the process includes recycling at least a portion of the saturated hydrocarbons stream to the hydrogenation zone.

[0011] In a second aspect of the present invention, the present invention may be generally characterized as provid-

ing a process for producing jet range hydrocarbons by: passing a renewable olefin feedstock comprising C_3 to C_8 olefins to an oligomerization reaction zone comprising an oligomerization reactor containing a catalyst and being operated under conditions to produce an oligomerized effluent; passing the oligomerized effluent to a first separation zone to provide at least one stream comprising C_{7-} hydrocarbons and a C_8+ olefin stream; splitting the C_8+ olefin stream into a first portion and a second portion; and, recycling the first portion of the C_8+ olefin stream to the oligomerization reaction zone.

[0012] In one or more embodiments of the present invention, the process further comprises combining the first portion of the C_8+ olefin stream with the renewable C_4 olefin feedstock to provide a combined stream and passing the combined stream into the oligomerization reactor.

[0013] In at least one embodiment of the present invention, the first separation zone produces a light hydrocarbon stream and a naphtha hydrocarbon stream.

[0014] In some of the embodiments of the present invention, the process further comprises passing the second portion of the C_8+ olefin stream to a hydrogenation zone having a hydrogenation reactor containing a catalyst and being operated to provide a hydrogenated effluent. It is contemplated that the process includes passing the hydrogenated effluent to second separation zone to provide at least a vent gas stream and a saturated jet range stream. It is also contemplated that the process includes recycling a portion of the hydrogenated effluent to the hydrogenation zone as a recycle stream. It is further contemplated that the process includes combining the recycle stream and the second portion of the C_8+ olefin stream into a combined stream and, passing the combined stream to the hydrogenation reactor.

[0015] In one or more of the embodiments of the present invention, the process further comprises passing the hydrogenated effluent to a second separation zone having at least two columns. It is contemplated that a first column in the second separation zone separates the hydrogenated effluent into a vent gas stream and a saturated hydrocarbon stream. It is also contemplated that a second column in the second separation zone separates the saturated hydrocarbon stream into a saturated jet range stream and a saturated diesel stream. It is further contemplated that the process includes passing at least a portion of the saturated hydrocarbon stream to the hydrogenation reaction zone as a recycle stream.

[0016] In at least one of the embodiments of the present invention, the process further comprises controlling a temperature rise in the oligomerization reactor by adjusting a flow rate of the first portion of the C_8+ olefin stream.

[0017] In some of the embodiments of the present invention, the process further comprises increasing a flow rate of the first portion of the C_8+ olefin stream to decrease a temperature rise in the oligomerization reactor.

[0018] Additional aspects, embodiments, and details of the invention, which may be combined in any manner, are set forth in the following detailed description of the invention.

DETAILED DESCRIPTION OF THE DRAWINGS

[0019] One or more exemplary embodiments of the present invention will be described below in conjunction with the following drawing FIGURE, in which:

[0020] the FIGURE shows a process flow diagram of one or more processes according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0021] As used herein, the term “stream” can include various hydrocarbon molecules and other substances. Moreover, the term “stream comprising C_x hydrocarbons” or “stream comprising C_x olefins” can include a stream comprising hydrocarbon or olefin molecules, respectively, with “x” number of carbon atoms, suitably a stream with a majority of hydrocarbons or olefins, respectively, with “x” number of carbon atoms and preferably a stream with at least 75 wt % hydrocarbons or olefin molecules, respectively, with “x” number of carbon atoms. Moreover, the term “stream comprising C_x+ hydrocarbons” or “stream comprising C_x+ olefins” can include a stream comprising a majority of hydrocarbon or olefin molecules, respectively, with more than or equal to “x” carbon atoms and suitably less than 10 wt % and preferably less than 1 wt % hydrocarbon or olefin molecules, respectively, with x-1 carbon atoms. Lastly, the term “ C_x- stream” can include a stream comprising a majority of hydrocarbon or olefin molecules, respectively, with less than or equal to “x” carbon atoms and suitably less than 10 wt % and preferably less than 1 wt % hydrocarbon or olefin molecules, respectively, with x+1 carbon atoms.

[0022] As used herein, the term “zone” can refer to an area including one or more equipment items and/or one or more sub-zones. Equipment items can include one or more reactors or reactor vessels, heaters, exchangers, pipes, pumps, compressors, controllers and columns. Additionally, an equipment item, such as a reactor, dryer, or vessel, can further include one or more zones or sub-zones.

[0023] As used herein, the term “substantially” can mean an amount of at least generally about 70%, preferably about 80%, and optimally about 90%, by weight, of a compound or class of compounds in a stream.

[0024] As used herein, the term “gasoline” can include hydrocarbons having a boiling point temperature in the range of about 25 to about 200° C. (68 to 392° F.) at atmospheric pressure.

[0025] As used herein the term “naphtha” can mean C_5 hydrocarbons up to hydrocarbons having a boiling point of 150° C. (302° F.) (i.e., hydrocarbons having a boiling point in the range of 30 to 150° C. (86 to 302° F.)).

[0026] As used herein the term “diesel” can include hydrocarbons having a boiling point temperature in the range of about 250 to about 400° C. (482 to 752° F.) at atmospheric pressure.

[0027] As used herein the term “jet-range hydrocarbons,” “jet-range paraffins,” “jet-range fuels,” or “jet fuels” can include hydrocarbons having a boiling point temperature in the range of about 130 to about 300° C. (266 to 572° F.), preferably 150 to 260° C. (302 to 500° F.), at atmospheric pressure. Additionally, as used herein, the terms “jet-range hydrocarbons,” “jet-range paraffins,” “jet-range fuels,” or “jet fuels” refer to a mixture of primarily C_8 to C_{16} hydrocarbons with a freezing point of about -40° C. (-40° F.) or about -47° C. (-52.6° F.).

[0028] As used herein, the term “distillate” comprises a mixture of diesel and jet-range hydrocarbons and can include hydrocarbons having a boiling point temperature in the range of about 150 to about 400° C. (302 to 752° F.) at atmospheric pressure.

[0029] As used herein, the phrase “a mixture of primarily . . . ” or “comprising primarily . . . ” a specified range of carbon-numbered hydrocarbons means that the group or category of hydrocarbons being described may also contain very small amounts of hydrocarbons outside the stated carbon number range, without altering the general characteristics (e.g., boiling point) of the group or category being described. For example, the description that jet fuels are a mixture of primarily C_8 to C_{16} hydrocarbons means that jet fuels contain at least 80 wt % of hydrocarbon molecules each having from about 8 to about 16 carbon atoms with, possibly, very small amounts of hydrocarbon molecules each having less than about 8 carbon atoms, as well as very small amounts of hydrocarbon molecules each having more than 16 carbon atoms, such that the freezing point remains about -40°C . to about -47°C . (-40 to 52.6°F .). There are multiple standards, established by various industries and governments, that are useful for ensuring that particular types of jet fuels have uniform characteristics that fall within expected ranges. For example, one type of jet fuel, known as Aviation Turbine Fuel, Jet A, or Jet A-1 fuel, is composition of hydrocarbons that boil in a range such that the volatility characteristics of the hydrocarbon (or paraffinic form of the hydrocarbon after hydrogenation) substantially conform to the volatility standards of flash point (typically minimum of 38°C . (100°F .), distillation range (T10 boiling point maximum of 205°C . (401°F .)) and final boiling point (maximum of 300°C . (572°F .)), with all distillation valves measured by D86 or D2887 values converted to D86) set forth in ASTM D7566-11a, “Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons,” promulgated by ASTM International, Inc. of West Conshohocken, Pa. Other standards that provide parameters useful for characterizing and defining the jet fuels prepared using the methods and apparatus contemplated and described herein include Jet Propellant (JP)-5 and JP-8, which are set forth in the United States military specifications found at MIL-DTL-83133, as well as in British Defence Standard 91-87.

[0030] The term “column” means a distillation column or columns for separating one or more components of different volatilities. Unless otherwise indicated, each column includes a condenser on an overhead of the column to condense and reflux a portion of an overhead stream back to the top of the column and a reboiler at a bottom of the column to vaporize and send a portion of a bottom stream back to the bottom of the column. Feeds to the columns may be preheated. The top pressure is the pressure of the overhead vapor at the outlet of the column. The bottom temperature is the liquid bottom outlet temperature. Overhead lines and bottom lines refer to the net lines from the column downstream of the reflux or reboil to the column.

[0031] As used herein, the term “boiling point temperature” means atmospheric equivalent boiling point (AEBP) as calculated from the observed boiling temperature and the distillation pressure, as calculated using the equations furnished in ASTM D1160 appendix A7 entitled “Practice for Converting Observed Vapor Temperatures to Atmospheric Equivalent Temperatures.”

[0032] As used herein, “taking a stream from” means that some or all of the original stream is taken.

[0033] Disclosed herein are methods and apparatus for producing jet-range hydrocarbons from one or more biorenewable C_3 to C_8 olefins via oligomerization. As mentioned above, the oligomerization reaction is highly exothermic. In

order to control the temperature rise from the inlet to the outlet in the reactor (i.e., the “ ΔT ”), various processes utilize a diluent. However, it has been discovered that by using a portion of the heavy olefins produced in the oligomerization reactor, the temperature rise can be controlled without using paraffin hydrocarbons which can result in hydrogen transfer to the olefins in the oligomerization reactor. The heavy olefins have been found to resist further oligomerization, resulting in a diluent that can minimize yield loss. While these methods find greatest utility in converting feedstocks from alkanols, thereby allowing for production of jet fuels from renewable sources, this is not intended to limit the application of the methods of the present invention.

[0034] With these general principles in mind, one or more embodiments of the present invention will be described with the understanding that the following description is not intended to be limiting.

[0035] As shown in the FIGURE, one or more processes of the present invention include a renewable olefin feedstock **10** being passed to an oligomerization zone **12**. As used herein, the term “renewable” denotes that the carbon content of the olefin feedstock **10** is from a “new carbon” source as measured by ASTM test method D6866-05, “Determining the Bio-based Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis”, incorporated herein by reference in its entirety. This test method measures the $^{14}\text{C}/^{12}\text{C}$ isotope ratio in a sample and compares it to the $^{14}\text{C}/^{12}\text{C}$ isotope ratio in a standard 100% bio-based material to give percent bio-based content of the sample. Additionally, “bio-based materials” are organic materials in which the carbon comes from recently (on the order of centuries) fixated carbon dioxide present in the atmosphere using sunlight energy (photosynthesis). On land, this carbon dioxide is captured or fixated by plant life (e.g., agricultural crops or forestry materials). In the oceans, the carbon dioxide is captured or fixated by photosynthesizing bacteria or phytoplankton. For example, a bio-based material has a $^{14}\text{C}/^{12}\text{C}$ isotope ratio greater than zero. Contrarily, a fossil-based material has a $^{14}\text{C}/^{12}\text{C}$ isotope ratio of zero. The term “renewable” with regard to compounds such as alcohols or hydrocarbons (olefins, di-olefins, polymers, etc.) also refers to compounds prepared from biomass using thermochemical methods (e.g., Fischer-Tropsch catalysts), biocatalysts (e.g., fermentation), or other processes, for example as described herein.

[0036] A small amount of the carbon atoms in the carbon dioxide in the atmosphere is the radioactive isotope ^{14}C . This ^{14}C carbon dioxide is created when atmospheric nitrogen is struck by a cosmic ray generated neutron, causing the nitrogen to lose a proton and form carbon of atomic mass 14 (^{14}C), which is then immediately oxidized, to carbon dioxide. small but measurable fraction of atmospheric carbon is present in the form of ^{14}C .

[0037] Atmospheric carbon dioxide is processed by green plants to make organic molecules during the process known as photosynthesis. Virtually all forms of life on Earth depend on this green plant production of organic molecules to produce the chemical energy that facilitates growth and reproduction. Therefore, the ^{14}C that forms in the atmosphere eventually becomes part of all life forms and their biological products, enriching biomass and organisms which feed on biomass with ^{14}C . In contrast, carbon from fossil fuels does not have the signature $^{14}\text{C}/^{12}\text{C}$ ratio of renewable organic molecules derived from atmospheric carbon diox-

ide. Furthermore, renewable organic molecules that biodegrade to carbon dioxide do not contribute to an increase in atmospheric greenhouse gases as there is no net increase of carbon emitted to the atmosphere. Assessment of the renewably based carbon content of a material can be performed through standard test methods, e.g., using radiocarbon and isotope ratio mass spectrometry analysis. ASTM International (formally known as the American Society for Testing and Materials) has established a standard method for assessing the bio-based content of materials. The ASTM method is designated ASTM-D6866. The application of ASTM-D6866 to derive “bio-based materials” is built on the same concepts as radiocarbon dating, but without use of the age equations. The analysis is performed by deriving a ratio of the amount of radiocarbon (^{14}C) in an unknown sample compared to that of a modern reference standard. This ratio is reported as a percentage with the units “pMC” (percent modern carbon). If the material being analyzed is a mixture of present day radiocarbon and fossil carbon (containing very low levels of radiocarbon), then the pMC value obtained correlates directly to the amount of biomass material present in the sample. In an aspect, renewable carbon substantially comprises the renewable olefin feedstock **10**. The percentage of renewable carbon in the renewable olefin feedstock **10** may be greater than 80% or greater than 90% or greater than 95% or greater than 99% on a weight basis.

[0038] Returning to the FIGURE, the renewable olefin feedstock **10** includes at least C_4 olefins, preferably comprising C_3 to C_8 olefins. In an aspect, the renewable olefin stream may comprise one or more carbon number olefins such as C_3 to C_4 olefins or C_3 to C_5 olefins or C_4 to C_5 olefins or C_3 to C_6 olefins. The renewable olefins may be derived from their corresponding alcohols (i.e., C_4 alcohols, especially including isobutanol), which are typically formed by fermentation or by condensation reactions of synthesis gas. For example, a feedstock for the fermentation process can be any suitable fermentable feedstock known in the art, such as sugars derived from agricultural crops including sugarcane, corn, etc. Alternatively, the fermentable feedstock can be prepared by the hydrolysis of biomass, for example lignocellulosic biomass (e.g. wood, corn stover, switchgrass, herbage plants, ocean biomass, etc.). In another example, renewable alcohols, such as isobutanols, can be prepared photosynthetically, for example using cyanobacteria or algae engineered to produce isobutanol and/or other alcohols. When produced photosynthetically, the feedstock for producing the resulting renewable alcohols is light, water, and carbon dioxide, which is provided to the photosynthetic organism (e.g., cyanobacteria or algae). Additionally, other known methods, whether biorenewable or otherwise, for producing isobutanol are suitable for supplying the C_4 olefins; the methods described herein are not intended to be limited by the use of any particular renewable feed source. Typically, the renewable olefin feedstock **10** may comprise greater than 50 wt % olefins such as greater than 70 wt % or greater than 80 wt % or greater than 90 wt % olefins or greater than 95 wt % or greater than 99 wt % olefins.

[0039] Olefin isomer types of the renewable olefin feedstock **10**, and of the oligomers produced by oligomerization, can be denominated according to the degree of substitution of the double bond, as follows:

TABLE 1

Olefin Type	Structure	Description
I	$\text{R}-\text{HC}=\text{CH}_2$	Monosubstituted
II	$\text{R}-\text{HC}=\text{CH}-\text{R}$	Disubstituted
III	$\text{RRC}=\text{CH}_2$	Disubstituted
IV	$\text{RRC}=\text{CHR}$	Trisubstituted
V	$\text{RRC}=\text{CRR}$	Tetrasubstituted

wherein R represents an alkyl group, each R being the same or different. Type I compounds are sometimes described as α - or vinyl olefins and Type III as vinylidene olefins. Type IV is sometimes subdivided to provide a Type IVA, in which access to the double bond is less hindered, and Type IVB where it is more hindered. In an aspect, the renewable olefin feedstock **10** may comprise high quantities of Type III olefins such as greater than 50 wt % or greater than 70 wt % or greater than 85 wt % or greater than 90 wt % or greater than 95 wt % Type III olefins as a fraction of the total olefins in the renewable olefins stream.

[0040] As shown in the FIGURE, the renewable olefins (possibly derived and converted from the C_4 alcohols, for example by dehydration of the alcohol see, e.g., U.S. Pat. No. 4,423,251) are mixed with a diluent stream **14** (discussed in more detail below) prior to entering an oligomerization reactor **16** in the oligomerization zone **12**. Although depicted with a single oligomerization reactor **16**, the oligomerization zone **12** may contain any number of reactors.

[0041] In the oligomerization reactor **16**, at least a portion of the renewable olefins are converted into a mixture of heavier boiling hydrocarbons including jet range hydrocarbons via oligomerization by reacting the olefins using a zeolitic oligomerization catalyst under appropriate conditions. For example, the oligomerization zone **12** may, for example, without limitation, be operated at a temperature from about 100 to about 300° C. (212 to 572° F.) and a pressure of from about 689 to about 6895 kPa (100 to 1000 psig). For example, the operating temperature may be from about 120 to about 280° C. (248 to 536° F.), or even from about 160 to about 260° C. (320 to 402.8° F.). The operating pressure may, for example, be from about 1034 to about 5516 kPa (150 to 800 psi), or even from about 2068 to about 4964 kPa (300 to 720 psi).

[0042] The oligomerization catalyst in the oligomerization zone **12** is not limited to any particular catalyst and may comprise any catalyst suitable for catalyzing conversion of the one or more biorenewable C_3 to C_8 olefins in the olefin stream to olefinic oligomers comprising heavier boiling C_{5+} hydrocarbons, including jet-range hydrocarbons. The oligomerization catalyst may be any such catalyst known now or in the future.

[0043] Conventional oligomerization catalysts will generally convert an olefin to a mixture of dimers, trimers, tetramers, and sometimes pentamers, of the olefin. For example, where the C_3 to C_8 olefin is isobutylene, a C_4 olefin, the products of oligomerization in the presence of a conventional oligomerization catalyst include C_8 , C_{12} , C_{16} , and sometimes C_{20} olefins, together in a mixture. Conventional oligomerization catalysts include, without limitation, solid phosphoric acid (“SPA”) and certain ion exchange resins such as Amberlyst-36 (commercially available from The Dow Chemical Company of Midland, Mich., U.S.A.). The olefinic oligomer mixture produced using conventional oligomerization catalysts may be further subjected to a

separation process to produce a mixture of jet-range hydrocarbons suitable for use as jet fuels. These jet fuels often have a boiling point distribution that has well-defined boiling point steps corresponding to only a few isomers of the corresponding trimer, tetramer, and pentamer paraffins of the starting olefin, which is different from petroleum-derived jet fuels.

[0044] Alternative oligomerization catalysts comprising zeolite materials, on the other hand, catalyze oligomerization conversion of C_3 to C_8 olefins to dimers, trimers, tetramers, and sometimes pentamers of the C_3 to C_8 olefins, but also catalyze backcracking conversion of the resulting heavier olefinic oligomers back into lighter and more random and varied sizes of olefins including C_5 to C_{20+} hydrocarbons. In other words, under appropriate conditions, zeolitic catalysts such as, without limitation, MTT, TON, MFI, and MTW, yield C_{5+} hydrocarbons, including jet-range hydrocarbons, with an increased distribution and variety of carbon numbers than those made using conventional non-zeolitic catalysts. This means that jet-range fuel produced from biorenewable olefins via oligomerization in the presence of zeolite catalysts has a boiling range and compositional profile that is more similar to jet-range fuels produced from petroleum refining processes.

[0045] Suitable zeolite catalysts may comprise between 5 and 95 wt % of zeolite material. Suitable zeolite materials include zeolites having a structure from one of the following classes: MFI, MEL, ITH, IMF, TUN, FER, BEA, FAU, BPH, MEL, MSE, MWW, UZM-8, MOR, OFF, MTW, TON, MTT, AFO, ATO, and AEL. 3-letter codes indicating a zeotype are as defined by the Structure Commission of the International Zeolite Association and are maintained at <http://www.iza-structure.org/databases/>. UZM-8 is as described in U.S. Pat. No. 6,756,030. In a preferred aspect, the zeolite catalyst may comprise a zeolite with a framework having a ten-ring pore structure. Examples of suitable zeolites having a ten-ring pore structure include TON, MTT, MFI, MEL, AFO, AEL, EUO and FER. The oligomerization catalyst comprising a zeolite having a ten-ring pore structure may comprise a uni-dimensional pore structure. uni-dimensional pore structure indicates zeolite materials containing non-intersecting pores that are substantially parallel to one of the axes of the crystal. The pores preferably extend through the zeolite crystal. Suitable examples of zeolite materials having a ten-ring uni-dimensional pore structure may include MTT. In a further aspect, the oligomerization catalyst comprises an MTT zeolite.

[0046] The zeolite catalyst may be formed by combining the zeolite material with a binder, and then forming the catalyst into pellets. The pellets may optionally be treated with a phosphorus reagent to create a zeolite having a phosphorous component between 0.5 and 15 wt % of the treated catalyst. The binder is used to confer hardness and strength on the catalyst. Binders include alumina, aluminum phosphate, silica, silica-alumina, zirconia, titania and combinations of these metal oxides, and other refractory oxides, and clays such as montmorillonite, kaolin, palygorskite, smectite and attapulgite. preferred binder is an aluminum-based binder, such as alumina, aluminum phosphate, silica-alumina and clays.

[0047] One of the components of the zeolite catalyst binder utilized herein is alumina. The alumina source may be any of the various hydrous aluminum oxides or alumina gels such as alpha-alumina monohydrate of the boehmite or

pseudo-boehmite structure, alpha-alumina trihydrate of the gibbsite structure, beta-alumina trihydrate of the bayerite structure, and the like. suitable alumina is available from UOP LLC under the trademark Versal. preferred alumina is available from Sasol North America Alumina Product Group under the trademark Catapal. This material is an extremely high purity alpha-alumina monohydrate (pseudo-boehmite) which after calcination at a high temperature has been shown to yield a high purity gamma-alumina.

[0048] A suitable zeolite catalyst may be, for example, prepared by mixing proportionate volumes of zeolite and alumina to achieve the desired zeolite-to-alumina ratio. In an embodiment, the MTT content may be about 5 to 85 wt %, for example about 20 to 82 wt % MTT zeolite, and the balance alumina powder will provide a suitably supported catalyst. silica support is also contemplated.

[0049] Monoprotic acid such as nitric acid or formic acid may be added to the mixture in aqueous solution to peptize the alumina in the binder. Additional water may be added to the mixture to provide sufficient wetness to constitute a dough with sufficient consistency to be extruded or spray dried. Extrusion aids such as cellulose ether powders can also be added. preferred extrusion aid is available from The Dow Chemical Company under the trademark Methocel.

[0050] The paste or dough may be prepared in the form of shaped particulates, with the preferred method being to extrude the dough through a die having openings therein of desired size and shape, after which the extruded matter is broken into extrudates of desired length and dried. further step of calcination may be employed to give added strength to the extrudate. Generally, calcination is conducted in a stream of air at a temperature from about 260 to about 815° C. (500 to 1500° F.). The MTT catalyst is not selectivated to neutralize acid sites such as with an amine.

[0051] The extruded particles may have any suitable cross-sectional shape, i.e., symmetrical or asymmetrical, but most often have a symmetrical cross-sectional shape, preferably a spherical, cylindrical or polylobal shape. The cross-sectional diameter of the particles may be as small as 40 μ m; however, it is usually about 0.635 mm (0.25 inch) to about 12.7 mm (0.5 inch), preferably about 0.79 mm ($1/32$ inch) to about 6.35 mm (0.25 inch), and most preferably about 0.06 mm ($1/24$ inch) to about 4.23 mm ($1/6$ inch).

[0052] Returning to the FIGURE, An oligomerized effluent **18** from the oligomerization zone **12** may be passed to a separation zone **20** including, for example, a distillation column **22**. In the separation zone **20**, the oligomerized effluent **18** may be separated into a light hydrocarbon stream **24** comprising C_4 hydrocarbons, a naphtha hydrocarbon stream **26** comprising C_5 to C_7 hydrocarbons, and a heavy stream **28** comprising C_{8+} olefins. As will be appreciated, there may be some overlap between the components of the various streams. For example, the naphtha hydrocarbon stream **26** may include some C_4 hydrocarbons or some heavier hydrocarbons such as C_8 or C_9 hydrocarbons. It is preferred that such streams include at least 50% of the intended components (i.e., the naphtha hydrocarbon stream **26** comprises 80% C_5 to C_7 hydrocarbons).

[0053] The further processing of the light hydrocarbon stream **24** and the naphtha hydrocarbon stream **26** are not necessary for an understanding or practicing of the present invention. However, the naphtha hydrocarbon stream **26** may be recycled to the oligomerization reactor **16** to further react these hydrocarbons into the jet range. As shown in the

FIGURE, in the various embodiments of the present invention, the heavy stream **28** is split into a first portion **28a** and a second portion **28b**. The first portion **28a** of the heavy stream **28** is used to dilute the renewable olefin feedstock **10** as the diluent stream **14**. The further processing of the second portion **28b** of the heavy stream **28** is described below.

[0054] The heavy olefins in the first portion **28a** of the heavy stream **28** are relatively inert in the oligomerization reaction and have a low tendency to further react with smaller olefins. Thus, utilizing the first portion **28a** of the heavy stream **28** to control the temperature in the oligomerization reactor **16** is desirable because the heavy olefins are less likely than similar saturated diluents to transfer hydrogen to the smaller olefins resulting in yield loss. Accordingly, it is contemplated that the relative amounts of the first portion **28a** and second portion **28b** of the heavy stream **28** are adjusted based upon the amount C_{8+} olefins as well as the temperature and temperature rise in the oligomerization reactor **16**. If the temperature or temperature rise is too high, the amount of the first portion **28a** of the heavy stream **28** may be increased. The C_{8+} olefins that are used as a diluent will be separated out in the separation zone **20** and can be utilized again as a diluent to the oligomerization zone **12** or the C_{8+} olefins material can be processed further in the second portion **28b** of the heavy stream **28**. Across a single bed of oligomerization catalyst, the exothermic reaction will cause the temperature to rise. Consequently, the oligomerization reactor **16** should be operated to allow the temperature at the outlet to be over about 25° C. greater but no more than 60° C. greater than the temperature at the inlet. In some embodiments, this temperature difference between the outlet and the inlet of the oligomerization reactor **16**, the ΔT , is at least 25° C. but no more than 40° C. In still other embodiments, the ΔT is at least 25° C. but no more than 35° C.

[0055] As shown in the FIGURE, the second portion **28b** of the heavy stream **28**, along with a hydrogen containing gas **30** may be passed to a hydrogenation zone **32** having a hydrogenation reactor **34**. Hydrogenation is typically performed using a conventional hydrogenation or hydrotreating catalyst, which may include metallic catalysts containing, e.g., palladium, rhodium, nickel, ruthenium, platinum, rhenium, cobalt, molybdenum, or combinations thereof, and the supported versions thereof. Catalyst supports can be any solid, inert substance including, but not limited to, oxides such as silica, alumina, titania, calcium carbonate, barium sulfate, and carbons. The catalyst support can be in the form of powder, granules, pellets, or the like. Hydrogenation suitably occurs at a temperature of about 150° C. (300° F.) and at a pressure of about 6895 kPa (1000 psig). Other process conditions known by those of ordinary skill in the art may be utilized.

[0056] A hydrogenated effluent **36** from the hydrogenation zone **32** will substantially comprise saturated hydrocarbons (i.e., paraffins). The a stream of hydrogenated effluent **36** may be passed to a separation zone **38** having one or more vessels or columns **40a**, **40b** configured to separate the saturated hydrocarbons into one or more product streams **42a**, **42b**. Additionally, at least a portion of the saturated hydrocarbons may be used as a recycle stream to the hydrogenation zone.

[0057] For example, a first column **40a** may separate the hydrogenated effluent **36** into a vent gas stream **44** and a saturated distillate stream **46**. portion **46a** of the saturated

distillate stream **46** may be used as a recycle stream to the hydrogenation zone **32**. second column **40b** may separate the saturated distillate stream **46** into a saturated jet range stream **42a** and a saturated diesel range stream **42b**.

[0058] Thus, using the processes of the present invention, jet-range hydrocarbons can be produced from a renewable olefin feedstock with minimal yield loss due to hydrogen transfer to the lighter olefins from heavy hydrocarbons in a diluent stream.

[0059] It should be appreciated and understood by those of ordinary skill in the art that various other components such as valves, pumps, filters, coolers, etc. were not shown in the drawings as it is believed that the specifics of same are well within the knowledge of those of ordinary skill in the art and a description of same is not necessary for practicing or understating the embodiments of the present invention.

[0060] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims and their legal equivalents.

1. process for producing hydrocarbons comprising:
 - oligomerizing a renewable olefin feedstock comprising C_3 to C_8 olefins in an oligomerization reactor containing a catalyst comprising a MTT zeolite that has not been selectivated and operating the oligomerization reactor under conditions to produce an oligomerized effluent;
 - separating the oligomerized effluent to produce a light hydrocarbon stream, a naphtha hydrocarbon stream and a heavy stream comprising C_{8+} olefins;
 - splitting the heavy stream into a first portion and a second portion; and,
 - diluting the renewable olefin feedstock with the first portion of the heavy stream.
2. The process of claim 1 further comprising:
 - controlling a flow rate of the first portion of the heavy stream.
3. The process of claim 2 wherein the flow rate of the first portion of the heavy stream is controlled to obtain a ΔT from an inlet to an outlet in the oligomerization reactor of at least 25° C. and no more than 60° C.
4. The process of claim 1 further comprising:
 - hydrogenating the second portion of the heavy stream in a hydrogenation zone having a hydrogenation reactor to provide a hydrogenated stream.
5. The process of claim 4 further comprising:
 - separating the hydrogenated stream into a vent gas stream and a saturated distillate stream.
6. The process of claim 5 further comprising:
 - separating the saturated distillate stream into a saturated jet range stream and a saturated diesel range hydrocarbons stream.

7. The process of claim 5 further comprising:
recycling at least a portion of the saturated distillate stream to the hydrogenation zone.
8. process for producing hydrocarbons comprising:
passing a renewable olefin feedstock comprising C_3 to C_8 olefins to an oligomerization reaction zone comprising an oligomerization reactor containing a catalyst comprising a non-selectivated MTT zeolite and wherein said oligomerization reactor is operating under conditions to produce an oligomerized effluent;
passing the oligomerized effluent to a first separation zone to provide at least one stream comprising C_{7-} hydrocarbons and a C_{8+} olefin stream;
splitting the C_{8+} olefin stream into a first portion and a second portion; and,
recycling the first portion of the C_{8+} olefin stream to the oligomerization reaction zone.
9. The process of claim 8 further comprising:
combining the first portion of the C_{8+} olefin stream with the renewable olefin feedstock to provide a combined stream; and,
passing the combined stream into the oligomerization reactor.
10. The process of claim 8 wherein the first separation zone produces a light hydrocarbon stream and a naphtha hydrocarbon stream.
11. The process of claim 8 further comprising:
passing the second portion of the C_{8+} olefin stream to a hydrogenation zone having a hydrogenation reactor containing a catalyst and being operated to provide a hydrogenated effluent.

12. The process of claim 11 further comprising:
passing the hydrogenated effluent to second separation zone to provide at least a vent gas stream and a saturated jet range stream.
13. The process of claim 12 further comprising:
recycling a portion of the hydrogenated effluent to the hydrogenation zone as a recycle stream.
14. The process of claim 13 further comprising:
combining the recycle stream and the second portion of the C_{8+} olefin stream into a combined stream; and,
passing the combined stream to the hydrogenation reactor.
15. The process of claim 11 further comprising:
passing the hydrogenated effluent to a second separation zone having at least two columns.
16. The process of claim 15 wherein a first column in the second separation zone separates the hydrogenated effluent into a vent gas stream and a saturated distillate stream.
17. The process of claim 16 wherein a second column in the second separation zone separates the saturated distillate stream into a saturated jet range stream and a saturated diesel stream.
18. The process of claim 17 further comprising:
passing at least a portion of the saturated distillate stream to the hydrogenation reaction zone as a recycle stream.
19. The process of claim 8 further comprising:
controlling a temperature rise in the oligomerization reactor by adjusting a flow rate of the first portion of the C_{8+} olefin stream.
20. The process of claim 8 further comprising:
increasing a flow rate of the first portion of the C_{8+} olefin stream to decrease a temperature rise in the oligomerization reactor.

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