

**PROCESS FOR PRODUCING FUEL FROM
PETROLEUM-DERIVED AND RENEWABLE SOURCES**

FIELD OF THE INVENTION

[0001] The present invention relates to the field of producing fuel from renewable sources and, in particular, to a process for producing kerosene and/or diesel from renewable sources.

BACKGROUND OF THE INVENTION

[0002] The increased demand for energy resulting from worldwide economic growth and development has contributed to an increase in concentration of greenhouse gases in the atmosphere. This has been regarded as one of the most important challenges facing mankind in the 21st century. To mitigate the effects of greenhouse gases, efforts have been made to reduce the global carbon footprint. The capacity of the earth's system to absorb greenhouse gas emissions is already exhausted. Accordingly, there is a target to reach net-zero emissions by 2050. To realize these reductions, the world is transitioning away from solely conventional carbon-based fossil fuel energy carriers. A timely implementation of the energy transition requires multiple approaches in parallel, including, for example, energy conservation, improvements in energy efficiency, electrification, and efforts to use renewable resources for the production of fuels and fuel components and/or chemical feedstocks.

[0003] Vegetable oils, oils obtained from algae, and animal fats are seen as renewable resources. Also, deconstructed materials, such as pyrolyzed recyclable materials or wood, are seen as potential resources.

[0004] Renewable materials may comprise materials such as triglycerides with very high molecular mass and high viscosity, which means that using them directly or as a mixture in fuel bases is problematic for modern engines. On the other hand, the hydrocarbon chains that constitute, for example, triglycerides are essentially linear and their length (in terms of number of carbon atoms) is compatible with the hydrocarbons used in/as fuels. Thus, it is attractive to transform triglyceride-comprising feeds in order to obtain good quality fuel components.

[0005] Petroleum-derived jet fuels inherently contain both paraffinic and aromatic hydrocarbons. In general, paraffinic hydrocarbons offer the most desirable combustion cleanliness characteristics for jet fuels. Challenges in using paraffinic hydrocarbons from renewable sources include higher boiling point, due to chain length, and higher freeze point.

Solutions to these challenges include cracking to reduce chain length and/or isomerization to increase branching to improve cold flow properties.

[0006] When coprocessing, conventional processes send both the renewable and petroleum feedstocks to the same hydrotreating zone (see for example, Bertoncini et al. (US7,872,165B2, 2011 Jan 18) and Wexler et al. (US10,577,547B2, 2020 Mar 3))

[0007] Roberto Gomes et al. (US8,366,910B2, 2013 Feb 5) describes a process for hydrotreating a mineral oil in a first catalyst bed and injecting oils of animal and/or plant origin upstream of catalyst beds after the first bed. Likewise, Mayeur et al. (US9,062,258B2, 2015 Jun 23) introduces petroleum feed to a hydrotreating unit upstream of the biological feed so that hydrodeoxygenation takes place downstream of hydrodesulfurization of the petroleum feed.

[0008] Ziegelaar et al. (WO2023/278531A1, 2023 Jan 5) relates to a process for coprocessing a renewable feed and a petroleum feed by hydrotreating the petroleum feed in a first reaction zone and passing the effluent to a second reaction zone with a renewable feed. The reactions in the first reaction zone are one or more of hydrodesulfurization, hydrodenitrogenation, hydrodemetallization, isomerization, hydrogenation of aromatics, and hydrocracking. The reactions in the second reaction zone are one or more of hydrodeoxygenation, decarboxylation, decarbonylation, isomerization, and hydrogenation of olefins.

[0009] Rippstein et al. (US11,377,603B2, 2022 Jul 5) describes a process for coprocessing petroleum distillates and a bio-feed by hydrotreating the petroleum feed and passing the hydrotreated petroleum feed to a dewaxing bed. The dewaxed stream is processed with the bio-feed through liquid quenching beds to create a mixed stream that is processed in post-treatment beds.

[0010] Marchand et al. (US7,781,629B2, 2010 Aug 24) discloses hydrotreating a petroleum cut, introducing a quench stream of vegetable or animal origin to form a mixture with the hydrotreated petroleum cut, and then hydrotreating the mixture.

[0011] In Marker et al. (US8,314,274, 20 Nov 2012), a renewable feedstock is hydrogenated/hydrodeoxygenated and then isomerized and selectively hydrocracked to generate an effluent comprising branched paraffins. The effluent is separated to provide an overhead stream, an optional aviation product stream, a diesel stream and a stream having higher boiling points. A portion of the diesel boiling point range product is recycled to the isomerization and selective hydrocracking zone.

[0012] McCall et al. (US8,742,183, 3 Jun 2014) relates to a process for production of aviation fuel from biorenewable feedstock, which is subjected to hydrogenation and deoxygenation to provide n-paraffins. Three embodiments are illustrated for subsequent steps of (i) isomerizing the n-paraffins and selectively cracking the isomerized effluent, (ii) selectively cracking the n-paraffins and isomerizing the cracked effluent, or (iii) subjecting the n-paraffins to a combined selective cracking and isomerization zone.

[0013] A challenge with isomerization and selective cracking schemes is a tension between maximizing product yield and meeting product specification.

[0014] Anumakonda et al. (US8,058,492, 15 Nov 2011) describes a process for controlling production of transportation fuels from renewable feedstocks by determining a yield for diesel and aviation components, determining isomerization and selective hydrocracking conditions that results in the yields, hydrogenating and deoxygenating a renewable feedstock to produce n-paraffins, and isomerizing and selectively hydrocracking the n-paraffins. Diesel and aviation fuel components are fractionated under predetermined conditions. An overhead stream from the fractionator is further fractionated into LPG and naphtha streams. The naphtha stream is optionally recycled to the isomerization zone.

[0015] While Anumakonda et al. contemplates adjusting conditions to serve a predetermined yield, there is a limit to how effective the method can be when the deoxygenated product is subjected to the isomerization and selective cracking, as described therein.

[0016] Markkanen et al. (EP2141217B1, 25 Mar 2015; US9,005,429, 14 Apr 2015) describe a process for making aviation fuel by a first stage hydrodeoxygenation of a biological feedstock, followed by a second stage isomerization of the resulting n-paraffins. Effluent from the second stage is separated in a fractionator to yield a gas, a gasoline fraction, an aviation fuel fraction, a diesel fraction, and a heavy fraction boiling at or above 200°C (US'429) or 290°C (EP'217B1).

[0017] In one embodiment of Markkanen et al., the heavy fraction is combined with the hydrodeoxygenated effluent and isomerizing the combined stream. In another embodiment, the heavy fraction is isomerized in a first section of the second stage and, after adding the hydrodeoxygenated effluent, the isomerized heavy fraction is isomerized with the hydrodeoxygenated effluent. Finally, in a third embodiment, the hydrodeoxygenated effluent and the heavy fraction are separately isomerized in a second stage and third stage isomerization, respectively. In the third embodiment of separate isomerization, the catalyst for the heavy fraction may be selected as promoting cracking.

[0018] There remains a need for improving the effectiveness of coprocessing of petroleum-derived and renewable feedstocks and improving the yield of kerosene and/or diesel fuel from these feedstocks.

SUMMARY OF THE INVENTION

[0019] According to one aspect of the present invention, there is provided a process for producing fuel from a renewable feedstock and a petroleum-derived oil, the process comprising the steps of: reacting a renewable feedstock in a first hydrotreating zone under hydrotreating conditions sufficient to cause a hydrotreating reaction to produce a hydrotreated renewable oil; providing a hydrotreated petroleum-derived oil; reacting the hydrotreated renewable oil and the hydrotreated petroleum-derived oil effluent in a hydroisomerization zone under hydroisomerization conditions to cause a hydroisomerization reaction to produce an isomerized effluent; separating the isomerized effluent to produce an offgas stream, at least one fuel stream having a desired boiling point range, and a heavy fraction having a boiling point greater than the desired boiling point range; reacting the heavy fraction in a hydrocracking zone under hydrocracking conditions to cause a hydrocracking reaction to produce a hydrocracked effluent; and passing the hydrocracked effluent to the hydroisomerization zone.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The process of the present invention will be better understood by referring to the following detailed description of preferred embodiments and the drawings referenced therein, in which:

[0021] Figs. 1 and 2 are flow diagrams illustrating embodiments of the process of the present invention for hydrotreating a renewable feedstock and isomerizing the hydrotreated renewable oil with a hydrotreated petroleum-derived oil together with a hydrocracked recycle stream.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The present invention provides a process for producing fuel from a renewable feedstock and a petroleum-derived oil. A renewable feedstock is hydrotreated. A hydrotreated petroleum-derived oil is provided. The hydrotreated renewable oil and the hydrotreated petroleum-derived oil are combined. A combined liquid is passed to a hydroisomerization zone. The isomerized effluent preferably has improved cold flow properties. The isomerized effluent

is separated to produce an offgas stream, at least one fuel stream having a desired boiling point range, and a heavy fraction having a boiling point greater than the desired boiling point range. The heavy fraction is hydrocracked, and the hydrocracked effluent is sent to the hydroisomerization zone.

[0023] It is generally understood that the renewable feedstock and the petroleum-derived feedstock are co-processed in a hydrotreater. However, when the renewable feedstock and the petroleum-derived feedstocks are combined for treating in an existing petroleum refinery, the percentage of renewable oil feedstock must be maintained at a level generally below 10 wt.% to avoid problems associated with metallurgy of conventional petroleum-derived oil hydrotreater, reaction heat release, process safety, and the like. The inventors have surprisingly discovered that by separately hydrotreating the renewable and petroleum-derived feedstocks and combining isomerisation, capital costs may be reduced for higher percentages of co-processing, especially when revamping an existing petroleum-derived oil refinery.

[0024] Further, it is generally understood that the hydroisomerization zone should be operated at high severity to maximize yield of isomerized product. However, when the hydroisomerization severity is high, there is an increased yield of undesirable and/or less valuable off-gas and/or naphtha. The inventors have surprisingly discovered that by operating at a lower hydroisomerization severity, the yield of heavy fraction is increased, and by passing the heavy fraction to a hydrocracking zone and then isomerizing the hydrocracked effluent, the yield of desirable isomerized product can be increased.

[0025] The process of the present invention is important for the energy transition and can improve the environment by producing low carbon energy and/or chemicals from renewable sources, and, in particular, from degradable waste sources, whilst improving the efficiency of the process.

[0026] A common challenge for processing renewable feedstocks to produce fuel, such as kerosene and/or diesel, is the variability of renewable feedstocks. Variability of renewable feedstocks may include a change from one type of feedstock to another, for example, due to supply and/or markets, changes in feedstock quality and/or composition profile, seasonal variations, variations between sources of same feedstock, and the like. Reaction schemes, operating conditions, heat generation, process efficiency, product composition, and/or product yield may each be impacted by such variability. A further challenge for meeting product specifications is that the product component yields change as catalyst activity changes, and/or from start-of-run to end-of-run. The process of the present invention provides flexibility and

robustness to allow for feedstock variability, changes in catalyst activity, and/or changes in desired products, while reducing energy consumption, operating costs, and/or carbon footprint. Further, the process of the present invention is more flexible in operating conditions and enables revamp of existing process schemes used for processing petroleum-derived feedstock.

[0027] Embodiments of process units for carrying out the method of the present invention are described below and/or illustrated in the drawings. For ease of discussion, additional equipment and process steps that may be used in a process for producing fuel from a renewable feedstock are not shown. The additional equipment and/or process steps may include, for example, without limitation, pre-treaters, heaters, chillers, air coolers, heat exchangers, mixing chambers, valves, pumps, compressors, condensers, quench streams, recycle streams, slip streams, purge streams, reflux streams, and the like.

[0028] Fig. 1 illustrates one embodiment of the process of the present invention 10. A renewable feedstock 12 is reacted in a hydrotreating zone 14 to produce a hydrotreated renewable oil 16. Hydrogen may be combined with the renewable feedstock 12 stream before it is introduced the hydrotreating zone 14, co-fed with the renewable feedstock 12, or added to the hydrotreating zone 14 independently of the renewable feedstock 12. Hydrogen may be fresh and/or recycled from the reactor effluent and/or another unit in the process and/or produced in a HMU (not shown). In another embodiment, the hydrogen may be produced, for example, without limitation, by water electrolysis. The water electrolysis process may be powered by renewable energy (such as solar photovoltaic, wind or hydroelectric power) to generate green hydrogen, nuclear energy or by non-renewable power from other sources (grey hydrogen).

[0029] The hydrotreated renewable oil 16 is combined with a hydrotreated petroleum-derived oil 26 and passed to a hydroisomerization unit 32. Preferably, the isomerized effluent is directed to a product recovery zone 34. Various embodiments for the product recovery zone 34 may be considered. The embodiments of the product recovery zone 34 may be comprised of one or more unit operations. For example, the product recovery zone 34 may include a product stripper for stripping entrained and/or dissolved gases from the hydroisomerization zone effluent, a naphtha stripper to produce the stripper offgas stream and a naphtha stream, a naphtha stabilizer column, a naphtha rectification column, a naphtha recovery column, an overhead separator, a vacuum fractionator, an atmospheric fractionator, and combinations thereof. For example, without limitation, the product recovery zone 34 may be as described in WO2023043764 (23 Mar 2023) or WO2023043792 (23 Mar 2023), incorporated by reference

herein. The product recovery zone 34 includes one or more product recovery units resulting in desired product streams.

[0030] As used herein, the terms “renewable feedstock,” “renewable feed,” and “material from renewable sources” mean a feedstock from a renewable source. A renewable source may be animal, vegetable, microbial, and/or bio-derived or mineral-derived waste materials suitable for the production of fuels, fuel components and/or chemical feedstocks. For example, vegetable oils, oils obtained from algae, and animal fats are suitable renewable feedstocks. Also, deconstructed materials, such as pyrolyzed recyclable materials or wood, are seen as potential resources.

[0031] A preferred class of renewable materials are bio-renewable fats and oils comprising triglycerides, diglycerides, monoglycerides, free fatty acids, and/or fatty acid esters derived from bio-renewable fats and oils. Examples of fatty acid esters include, but are not limited to, fatty acid methyl esters and fatty acid ethyl esters. The bio-renewable fats and oils include both edible and non-edible fats and oils. Examples of bio-renewable fats and oils include, without limitation, algal oil, brown grease, canola oil, carinata oil, castor oil, coconut oil, colza oil, corn oil, cottonseed oil, fish oil, hempseed oil, jatropha oil, lard, linseed oil, milk fats, mustard oil, olive oil, palm oil, peanut oil, rapeseed oil, sewage sludge, soy oils, soybean oil, sunflower oil, pongamia oil, tall oil, tall oil fatty acids (TOFA), tallow, used cooking oil, yellow grease, white grease, and combinations thereof.

[0032] Another preferred class of renewable materials are liquids derived from biomass and waste liquefaction processes. Examples of such liquefaction processes include, but are not limited to, (hydro)pyrolysis, hydrothermal liquefaction, plastics liquefaction, and combinations thereof. Renewable materials derived from biomass and waste liquefaction processes may be used alone or in combination with bio-renewable fats and oils.

[0033] The renewable materials to be used as feedstock in the process of the present invention may contain impurities. Examples of such impurities include, but are not limited to, solids, iron, chloride, phosphorus, alkali metals, alkaline-earth metals, polyethylene, and unsaponifiable compounds. If required, these impurities can be removed from the renewable feedstock before being introduced to the process of the present invention. Methods to remove these impurities are known to the person skilled in the art.

[0034] The hydrotreated petroleum-derived oil 26 is produced by hydrotreating petroleum-derived hydrocarbons including, without limitation, all fractions from petroleum crude oil, natural gas condensate, tar sands, shale oil, synthetic crude, and combinations thereof. In the

embodiment of Fig. 1, the hydrotreated petroleum-derived oil 26 is provided to the process of the present invention 10 from another process and/or refinery. In the embodiment of Fig. 2, the process 10 includes a hydrotreater 24 for hydrotreating a petroleum-derived feedstock 22 to produce the hydrotreated petroleum-derived oil 26.

[0035] In the hydrotreating zone 14, renewable feedstock 12 is reacted under hydrotreating conditions sufficient to cause a reaction selected from a hydrotreating reaction including, without limitation, hydrodeoxygenation, hydrodenitrogenation, hydrodesulphurization, hydrodearomatization, hydrogenation, hydrodemetallization, and combinations thereof. In the hydrotreating zone 24, petroleum-derived feedstock 22 is reacted under hydrotreating conditions sufficient to cause a reaction selected from a hydrotreating reaction including, without limitation, hydrodenitrogenation, hydrodesulphurization, hydrodearomatization, hydrogenation, hydrodemetallization, and combinations thereof. The reactions in the hydrotreating zones 14, 24 are both preferably catalytic reactions, but each may independently include non-catalytic reactions, such as thermal processing and the like. Each of the hydrotreating zones 14, 24 may independently be single-stage or multi-stage. In the case of catalytic reactions, the hydrotreating zones 14, 24 may independently be operated in a slurry, moving bed, fluidized bed, and/or fixed bed operation. In the case of a fixed bed operation, each reactor may have a single catalyst bed or multiple catalyst beds. The hydrotreating zones 14, 24 may be comprised of a single reactor or multiple reactors. The hydrotreating zones 14, 24 may be operated in a co-current flow, counter-current flow, or a combination thereof. Preferably, the hydrotreating zones 14, 24 are each independently operated in a co-current flow.

[0036] The catalyst may be the same or different throughout the hydrotreating zones 14, 24. The hydrotreating zones 14, 24 may comprise a single catalyst bed or multiple catalyst beds. The catalyst may be the same throughout the single catalyst bed, optionally there is a mixture of catalysts, or different catalysts may be provided in two or more layers in the catalyst bed. In an embodiment of multiple catalyst beds, the catalyst may be same or different for each catalyst bed.

[0037] In one embodiment, the hydrotreating zones 14, 24 independently further comprise a hydrogenation catalyst in advance of the hydrotreating catalyst. The hydrogenation components may be used in bulk metal form, or the metals may be supported on a carrier. Active metals for hydrogenation include catalytically active metals of Group VIII and/or Group VIB, including, without limitation, Ni, Co, Mo, W, and combinations thereof. Suitable carriers include refractory oxides, molecular sieves, and combinations thereof. Examples of suitable

refractory oxides include, without limitation, alumina, amorphous silica-alumina, titania, silica, and combinations thereof. Examples of suitable molecular sieves include, without limitation, zeolite Y, zeolite beta, ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-48, SAPO-11, SAPO-41, ferrierite, and combinations thereof.

[0038] The hydrotreating catalyst may be any catalyst known in the art that is suitable for hydrotreating. Catalyst metals are often in an oxide state when charged to a reactor and preferably activated by reducing or sulphiding the metal oxide. Preferably, the hydrotreating catalyst comprises catalytically active metals of Group VIII and/or Group VIB, including, without limitation, Pd, Pt, Ni, Co, Mo, W, and combinations thereof. Hydrotreating catalysts are generally more active in a sulphided form as compared to an oxide form of the catalyst. A sulphiding procedure is used to transform the catalyst from a calcined oxide state to an active sulphided state. Catalyst may be pre-sulphided or sulphided in situ. Because renewable feedstocks generally have a low sulphur content, a sulphiding agent is often added to the feed to maintain the catalyst in a sulphided form.

[0039] Preferably, the hydrotreating catalyst comprises sulphided catalytically active metals. Examples of suitable catalytically active metals include, without limitation, sulphided nickel, sulphided cobalt, sulphided molybdenum, sulphided tungsten, sulphided CoMo, sulphided NiMo, sulphided MoW, sulphided NiW, and combinations thereof. A catalyst bed/zone may have a mixture of two or more types of catalysts and/or successive beds/zones, including stacked beds, and may have the same or different catalysts and/or catalyst mixtures. In case of such sulphided hydrotreating catalyst, a sulphur source will typically be supplied to the catalyst to keep the catalyst in sulphided form during the hydroprocessing step.

[0040] The hydrotreating catalyst may be sulphided in-situ or ex-situ. In-situ sulphiding may be achieved by supplying a sulphur source, usually H₂S or an H₂S precursor (i.e., a compound that easily decomposes into H₂S such as, for example, dimethyl disulphide, di-tert-nonyl polysulphide or di-tert-butyl polysulphide) to the hydrotreating catalyst during operation of the process. The sulphur source may be supplied with the feed, the hydrogen stream, or separately. An alternative suitable sulphur source is a sulphur-comprising hydrocarbon stream boiling in the diesel or kerosene boiling range that is co-fed with the feedstock. In addition, added sulphur compounds in feed facilitate the control of catalyst stability and may reduce hydrogen consumption.

[0041] The hydrotreating zones 14, 24 may independently be operated as a single-stage process or a multi-stage process. In one preferred embodiment, the hydrotreating zones 14, 24 are each operated as a single-stage process, in a co-current mode with one or more fixed beds.

[0042] The hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26 may be combined within the hydroisomerization unit 32, for example, by concurrent injection and/or using a fluid mixer internal known to those skilled in the art.

[0043] Fig. 2 illustrates a preferred embodiment wherein the hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26 are combined in a separation zone 40 or a portion thereof. For example, the effluent from hydrotreating zone 14 may be sent to a high-pressure separator and the liquid from the high-pressure separator may then be passed to a stripper, preferably a low-pressure stripper where it is combined with the hydrotreated petroleum oil 26. In some embodiments, the low-pressure stripper may be directly connected to one of the hydrotreating zones 14, 24.

[0044] As depicted in Fig. 2, the effluents of the hydrotreating zones 14, 24 are directed to the separation zone 40 for separating the hydrotreating effluents 16, 26 into a vapor phase effluent and a liquid hydrotreated effluent. Where the catalyst used for hydroisomerization has a noble metal, the separation zone 40 is provided to remove or at least substantially reduce components that poison or otherwise adversely impact the hydroisomerization catalyst.

[0045] When the separation zone 40 is included, the separation zone 40 has one or more separation units including, for example, without limitation, gas/liquid separators, including hot high- and low-pressure separators, intermediate high- and low-pressure separators, cold high- and low-pressure separators, high- and low-pressure strippers, integrated strippers, and combinations thereof. Integrated strippers include strippers that are integrated with hot high- and low-pressure separators, intermediate high- and low-pressure separators, cold high- and low-pressure separators. It will be understood by those skilled in the art that high-pressure separators operate at a pressure that is close to the hydrotreating zone 14 pressure, suitably 0 - 10 bar (0 - 1 MPa) below the reactor outlet pressure, while a low-pressure separator is operated at a pressure that is lower than a preceding reactor in the hydrotreating zone 14 pressure or a preceding high-pressure separator, suitably 0 - 15 barg (0 - 1.5 MPaG). Similarly, it will be understood by those skilled in the art that hot means that the hot-separator is operated at a temperature that is close to a preceding reactor in the hydrotreating zone 14 temperature, suitably sufficiently above water dew point (e.g., $\geq 10^{\circ}\text{C}$, preferably $\geq 20^{\circ}\text{C}$, above the water dew point) and sufficiently greater than salt deposition temperatures (e.g., $\geq 10^{\circ}\text{C}$, preferably

$\geq 20^{\circ}\text{C}$, above the salt deposition temperature), while intermediate- and cold-separators are at a reduced temperature relative to the preceding reactor in the hydrotreating zone 14. For example, a cold-separator is suitably at a temperature that can be achieved via an air cooler. A hot-separator preferably operates at a temperature in a range from 150 to 250°C, while a cold-separator preferably operates at a temperature in a range from 40 to 120°C. An intermediate temperature will be understood to mean any temperature between the temperature of a hot- or cold-separator.

[0046] In conventional renewable hydrotreating, the separation zone can have many different configurations, for example, comprising multiple high-pressure separators, including a high-pressure stripper. The inventors surprisingly discovered that a particular advantage of the process of the present invention 10 is that it enables the use of a low-pressure stripper to replace the high-pressure stripper, while improving stripping efficiency, improving isomerization feed quality, and reducing equipment and operating costs.

[0047] There are a variety of configurations for petroleum refining for fuel production. However, the configurations typically have one or two hydrodesulfurization units and a separation zone for separating hydrotreated oil from gas phase products exiting the hydrodesulfurization unit. The separation zone can have many different configurations and combinations of separators. Often the separation zone in a conventional petroleum refinery will have a stripper. While the stripper can be a high-pressure stripper, an existing refinery often has a low-pressure stripper.

[0048] The process of the present invention is particularly advantageous for efficiently and effectively revamping an existing petroleum refinery. A challenge for revamping an existing hydrodesulfurization unit is that the typical hydrodesulfurization unit is produced using a metallurgy that is not compatible with renewable feedstocks at a concentration of greater than about 10 wt.%. Another challenge is that, when the renewable feedstock content is greater than about 10 wt.%, the heat of reaction is typically too high for conventional petroleum hydrotreaters. Accordingly, additional catalyst beds and increased quenching are typically required. It is difficult to change the number of catalyst beds in an existing petroleum hydrotreater.

[0049] The process of the present invention 10 solves the problem by separately hydrotreating the renewable feedstock 12 and the petroleum-derived feedstock 22 in independent hydrotreating zones 14, 24 and then combining the hydrotreated oils 16, 26 for co-processing in a hydroisomerization unit.

[0050] As well, the inventors have discovered that a stripper, preferably an existing stripper from an existing refinery, more preferably an existing low-pressure stripper, is a preferred location for combining the hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26.

[0051] In addition, the separation zone 40 may include one or more treating units including, for example, without limitation, a membrane separation unit, an amine scrubber, a pressure swing adsorption (PSA) unit, a caustic wash, and combinations thereof. The treating units are preferably selected to separate desired gas phase molecules. For example, an amine scrubber is used to selectively separate H₂S and/or carbon oxides from H₂ and/or hydrocarbons. As another example, a PSA unit may be used to purify a hydrogen stream for recycling to a stripper and/or a reactor in one or both of the hydrotreating zones 14, 24.

[0052] A portion of the hydrotreated renewable oil 16 from one or more separator units may be returned to a hydrotreating zone 14, for example, as a quench stream (not shown) or as a diluent (not shown) of feedstock 12. The volumetric ratio of diluent to fresh renewable feedstock 12 is preferably in a range of from 1:1 to 30:1. The quench stream is used to control temperature in the hydrotreating zone 14 and therefore typically cooled using, for example, an air cooler (not shown) or a heat exchanger (not shown). One or more quench streams may be added between catalyst beds/zones in the hydrotreating zone 14.

[0053] The hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26 (with or without a separation step) is passed to a hydroisomerization zone 32 under hydroisomerization conditions to cause a hydroisomerization reaction.

[0054] By separately hydrotreating the renewable feedstock 12 and the petroleum-derived feedstock 22 and later combining the hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26 for isomerization in the hydroisomerization zone 32, a higher percentage of renewable content can be processed, as compared with conventional coprocessing processes. Preferably, the hydrotreated renewable oil 16 is present in an amount of 10 – 95 wt.% in the combined liquid, preferably 30 – 90 wt.%, more preferably from 40 – 80 wt.%. A further advantage of the process of the present invention 10 is that the renewable oil content may be changed during the process without the need for changes in reactor design, as would be required in other coprocessing configurations where the renewable feedstock and the petroleum-derived feedstock are hydrotreated together in one hydrotreater.

[0055] Isomerization has the effect of improving cold flow properties of the hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26.

[0056] The hydroisomerization catalyst may be any suitable catalyst composition known to those skilled in the art. Preferably, the hydroisomerization catalyst comprises a Group VIII metal. More preferably, the hydroisomerization catalyst further comprises a zeolitic material. The hydroisomerization catalyst may further comprise a binder and/or carrier, such as, without limitation, silica, alumina, silica-alumina, and combinations thereof. Preferably, the Group VIII metal is selected from the group consisting of platinum, palladium, nickel, and combinations thereof. When the Group VIII metal is Ni, the hydroisomerization preferably includes a Group VI metal, preferably Mo or W.

[0057] The zeolitic material is preferably selected from the group consisting of Beta, COK-7, EU-1, EU-2, EU-11, IZM-1, MCM-22, NU-10, ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-30, ZSM-35, ZSM-48, ZSM-50, ZSM-57, and combinations thereof.

[0058] The catalyst may be the same or different throughout the hydroisomerization zone 32. The hydroisomerization zone 32 may comprise a single catalyst bed or multiple catalyst beds. The catalyst may be the same throughout the single catalyst bed, optionally there is a mixture of catalysts, or different catalysts may be provided in two or more layers in the catalyst bed. In an embodiment of multiple catalyst beds, the catalyst may be same or different for each catalyst bed.

[0059] The hydroisomerization zone 32 is operated in the presence of hydrogen at a pressure in a range of from 1 MPa to 30 MPa and at a temperature in a range of from 260°C to 400°C. Preferably, the pressure is in a range of from 2 MPa to 17 MPa, and the temperature is in a range of from 300°C to 380°C. The LHSV is in a range of from 0.2 h⁻¹ to 4 h⁻¹ based on the hydrotreated oils 16, 26. The ratio of the hydrogen gas to the combined liquid supplied to the hydroisomerization zone 32 is in a range of from 100 to 1500 normal L (at standard conditions of 0 °C and 1 atm (0.1 MPa)) per kg of the combined liquid.

[0060] Hydroisomerization is particularly advantageous for improving the production of kerosene for jet fuel. To increase kerosene production, the WABT (weighted average bed temperature) in the hydroisomerization zone 32 is typically increased. WABT is a representative temperature, assuming an adiabatic reactor having no loss or gain from its surroundings, for the catalyst bed. Those skilled in that art understand that the temperature profile will typically increase from inlet to outlet.

[0061] As shown in Figs. 1 and 2, the product recovery zone 34 produces, for example, without limitation, an off-gas stream 36, a naphtha boiling point range stream 42, a kerosene boiling point range 38, a diesel boiling point range stream 44, and/or a heavy fraction 52. The

product streams are dependent on the composition of the feedstocks 12, 22 and/or the components and/or the operating conditions of the product recovery zone 34.

[0062] As shown in the embodiment of Fig. 1, the product recovery zone 34 produces an off-gas stream 36, a naphtha boiling point range stream 42, a kerosene boiling point range stream 38, and a heavy fraction 52. In this embodiment, the off-gas stream 36 suitably comprises C1-C5 hydrocarbons, while the naphtha boiling point range 42 suitably comprises C4-C12 hydrocarbons in a boiling point range of from -12°C to 204°C. The kerosene boiling point range stream 38 is preferably comprised of C6-C18 hydrocarbons having a boiling point range of from 90°C to 300°C. In this embodiment, the heavy fraction 52 has C17+ hydrocarbons having a boiling point greater than 250°C.

[0063] In another embodiment, as illustrated in Fig. 2, the product recovery zone 34 produces an off-gas stream 36, a naphtha boiling point range stream 42, a kerosene boiling point range stream 38, a diesel boiling point range stream 44, and a heavy fraction 52. In this embodiment, the off-gas stream 36 suitably comprises C1-C5 hydrocarbons, while the naphtha boiling point range 42 suitably comprises C4-C12 hydrocarbons in a boiling point range of from -12°C to 204°C. The kerosene boiling point range stream 38 is preferably comprised of C6-C18 hydrocarbons having a boiling point range of from 90°C to 300°C. The diesel boiling point range stream 44 comprises C8-C26 hydrocarbons having a boiling point range of from 120°C to 400°C, while the heavy fraction 52 has C17+ hydrocarbons having a boiling point greater than 250°C.

[0064] In a preferred embodiment, the process 10 is directed towards improving the yield of the kerosene boiling point range stream 38. In particular, in a preferred embodiment, the process 10 is directed toward a kerosene product meeting the specifications of ASTM D7566, wherein a synthesized paraffinic kerosene from hydroprocessed esters and fatty acids has a T10 distillation temperature (using ASTM Test Method D86) maximum of 205°C and a final boiling maximum of 300°C.

[0065] In this case, as shown in Fig. 2, at least a portion of the diesel boiling point range stream 44 is recycled with the heavy fraction 52. Another portion of the diesel boiling point range stream 44 may be drawn off as a bleed stream. The product recovery zone 34 may include a further separation of the diesel boiling point range stream 44 into a light diesel stream that may be drawn off as a bleed stream, for example, while the heavy diesel stream is recycled with the heavy fraction 52.

[0066] Additionally, or alternatively, the product recovery zone 34 may include a further separation of heavy contaminants from the heavy fraction 52. Depending on the original feedstock and/or processing conditions, it is possible that heavy contaminants are present that may not be reactive in a subsequent hydrocracking and/or hydroisomerization zones. In this case, it is preferred to provide a bleed stream of a heaviest portion of the heavy fraction 52. In one embodiment, the bleed stream has substantially the same composition as the heavy fraction 52. In another embodiment, the bleed stream may be the product of a further treatment and/or separation of the heavy fraction 52 to selectively remove contaminants from the heavy fraction 52.

[0067] In the Fig. 1 embodiment, the diesel boiling point range hydrocarbons are part of the heavy fraction 52 and are recycled for cracking and isomerization to extinction.

[0068] In the Fig. 2 embodiment, at least a portion of the heavy fraction 52 is directed to a hydrocracking zone 54 under hydrocracking conditions sufficient to cause a hydrocracking reaction to produce a hydrocracked effluent. In one embodiment, another portion of the heavy fraction 52 may be directed to further processing for valorizing the heavy fraction 52.

[0069] In the embodiments of Figs. 1 and 2, the hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26 are combined and introduced to the effluent from the hydrocracking zone 54 in advance of the hydroisomerization zone 32.

[0070] The hydrocracking catalyst may be any suitable catalyst composition known to those skilled in the art. Preferably, the hydrocracking catalyst comprises a Group VIII metal. More preferably, the hydrocracking catalyst further comprises an acidic material.

[0071] The acidic material may be an amorphous acidic material, a crystalline acidic material, or a combination thereof. The amorphous acidic material may be, for example, without limitation, amorphous silica alumina. The crystalline acidic material may be selected from the group consisting of Beta, COK-7, EU-1, EU-2, EU-11, IZM-1, MCM-22, NU-10, ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-30, ZSM-35, ZSM-48, ZSM-50, ZSM-57, and combinations thereof.

[0072] Preferably, the Group VIII metal is selected from the group consisting of platinum, palladium, nickel, and combinations thereof. When the Group VIII metal is Ni, the hydroisomerization catalyst preferably includes a Group VI metal, preferably Mo or W.

[0073] The hydrocracking catalyst may further comprise a binder and/or carrier, such as, without limitation, silica, alumina, silica-alumina, and combinations thereof.

[0074] The hydrocracking zone 54 is operated in the presence of hydrogen at a pressure in a range of from 1 MPa to 30 MPa and at a temperature in a range of from 260°C to 400°C. Preferably, the pressure is in a range of from 2 MPa to 18 MPa, and the temperature is in a range of from 280°C to 400°C.

[0075] The hydrocracking conditions and catalyst are selected to favour cracking over branching.

[0076] In the embodiment of Fig. 1, the hydrocracking zone 54 is provided in a single-stage configuration above the hydroisomerization zone 32. In this embodiment, the heavy fraction 52 is recycled to a single stage reactor comprising both the hydrocracking zone 54 and a hydroisomerization zone 32. The heavy fraction 52 is first reacted in the hydrocracking zone 54. The hydrocracked effluent from the hydrocracking zone 54 is then passed to the hydroisomerization zone 32 where it is combined with the hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26 for isomerizing the hydrocracked effluent and the hydrotreated oils 16, 26 concurrently.

[0077] In the embodiment of Fig. 2, the hydrocracking zone 54 and the hydroisomerization zone 32 are provided in a two-stage configuration. The heavy fraction 52 is first reacted in the hydrocracking zone 54. The hydrocracked effluent from the hydrocracking zone 54 is then passed to the hydroisomerization zone 32 where it is combined with the hydrotreated renewable oil 16 and the hydrotreated petroleum-derived oil 26 for isomerizing the hydrocracked effluent and the hydrotreated oils 16, 26 concurrently.

[0078] In each of the embodiments of Figs. 1 and 2, the hydroisomerization zone 32 optionally includes a hydrofinishing zone (not shown). During the hydroisomerization step and/or depending on the feedstock used, some aromatics and/or trace olefins may be present in the effluent of the hydroisomerization zone.

[0079] The hydrofinishing components may be used in bulk metal form, or the metals may be supported on a carrier. Active metals for hydrogenation include catalytically active metals of Group VIII and/or Group VIB, including, without limitation, Ni, Co, Mo, W, and combinations thereof. Preferably, the Group VIII metal is selected from the group consisting of platinum, palladium, nickel, and combinations thereof. Suitable carriers include refractory oxides. Examples of suitable refractory oxides include, without limitation, alumina, amorphous silica-alumina, titania, silica, and combinations thereof.

[0080] In the process of the present invention 10, the amount of recycle for the heavy fraction 52 can be selected to be 20-200 wt.% of the total of the renewable feedstock 12 and

the petroleum-derived feedstock 22 to the isomerisation bed, preferably in the range of 30-100 wt.% of the total of the renewable feedstock 12 and the petroleum-derived feedstock 22.

[0081] While the embodiments are described with reference to various implementations and exploitations, it will be understood that these embodiments are illustrative and that the scope of the inventive subject matter is not limited to them. Many variations, modifications, additions, and improvements are possible. Various combinations of the techniques provided herein may be used.

CLAIMS

1. A process for producing fuel from a renewable feedstock and a petroleum-derived oil, the process comprising the steps of:
 - reacting a renewable feedstock in a first hydrotreating zone under hydrotreating conditions sufficient to cause a hydrotreating reaction to produce a hydrotreated renewable oil;
 - providing a hydrotreated petroleum-derived oil;
 - reacting the hydrotreated renewable oil and the hydrotreated petroleum-derived oil effluent in a hydroisomerization zone under hydroisomerization conditions to cause a hydroisomerization reaction to produce an isomerized effluent;
 - separating the isomerized effluent to produce an offgas stream, at least one fuel stream having a desired boiling point range, and a heavy fraction having a boiling point greater than the desired boiling point range;
 - reacting the heavy fraction in a hydrocracking zone under hydrocracking conditions to cause a hydrocracking reaction to produce a hydrocracked effluent; and
 - passing the hydrocracked effluent to the hydroisomerization zone.
2. The process of claim 1, wherein the hydrotreated petroleum-derived oil is generated by reacting a petroleum-derived feedstock in a second hydrotreating zone separate from the first hydrotreating zone.
3. The process of claim 1, wherein the combining step includes a step of separating the combined hydrotreated renewable oil and hydrotreated petroleum-derived oil into a liquid stream and a gaseous stream.
4. The process of claim 1, wherein the combining step is conducted in a stripper.
5. The process of claim 4, wherein the stripper is a low-pressure stripper.
6. The process of claim 2, further comprising the step of revamping a refinery used for producing a fuel from a petroleum-derived oil, the refinery comprising at least one hydrodesulfurization reactor and a stripper, wherein the at least one hydrodesulfurization reactor is the second hydrotreating zone and the combining step is conducted in the stripper.

7. The process of claim 1, wherein the at least one fuel stream is selected from the group consisting of a naphtha boiling point range product stream, a kerosene boiling point range product stream, a diesel boiling point range product stream, and combinations thereof.
8. The process of claim 1, wherein the hydroisomerization conditions and hydroisomerization catalyst are selected to favour branching over cracking.
9. The process of claim 1, wherein the hydrocracking conditions and the hydrocracking catalyst are selected to favour cracking over branching.
10. The process of claim 1, wherein the hydroisomerization conditions include a temperature in a range of from 260°C to 400°C, preferably in a range of from 300°C to 380°C, and a pressure in a range of from 1 to 30 MPa, preferably in a range of from 2 to 17 MPa.
11. The process of claim 1, wherein the hydroisomerization conditions and hydroisomerization catalyst are selected to operate at a mild or moderate hydroisomerization severity.
12. The process of claim 1, wherein the hydroisomerization step is conducted with a hydroisomerization catalyst comprising a Group VIII metal and a zeolitic material.
13. The process of claim 1, wherein the hydrocracking conditions include a temperature in a range of from 260°C to 400°C, preferably in a range of from 280°C to 400°C, and a pressure in a range of from 1 to 30 MPa, preferably in a range of from 2 to 18 MPa.
14. The process of claim 1, wherein the hydrocracking step is conducted with a hydrocracking catalyst comprising a Group VIII metal.
15. The process of claim 14, wherein the hydrocracking catalyst further comprises an acidic material.
16. The process of claim 1, wherein the hydrotreating zone further comprises a separation zone for separating a product of the hydrotreating reaction into a vapor phase effluent and a liquid hydrotreated effluent.

17. The process of claim 1, wherein the renewable feedstock is selected from the group consisting of one or more bio-renewable fats and oils, liquid derived from a biomass liquefaction process, liquid derived from a waste liquefaction process, and combinations thereof.
18. The process of claim 1, further comprising the step of hydrofinishing the isomerized effluent.