

METHODS AND APPARATUSES FOR PROCESSING RENEWABLE FEEDSTOCKS

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 13/853,631 which was
5 filed March 29, 2013, the contents of which are hereby incorporated by reference in its
entirety.

TECHNICAL FIELD

[0002] The technical field relates generally to methods and apparatuses for processing
renewable feedstocks, and more particularly relates to methods and apparatuses that
10 deoxygenate renewable feedstocks to form normal paraffins and that isomerize normal
paraffins at relatively low hydrogen partial pressure to form branched paraffins for fuel
products.

BACKGROUND

[0003] As the demand for diesel and jet boiling range fuels increase worldwide, there is
15 increasing interest in feedstock sources other than petroleum crude oil. One such source is
what has been termed “renewable feedstocks.” Renewable feedstocks are biological
feedstocks that include, but are not limited to, plant oils such as corn, jatropha, camelina,
rapeseed, canola, and soybean oil; algal oils; and animal fats such as tallow and fish oils.
The common feature of these sources is that they are composed of glycerides and free fatty
20 acids (FFA). Both of these classes of compounds contain n-aliphatic hydrocarbon chains
having from 8 to 24 carbon atoms. The aliphatic hydrocarbon chains in the glycerides or
FFAs can be fully saturated and/or mono-, di-, and/or poly-unsaturated.

[0004] The glycerides and FFAs in biological oils and fats can be converted into diesel
or jet fuel using many different processes, such as hydro-deoxygenation and hydro-
25 isomerization processes. One such approach uses both hydro-deoxygenation and hydro-
isomerization to process renewable feedstocks for diesel or jet fuel production. In
particular, a continuous feed of renewable feedstock is introduced to a deoxygenating
reaction zone and make-up hydrogen is initially passed through an isomerization reaction
zone and subsequently to the deoxygenating reaction zone. The renewable feedstock is

deoxygenated in the deoxygenating reaction zone in the presence of hydrogen to hydrogenate the olefinic or unsaturated portions of the aliphatic hydrocarbon chains to increase the normal paraffin content of the oil. The normal paraffin-containing oil is then isomerized in the isomerization reaction zone in the presence of hydrogen to convert at least a portion of the normal paraffins to branched paraffins.

[0005] Forming diesel or jet fuels having relatively low temperature cloud points and/or freeze points is desirable for certain applications particularly those applications occurring in lower temperature environments. Increasing the branched paraffin content of diesel or jet fuels has been found to lower the cloud point and/or freeze point temperatures of fuel products. Unfortunately, further improvements are needed for processing renewable feedstocks to produce diesel or jet fuels with increased branched paraffin content to lower their corresponding cloud and/or freeze points.

[0006] Accordingly, it is desirable to provide methods and apparatuses for processing renewable feedstocks to produce a diesel or jet fuel with increased branched paraffin content, for example, to lower the cloud point and/or freeze point of the fuel product. Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and this background.

BRIEF SUMMARY

[0007] Methods and apparatuses for processing a renewable feedstock are provided herein. In accordance with an exemplary embodiment, a method for processing a renewable feedstock comprises the steps of dividing a H₂-rich make-up stream into a first H₂-rich portion and a second H₂-rich portion. The second H₂-rich portion has a lower mass flow rate than the first H₂-rich portion. The renewable feedstock is deoxygenated in the presence of the first H₂-rich portion at hydroprocessing conditions effective to form a deoxygenating reaction zone effluent that contains normal paraffins. At least a portion of the deoxygenating reaction zone effluent is isomerized in the presence of the second H₂-rich portion at isomerization conditions effective to form an isomerization reaction zone effluent that contains branched paraffin. The isomerization conditions include a first hydrogen partial pressure of 4,140 kPa gauge or less.

[0008] In accordance with another exemplary embodiment, a method for processing a renewable feedstock is provided. The method comprises the steps of separating H₂, C₃⁻ hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O from a deoxygenating reaction zone effluent that contains normal paraffins using a first H₂-rich portion of a H₂-rich make-up stream to form a liquid normal paraffin-containing stream. A second H₂-rich portion of the H₂-rich make-up stream is fluidly communicated to an isomerization reaction zone. The second H₂-rich portion has a lower mass flow rate than the first H₂-rich portion. The liquid normal paraffin-containing stream is contacted with an isomerization catalyst in the presence of the second H₂-rich portion in the isomerization reaction zone that is operating at isomerization conditions effective to form an isomerization reaction zone effluent that contains branched paraffin. The isomerization conditions include a first hydrogen partial pressure of 4,140 kPa gauge or less.

[0009] In accordance with another exemplary embodiment, an apparatus for processing a renewable feedstock is provided. The apparatus comprises a control valve configured to divide a H₂-rich make-up stream into a first H₂-rich portion and a second H₂-rich portion. The second H₂-rich portion has a lower mass flow rate than the first H₂-rich portion. A deoxygenating reaction zone contains a hydroprocessing catalyst and is configured to deoxygenate the renewable feedstock in the presence of the first H₂-rich portion at hydroprocessing conditions effective to form a deoxygenating reaction zone effluent that contains normal paraffins. An isomerization reaction zone contains an isomerization catalyst and is configured to isomerize at least a portion of the deoxygenating reaction zone effluent in the presence of the second H₂-rich portion at isomerization conditions effective to form an isomerization reaction zone effluent that contains branched paraffin. The isomerization conditions include a hydrogen partial pressure of 4,140 kPa gauge or less.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The various embodiments will hereinafter be described in conjunction with the following drawing figures, wherein like numerals denote like elements, and wherein:

[0011] FIG. 1 schematically illustrates an apparatus and method for processing a renewable feedstock in accordance with an exemplary embodiment; and

[0012] FIG. 2 schematically illustrates an apparatus and method for processing a renewable feedstock in accordance with another exemplary embodiment.

DETAILED DESCRIPTION

[0013] The following Detailed Description is merely exemplary in nature and is not intended to limit the various embodiments or the application and uses thereof. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0014] Various embodiments contemplated herein relate to methods and apparatuses for processing a renewable feedstock. The exemplary embodiments taught herein contact the renewable feedstock with a hydroprocessing catalyst in the presence of hydrogen in a deoxygenating reaction zone at hydroprocessing conditions effective to form a deoxygenating reaction zone effluent. As used herein, the term “zone” refers 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, and controllers. Additionally, an equipment item, such as a reactor, dryer, or vessel, can further include one or more zones or sub-zones. The deoxygenating reaction zone effluent contains normal paraffins and hydrogen (H_2), C_3^- hydrocarbons, carbon monoxide (CO), carbon dioxide (CO_2), ammonia (NH_3), hydrogen sulfide (H_2S), and/or water (H_2O). As used herein, C_x means hydrocarbon molecules that have “X” number of carbon atoms, C_x^+ means hydrocarbon molecules that have “X” and/or more than “X” number of carbon atoms, and C_x^- means hydrocarbon molecules that have “X” and/or less than “X” number of carbon atoms.

[0015] In an exemplary embodiment, a H_2 -rich make-up stream is divided into a first H_2 -rich portion and a second H_2 -rich portion. The second H_2 -rich portion has a lower mass flow rate than the first H_2 -rich portion. H_2 , C_3^- hydrocarbons, CO, CO_2 , NH_3 , H_2S , and/or H_2O are separated from the deoxygenating reaction zone effluent using the first H_2 -rich portion of the H_2 -rich make-up stream to form a liquid normal paraffin-containing stream. In an exemplary embodiment, after being used to separate components from the deoxygenating reaction zone effluent, the first H_2 -rich portion of the H_2 -rich make-up stream is fluidly communicated to the deoxygenating reaction zone to replenish consumed hydrogen.

[0016] The second H₂-rich portion of the H₂-rich make-up stream is fluidly communicated to an isomerization reaction zone. The liquid normal paraffin-containing stream is contacted with an isomerization catalyst in the presence of the second H₂-rich portion in the isomerization reaction zone that is operating at isomerization conditions effective to form an isomerization reaction zone effluent. In an exemplary embodiment, the isomerization conditions include a relatively low hydrogen partial pressure of 4,140 kPa gauge or less. The isomerization reaction zone effluent contains branched paraffin. It has been found that by dividing the H₂-rich make-up stream into the first and second H₂-rich portions and directing the second H₂-rich portion that has a lower mass flow rate than the first H₂-rich portion to the isomerization reaction zone that is operating at a relatively low hydrogen partial pressure, the conversion of normal paraffins to branched paraffins is increased compared to conventional renewable feedstock processes to provide an isomerization reaction zone effluent with improved branched paraffin content. As such, the isomerization reaction zone effluent can be further processed, for example, to provide a fuel product such as a diesel or jet fuel that is enriched with branched paraffins to lower the cloud point and/or freeze point of the fuel product.

[0017] Referring to FIG. 1, an apparatus 10 for processing a renewable feedstock 12 to produce a hydrocarbon product stream 14 useful as a diesel or aviation fuel or blending component in accordance with an exemplary embodiment is provided. The renewable feedstock 12 is meant to include feedstocks other than those obtained from petroleum crude oil. The renewable feedstocks that can be used in the methods and apparatuses contemplated herein include any of those that comprise glycerides, fatty acid alkyl esters (FAAE), and/or free fatty acids (FFA). Most of the glycerides will be triglycerides, but monoglycerides and diglycerides may be present and processed as well. Examples of these feedstocks include, but are not limited to, canola oil, corn oil, soy oils, rapeseed oil, soybean oil, colza oil, tall oil, sunflower oil, hempseed oil, olive oil, linseed oil, coconut oil, castor oil, peanut oil, palm oil, mustard oil, cottonseed oil, jatropha oil, inedible tallow, yellow and brown greases, lard, train oil, fats in milk, fish oil, algal oil, sewage sludge, cuphea oil, camelina oil, curcas oil, babassu oil, palm kernel oil, crambe oil, fatty acid methyl esters, lard, and the like. Additional examples of renewable feedstocks include non-edible vegetable oils from the group comprising *Jatropha curcas* (Ratanjoy, Wild Castor, Jangli Erandi), *Madhuca indica* (Mohuwa), *Pongamia pinnata* (Karanji

Honge), and Azadiracta indica (Neem). The renewable feedstocks may include ratanjay oil, wild castor oil, jangli oil erandi oil, mohuwa oil, karanji honge oil, neem oil, or any oil from a natural source or produced through microbial action. The glycerides, FAAEs and FFAs of the typical vegetable or animal fat contain aliphatic hydrocarbon chains in their structure which have 8 to 24 carbon atoms, with a majority of the fats and oils containing high concentrations of fatty acids with 16 and 18 carbon atoms.

[0018] Mixtures or co-feeds of renewable feedstocks and petroleum-derived hydrocarbons may also be used as the renewable feedstock 12. Other feedstock components which may be used, especially as a co-feed component in combination with the above listed feedstocks, include spent motor oils and industrial lubricants; used paraffin waxes; liquids derived from the gasification of coal, biomass, or natural gas followed by a downstream liquefaction step such as Fischer-Tropsch technology; liquids derived from thermal or chemical depolymerization of waste plastics such as polypropylene, high density polyethylene, and low density polyethylene; and other synthetic oils generated as byproducts from petrochemical and chemical processes. Mixtures of the above feedstocks may also be used as co-feed components. In some applications, a co-feed component is the transformation of what may have been considered to be a waste product from a petroleum-based or other process into a valuable co-feed component to the current process.

[0019] As illustrated and discussed in further detail below, the apparatus 10 includes a deoxygenating reaction zone 16, an isomerization reaction zone 18 that is downstream from the deoxygenating reaction zone 16, and a product recovery zone 20 that is downstream from the isomerization reaction zone 18. The deoxygenating reaction zone 16 and the isomerization reaction zone 18 are cooperatively configured with the product recovery zone 20 to process the renewable feedstock 12 to produce the hydrocarbon product stream 14.

[0020] In an exemplary embodiment, the renewable feedstock 12 is passed through a feed surge drum 22 and a pump 24 and is combined with a recycle H₂-containing gas stream 26 and a liquid deoxygenated recycle stream 28 (both discussed in further detail below) to form a combined feed stream 30. The combined feed stream 30 is heat exchanged with a deoxygenating reaction zone effluent 32 in a heat exchanger 34 and is

passed through and heated in a heater 36 for introduction to the deoxygenating reaction zone 16. In an exemplary embodiment, the combined feed stream 30 is introduced to the deoxygenating reaction zone 16 at a temperature of from 200 to 400°C.

[0021] As illustrated, the deoxygenating reaction zone 16 includes an optional guard reactor 38 and a deoxygenating reactor 40 that is downstream from the guard reactor 38. The renewable feedstock 12 can contain impurities such as alkali metals, e.g., sodium, potassium, and phosphorus as well as solids, water, and detergent. As such, the guard reactor 38 has one or more catalyst beds 42, 44, and 46 each containing a catalyst such as a demetallation catalyst for removing impurities. Non-limiting examples of demetallation catalysts include alumina with nickel and/or cobalt. Other demetallation catalysts and/or other catalysts for hydroprocessing known to those skilled in the art may also be used.

[0022] The combined feed stream 30 is introduced to the guard reactor 38 operating at hydroprocessing conditions and contacts the demetallation catalyst in the presence of hydrogen to remove metal contaminants and other impurities from the combined feed stream 30. In an exemplary embodiment, the hydroprocessing conditions include a reaction temperature of from 200 to 450°C and a reaction hydrogen partial pressure of 4,140 kPa gauge or greater, such as from 4,140 to 8,270 kPa gauge. Additionally, the combined feed stream 30 may be partially deoxygenated in the guard reactor 38 to remove some oxygen from the renewable feedstock 12. As illustrated, liquid deoxygenated recycle quench streams 48 and 50 may also be introduced to the guard reactor 38 between the catalyst beds 42, 44, and 46 to limit a temperature increase inside the guard reactor 38 due to the exothermic reaction(s).

[0023] A partially treated effluent 52 is removed from the guard reactor 38 and is combined with a liquid deoxygenated recycle quench stream 54 to form a combined partially treated feed stream 56. The combined partially treated feed stream 56 is introduced to the deoxygenating reactor 40. As illustrated, the deoxygenating reactor 40 has one or more catalyst beds 58 and 60 each containing a hydroprocessing catalyst capable of catalyzing decarboxylation and/or hydrodeoxygenation of the combined partially treated feed stream 56 to remove oxygen. Non-limiting examples of hydroprocessing catalyst include nickel, nickel/molybdenum, and/or a noble metal(s) such as platinum (Pt) and palladium (Pd) dispersed on a high surface area support such as

alumina, zeolite, or the like. Other hydroprocessing or hydrotreating catalysts known to those skilled in the art may also be used.

[0024] The deoxygenating reactor 40 is operating at hydroprocessing conditions and the combined partially treated feed stream 56 contacts the hydroprocessing catalyst in the presence of hydrogen to further deoxygenate the combined partially treated feed stream 56 and form the deoxygenated reaction zone effluent 32. In an exemplary embodiment, the hydroprocessing conditions include a reaction temperature of from 200 to 450°C and a reaction hydrogen partial pressure of 4,140 kPa gauge or greater, such as from 4,140 to 8,270 kPa gauge. Optionally, a liquid deoxygenated recycle quench stream 62 can be introduced between the catalyst beds 58 and 60 to limit a temperature increase inside the deoxygenating reactor 40 due to the exothermic reaction(s). The deoxygenating reaction zone effluent 32 contains products of the decarboxylation and/or hydrodeoxygenation reactions such as a liquid component containing largely normal paraffins in the diesel boiling range and a gaseous component containing largely H₂, vaporous water (H₂O), CO, CO₂ and C₃⁻ hydrocarbons such as propane. Additional impurities may include NH₃ and sulfur containing compounds such as H₂S.

[0025] The deoxygenating reaction zone effluent 32 is heat exchanged with a combined stream 64 (discussed in further detail below) via a heat exchanger 66 and is then passed through the heat exchanger 34 (discussed above) and a cooler 68 to a hot separator 70. In an exemplary embodiment, the deoxygenating reaction zone effluent 32 is cooled to a temperature of from 100 to 350°C (e.g., 200 to 210°C) for introduction to the hot separator 70. The hot separator 70 at least partially separates H₂, C₃⁻ hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O from the deoxygenating reaction zone effluent 32 to form an intermediate liquid normal paraffin-containing stream 72 and a vapor stream 74. In an exemplary embodiment, the intermediate liquid normal paraffin-containing stream 72 comprises primarily normal paraffins and some dissolved and/or residual H₂, C₃⁻ hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O and the vapor stream 74 comprises primarily H₂ and C₃⁻ hydrocarbons as well as some CO, CO₂, NH₃, H₂S, and/or H₂O.

[0026] The intermediate liquid normal paraffin-containing stream 72 is passed through a pump 76 and is divided into portion 78 and portion 80. Portion 78 of the intermediate liquid normal paraffin-containing stream 72 is advanced downstream and divided to form

the liquid deoxygenated recycle/quench streams 28, 48, 50, 54, and 62 as discussed above. The portion 80 of the intermediate liquid normal paraffin-containing stream 72 is passed along and introduced to an enhanced hot separator 82 for further separation as will be discussed in further detail below.

5 [0027] Downstream from the enhanced hot separator 82, a H₂-rich make-up stream 84 is passed through a compressor 86 to a control valve 88. In an exemplary embodiment, the compressor 86 increases the pressure of H₂-rich make-up stream 84 to coincide with the hydroprocessing conditions associated with the deoxygenating reaction zone 16 as discussed above. The control valve 88 divides the H₂-rich make-up stream 84 into a H₂-
10 rich portion 90 and a H₂-rich portion 92 such that the H₂-rich portion 92 has a lower mass flow rate than the H₂-rich portion 90. In an exemplary embodiment, the H₂-rich portion 92 has a mass flow rate that is 75% or less of a mass flow rate of the H₂-rich portion 90, such as from 10 to 75% of the mass flow rate of the H₂-rich portion 90, such as from 10 to 50% of the mass flow rate of the H₂-rich portion 90, for example from 10 to 40% of the
15 mass flow rate of the H₂-rich portion 90. In an exemplary embodiment, the control valve 88 controls (e.g., shown as a single 3-way valve but may be configured as multiple valves, e.g., two 2-way valves, or the like) the hydrogen partial pressures of the H₂-rich portions 90 and 92 such that the H₂-rich portion 90 has a hydrogen partial pressure that corresponds to the hydroprocessing conditions of the deoxygenating reaction zone 16 and the H₂-rich
20 portion 92 has a hydrogen partial pressure that corresponds to the isomerization conditions of the isomerization reaction zone 18 as discussed in further detail below.

[0028] The H₂-rich portion 90 of the H₂-rich make-up stream 84 is directed to the enhanced hot separator 82. In the enhanced hot separator 82, the dissolved and/or residual gaseous components of the portion 80 of the intermediate liquid normal paraffin-
25 containing stream 72 are selectively stripped or removed using the H₂-rich portion 90 in countercurrent contacting flow with the portion 80 to form a vapor stream 94 and a liquid normal paraffin-containing stream 96. The dissolved and/or residual gaseous components comprise H₂, at least a portion of C₃⁻ hydrocarbons, and CO, CO₂, NH₃, H₂S, and/or H₂O. In an exemplary embodiment, the gaseous components are separated in the enhanced hot
30 separator 82 at a temperature of from 100 to 350°C (e.g., 200 to 210°C). In an exemplary embodiment, the vapor stream 94 comprises primarily H₂, C₃⁻ hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O and the liquid normal paraffin-containing stream 96

comprises primarily normal paraffins having a carbon number from 8 to 24 with a cetane number of 60 to 100.

[0029] As illustrated, the vapor streams 74 and 94 are combined to form a combined vapor stream 98. The combined vapor stream 98 is passed through an air cooler 100 to form a partially cooled, combined vapor stream 102 that is introduced to a cold separator 104. In an exemplary embodiment, the partially cooled, combined vapor stream 102 has a temperature of from 30 to 100°C. In the cold separator 104, a gaseous portion of the partially cooled, combined vapor stream 102 comprising primarily H₂, and some CO, CO₂, NH₃, and/or H₂S is separated to form a vapor stream 106. Also, as illustrated, a water byproduct stream 108 and a condensed/liquid hydrocarbon stream 110 containing C₃⁻ hydrocarbons (e.g., propane) and some C₃⁺ hydrocarbons are separated and removed from the cold separator 104.

[0030] The vapor stream 106 from the cold separator 104 is passed along to a scrubbing zone 112 to remove CO₂, NH₃, and/or H₂S and form the recycle H₂-containing gas stream 26. As illustrated, CO₂, H₂S and/or NH₃ are removed from the scrubbing zone 112 along line 114. In an exemplary embodiment, the recycle H₂-containing gas stream 26 is passed through a compressor 116 to raise its hydrogen partial pressure to correspond to the hydroprocessing conditions of the deoxygenating reaction zone 16. In one example, the compressor 116 compresses the recycle H₂-containing gas stream 26 to a hydrogen partial pressure of from 4,140 to 8,270 kPa gauge. As discussed above, the recycle H₂-containing gas stream 26, which includes the H₂-rich portion 90 from the H₂-rich make-up stream 84, is combined with the renewable feedstock 12 for introduction to the deoxygenating reaction zone 16. As such, the H₂-rich portion 90 is used to replenish consumed hydrogen in the deoxygenating reaction zone 16.

[0031] In an exemplary embodiment, because the liquid normal paraffin-containing stream 96 comprises essentially all normal paraffins, it will have poor cold flow properties related to, for example, its cloud point and/or freeze point. Many diesel and aviation fuels and blending components must have better cold flow properties which can be improved by converting normal paraffins to branched paraffins. Accordingly, in an exemplary embodiment, the liquid normal paraffin-containing stream 96 is directed to the isomerization reaction zone 18 by initially passing the liquid normal paraffin-containing

stream 96 through a control valve 118 and combining the stream 96 with the H₂-rich portion 92 of the H₂-rich make-up stream 84 to form the combined stream 64. As such, the combined stream 64 comprises H₂ and normal paraffins. As discussed above, the combined stream 64 is passed through the heat exchanger 66 and a heater 119 and is introduced to the isomerization reaction zone 18. In an exemplary embodiment, the combined stream 64 is introduced to the isomerization reaction zone 18 at a temperature of from 100 to 400°C and a hydrogen partial pressure of 4,140 kPa gauge or less, such as 3,450 kPa gauge or less, such as from 1,380 to 3,450 kPa gauge, for example from 1,380 to 3,280 kPa gauge.

[0032] As illustrated, the isomerization reaction zone 18 comprises an isomerization reactor 120. The isomerization reactor 120 has one or more catalyst beds 122 and 124 each containing an isomerization catalyst. Non-limiting examples of isomerization catalyst include catalyst comprising a metal of Group VIII (IUPAC 8-10) of the Periodic Table and a support material. Suitable Group VIII metals include platinum and palladium, each of which may be used alone or in combination. The support material may be amorphous or crystalline. Suitable support materials include aluminas, amorphous aluminas, amorphous silica-aluminas, ferrierite, laumontite, cancrinite, offretite, hydrogen form of stillbite, magnesium or calcium form of mordenite, and magnesium or calcium form of partheite, each of which may be used alone or in combination. Many natural zeolites, such as ferrierite, that have an initially reduced pore size can be converted to forms suitable for olefin skeletal isomerization by removing associated alkali metal or alkaline earth metal by ammonium ion exchange and calcination to produce the substantially hydrogen form. The isomerization catalyst may also comprise a modifier selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, and mixtures thereof. Other isomerization catalysts known to those skilled in the art may also be used.

[0033] In the isomerization reactor 120, the combined stream 64 contacts the isomerization catalyst in the presence of hydrogen at isomerization conditions effective to isomerize the normal paraffins into branched paraffins and form an isomerization reaction zone effluent 126. The isomerization reaction zone effluent 126 contains a gaseous portion of H₂ and C₃⁻ hydrocarbons (e.g., propane) and a branched-paraffin-enriched liquid

portion. In an exemplary embodiment, the isomerization conditions include a reaction temperature of from 100 to 400°C and a reaction hydrogen partial pressure of 4,140 kPa gauge or less, such as 3,450 kPa gauge or less, such as from 1,380 to 3,450 kPa gauge, for example from 1,380 to 3,280 kPa gauge. It has been found that by dividing the H₂-rich make-up stream 84 into the H₂-rich portions 90 and 92 and directing the H₂-rich portion 92 that has a lower mass flow rate than the H₂-rich portion 90 to the isomerization reaction zone 18 that is operating at a relatively low hydrogen partial pressure, the conversion of normal paraffins to branched paraffins is increased compared to conventional renewable feedstock processes to provide the isomerization reaction zone effluent 126 with improved branched paraffin content. In an exemplary embodiment, the isomerization reaction zone effluent 126 has a weight ratio of branched C₉⁺ paraffins to C₉⁺ n-paraffins of 2:1 or greater, such as from 2:1 to 20:1, for example from 4:1 to 10:1.

[0034] As illustrated, the isomerization reaction zone effluent 126 is passed through a control valve 128 (e.g., used to help control the hydrogen partial pressure in the isomerization reaction zone 18) and combined with the condensed/liquid hydrocarbon stream 110 to form a combined stream 130. The combined stream 130 is introduced to the product recovery zone 20. In the product recovery zone 20, the combined stream 130 is separated such that components having higher relative volatilities form a lean gas stream 132, components within the boiling range of diesel and/or aviation fuel form the hydrocarbon product stream 14, C₃/C₄ hydrocarbons form a liquefied petroleum gas (LPG) stream 134, and components having a boiling range of from 30 to 130°C form a naphtha stream 136. In an exemplary embodiment, because the isomerization reaction zone effluent 126 is enriched with branched paraffins, the hydrocarbon product stream 14 is correspondingly enriched with branched paraffins. As such, the hydrocarbon product stream 14 has improved cold flow properties such as a lower the cloud point and/or freeze point.

[0035] In an exemplary embodiment, and as described in relation to FIG. 1, the make-up hydrogen for the isomerization reaction zone 18 follows a “once through” flow scheme. In particular, the make-up hydrogen fluid circuit for the isomerization reaction zone 18 is defined by the H₂-rich portion 92 along lines 92, 64, 126, and 130 where any residual or

unconsumed portion of the H₂-rich portion 92 is separated out in the product recovery zone 20 and is removed from the apparatus 10 in the lean gas stream 132.

[0036] FIG. 2 schematically illustrates, in accordance with an alternative embodiment, a portion of the apparatus 10 shown in FIG. 1 with the exception that any residual or unconsumed portion of the make-up hydrogen from the isomerization reaction zone 18 forms part of the recycle H₂-containing gas 26 that is directed to the deoxygenating reaction zone 16 (see FIG. 1). In particular, the portion of the apparatus 10 shown in FIG. 2 illustrates an alternative embodiment for the make-up hydrogen fluid circuit for the isomerization reaction zone 18.

[0037] As illustrated, the H₂-rich portion 92 of the H₂-rich make-upstream 84 is advanced downstream from the control valve 88 and combined with the liquid normal paraffin-containing stream 96 to form the combined stream 64. As discussed above, the combined stream 64 is passed through the heat exchanger 66 and the heater 119 to the isomerization reaction zone 18. The isomerization reaction zone 18 is operating at isomerization conditions effective to isomerize the normal paraffins in the combined stream 64 into branched paraffins and form the isomerization reaction zone effluent 126 as discussed above.

[0038] The isomerization reaction zone effluent 126 is removed from the isomerization reaction zone 18 and is heat exchanged with the condensed/liquid hydrocarbon stream 110 at heat exchanger 140. The condensed/liquid hydrocarbon stream 110 is passed along to the product recovery zone 20 for separation to form the hydrocarbon product stream 14, the lean gas stream 132, the LPG stream 134, and the naphtha stream 136 as discussed above. In an exemplary embodiment, the isomerization reaction zone effluent 126 is cooled in the heat exchanger 140 to a temperature of from 80 to 300°C.

[0039] The isomerization reaction zone effluent 126 is introduced to a flash drum 142. In the flash drum 142, the isomerization reaction zone effluent 126 is separated into a vapor portion 144 and a liquid portion 146. The vapor portion 144 contains the gaseous portion of the isomerization reaction zone effluent 126 such as primarily H₂ and C₃ hydrocarbons (e.g., propane) and the liquid portion 146 contains the branched-paraffin-enriched liquid portion of the isomerization reaction zone effluent 126.

[0040] The liquid portion 146 is combined with the combined vapor stream 98 to form a combined stream 148. The combined stream 148 is passed through the air cooler 100 to the cold separator 104 for separation to form the recycle H₂-containing gas stream 26, the water byproduct stream 108, and the condensed/liquid hydrocarbon stream 110 as discussed above.

[0041] The vapor portion 144 is removed from the flash drum 142 and is combined with the H₂-rich portion 90 of the H₂-rich make-up stream 84 to form a combined H₂-rich stream 148. The combined H₂-rich stream 148 is introduced to the enhanced hot separator 82 for separating the portion 80 of the intermediate liquid normal paraffin-containing stream 72 as discussed above. As such, the vapor stream 94 that is removed from the enhanced hot separator 82 contains H₂ from the combined H₂-rich stream 148 and therefore, also contains H₂ from the vapor portion 144 from the flash drum 142. The vapor stream 94 is combined with the vapor stream 74 to form the combined vapor stream 98 which is combined with the liquid portion 146 to form the combined stream 148 as discussed above.

[0042] Accordingly, methods and apparatuses for processing a renewable feedstock have been described. The exemplary embodiments taught herein contact the renewable feedstock with a hydroprocessing catalyst in the presence of hydrogen in a deoxygenating reaction zone at hydroprocessing conditions effective to form a deoxygenating reaction zone effluent. A H₂-rich make-up stream is divided into a first H₂-rich portion and a second H₂-rich portion. The second H₂-rich portion has a lower mass flow rate than the first H₂-rich portion. H₂, C₃⁻ hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O are separated from the deoxygenating reaction zone effluent using the first H₂-rich portion of the H₂-rich make-up stream to form a liquid normal paraffin-containing stream. In an exemplary embodiment, after being used to separate components from the deoxygenating reaction zone effluent, the first H₂-rich portion of the H₂-rich make-up stream is fluidly communicated to the deoxygenating reaction zone to replenish consumed hydrogen. The second H₂-rich portion of the H₂-rich make-up stream is fluidly communicated to an isomerization reaction zone. The liquid normal paraffin-containing stream is contacted with an isomerization catalyst in the presence of the second H₂-rich portion in the isomerization reaction zone that is operating at isomerization conditions effective to form

an isomerization reaction zone effluent. In an exemplary embodiment, the isomerization conditions include a relatively low hydrogen partial pressure. The isomerization reaction zone effluent contains branched paraffin and can be further processed, for example, to provide a fuel product that is enriched with branched paraffins to lower the cloud point and/or freeze point of the fuel product.

SPECIFIC EMBODIMENTS

[0043] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0044] A first embodiment of the invention is a method for processing a renewable feedstock, the method comprising the steps of dividing a H₂-rich make-up stream into a first H₂-rich portion and a second H₂-rich portion that has a lower mass flow rate than the first H₂-rich portion; deoxygenating the renewable feedstock in the presence of the first H₂-rich portion at hydroprocessing conditions effective to form a deoxygenating reaction zone effluent that contains normal paraffins; and isomerizing at least a portion of the deoxygenating reaction zone effluent in the presence of the second H₂-rich portion at isomerization conditions effective to form an isomerization reaction zone effluent that contains branched paraffin, wherein the isomerization conditions include a first hydrogen partial pressure of 4,140 kPa gauge or less. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the step of dividing comprises forming the first H₂-rich portion having a first mass flow rate and the second H₂-rich portion having a second mass flow rate that is 75% or less of the first mass flow rate. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the step of dividing comprises forming the second H₂-rich portion having the second mass flow rate that is from 10 to 75% of the first mass flow rate. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the step of isomerizing comprises isomerizing at least the portion of the deoxygenating reaction zone effluent at the first hydrogen partial pressure of from 1,380 to 3,450 kPa gauge. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first

embodiment in this paragraph, wherein the step of isomerizing comprises isomerizing at least the portion of the deoxygenating reaction zone effluent at the first hydrogen partial pressure of from 1,380 to 3,280 kPa gauge. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the step of deoxygenating comprises deoxygenating the renewable feedstock at a second hydrogen partial pressure that is substantially the same as the first hydrogen partial pressure. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the step of deoxygenating comprises deoxygenating the renewable feedstock at a second hydrogen partial pressure that is greater than the first hydrogen partial pressure. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the step of deoxygenating comprises deoxygenating the renewable feedstock at the second hydrogen partial pressure of 4,140 kPa gauge or greater. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the step of deoxygenating comprises deoxygenating the renewable feedstock at the second hydrogen partial pressure of from 4,140 to 8,270 kPa gauge.

[0045] A second embodiment of the invention is a method for processing a renewable feedstock, the method comprising the steps of separating H₂, C₃-hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O from a deoxygenating reaction zone effluent that contains normal paraffins using a first H₂-rich portion of a H₂-rich make-up stream to form a liquid normal paraffin-containing stream; fluidly communicating a second H₂-rich portion of the H₂-rich make-up stream to an isomerization reaction zone, wherein the second H₂-rich portion has a lower mass flow rate than the first H₂-rich portion; and contacting the liquid normal paraffin-containing stream with an isomerization catalyst in the presence of the second H₂-rich portion in the isomerization reaction zone that is operating at isomerization conditions effective to form an isomerization reaction zone effluent that contains branched paraffin, wherein the isomerization conditions include a first hydrogen partial pressure of 4,140 kPa gauge or less. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of separating comprises contacting at least a portion of the deoxygenating reaction zone effluent with the first H₂-rich portion in an enhanced hot

separator to remove H₂, C₃- hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O and form the liquid normal paraffin-containing stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of contacting comprises contacting at least the portion of the deoxygenating reaction zone effluent with the first H₂-rich portion in the enhanced hot separator at a temperature of from 100 to 350°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of separating comprises separating H₂, C₃- hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O from the deoxygenating reaction zone effluent in a hot separator to form an intermediate liquid normal paraffin-containing stream, and wherein the step of contacting comprises contacting the intermediate liquid normal paraffin-containing stream with the first H₂-rich portion in the enhanced hot separator to form the liquid normal paraffin-containing stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of separating comprises separating H₂, C₃- hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O from the deoxygenating reaction zone effluent in the hot separator at a temperature of from 100 to 350°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of separating in the hot separator and contacting in the enhanced hot separator form a first vapor stream and a second vapor stream, respectively, each comprising H₂ and C₃- hydrocarbons, and wherein the method further comprises the steps of combining the first and second vapor streams to form a combined H₂- , C₃- hydrocarbon-containing stream; and separating the combined H₂- , C₃- hydrocarbon-containing stream in a cold separator to form a H₂-rich stream that comprises the first H₂-rich portion. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising the step of deoxygenating the renewable feedstock in the presence of the H₂-rich stream at hydroprocessing conditions effective to form the deoxygenating reaction zone effluent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of separating the combined H₂- , C₃- hydrocarbon-containing stream comprises separating the combined H₂- , C₃- hydrocarbon-containing stream in the cold separator at a temperature of from 20

to 60°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising the step of fluidly communicating the isomerization reaction zone effluent from the isomerization reaction zone to a product recovery zone for separating the isomerization

5 reaction zone effluent into product streams. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising the steps of separating H₂ from the isomerization reaction zone effluent to form a H₂-rich stream and a liquid branched paraffin-containing stream; and combining the H₂-rich stream and the first H₂-rich portion to form a combined H₂-
10 rich stream, and wherein the step of separating comprises separating H₂, C₃-hydrocarbons, CO, CO₂, NH₃, H₂S, and/or H₂O from the deoxygenating reaction zone effluent using the combined H₂-rich stream to form the liquid normal paraffin-containing stream.

[0046] A third embodiment of the invention is an apparatus for processing a renewable
15 feedstock, the apparatus comprising a control valve configured to divide a H₂-rich make-up stream into a first H₂-rich portion and a second H₂-rich portion that has a lower mass flow rate than the first H₂-rich portion; a deoxygenating reaction zone containing a hydroprocessing catalyst and configured to deoxygenate the renewable feedstock in the presence of the first H₂-rich portion at hydroprocessing conditions effective to form a
20 deoxygenating reaction zone effluent that contains normal paraffins; and an isomerization reaction zone containing an isomerization catalyst and configured to isomerize at least a portion of the deoxygenating reaction zone effluent in the presence of the second H₂-rich portion at isomerization conditions effective to form an isomerization reaction zone effluent that contains branched paraffin, wherein the isomerization conditions include a
25 hydrogen partial pressure of 4,140 kPa gauge or less.

[0047] While at least one exemplary embodiment has been presented in the foregoing detailed description of the disclosure, 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,
30 applicability, or configuration of the disclosure 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 disclosure. 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 disclosure as set forth in the appended claims.

CLAIMS

What is claimed is:

1. A method for processing a renewable feedstock (12), the method comprising the steps of:
 - 5 dividing a H₂-rich make-up stream (84) into a first H₂-rich portion (90) and a second H₂-rich portion (92) that has a lower mass flow rate than the first H₂-rich portion (90);
 - deoxygenating the renewable feedstock (12) in the presence of the first H₂-rich portion (90) at hydroprocessing conditions effective to form a deoxygenating
 - 10 reaction zone effluent (32) that contains normal paraffins; and
 - isomerizing at least a portion of the deoxygenating reaction zone effluent (32) in the presence of the second H₂-rich portion (92) at isomerization conditions effective to form an isomerization reaction zone effluent (126) that contains branched paraffin, wherein the isomerization conditions include a first hydrogen
 - 15 partial pressure of 4,140 kPa gauge or less.
2. The method of claim 1, wherein the step of dividing comprises forming the first H₂-rich portion (90) having a first mass flow rate and the second H₂-rich portion (92) having a second mass flow rate that is 75% or less of the first mass flow rate.
- 20 3. The method of claim 2, wherein the step of dividing comprises forming the second H₂-rich portion (92) having the second mass flow rate that is from 10 to 75% of the first mass flow rate.
- 25 4. The method of claim 1, wherein the step of isomerizing comprises isomerizing at least the portion of the deoxygenating reaction zone effluent (32) at the first hydrogen partial pressure of from 1,380 to 3,450 kPa gauge.
- 30 5. The method of claim 1, wherein the step of isomerizing comprises isomerizing at least the portion of the deoxygenating reaction zone effluent (32) at the first hydrogen partial pressure of from 1,380 to 3,280 kPa gauge.

6. The method of claim 1, wherein the step of deoxygenating comprises deoxygenating the renewable feedstock (12) at a second hydrogen partial pressure that is substantially the same as the first hydrogen partial pressure.
- 5 7. The method of claim 1, wherein the step of deoxygenating comprises deoxygenating the renewable feedstock (12) at a second hydrogen partial pressure that is greater than the first hydrogen partial pressure.
8. The method of claim 7, wherein the step of deoxygenating comprises
10 deoxygenating the renewable feedstock (12) at the second hydrogen partial pressure of 4,140 kPa gauge or greater.
9. The method of claim 7, wherein the step of deoxygenating comprises deoxygenating the renewable feedstock (12) at the second hydrogen partial
15 pressure of from 4,140 to 8,270 kPa gauge.
10. The method of claim 1, wherein the step of isomerizing comprises isomerizing at least the portion of the deoxygenating reaction zone effluent (32) at the first hydrogen partial pressure of from 1,380 to 3,450 kPa gauge, and wherein the step
20 of deoxygenating comprises deoxygenating the renewable feedstock (12) at a second hydrogen partial pressure of 4,140 kPa gauge or greater.