

PROCESS FOR PRODUCING FUEL AND/OR CHEMICALS FROM RENEWABLE SOURCES

FIELD OF THE INVENTION

[0001] The present invention relates to the field of producing fuel and/or chemicals from renewable sources and, in particular, to a process for improving the yield of fuel and/or chemicals 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] For example, vegetable oils, oils obtained from algae, and animal fats are seen as new sources for low carbon fuel production. Also, deconstructed materials are seen as a potential source for low carbon renewable fuels materials, such as pyrolyzed recyclable materials or wood.

[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. As well, renewable feedstocks may comprise unsaturated compounds and/or oxygenates that are unsaturated compounds.

[0005] The renewable feedstocks are therefore hydrotreated to remove oxygen, sulphur, and nitrogen, as well as metals and olefins.

[0006] Typically, a bimetallic catalyst having a Group VIII metal and a Group VIB metal is used for hydrotreating. Particularly notable bimetallic catalysts are NiMo, NiW, and CoMo catalyst. A challenge for the bimetallic catalyst is that the yield of paraffins suffers by production of carbon oxides (CO and CO₂). Furthermore, the carbon oxide by-products must be treated to avoid potentially harmful effects on the environment.

[0007] Another option is to use a monometallic Group VIB metal, which has been shown to reduce the production level of carbon oxides. Reduction in carbon oxide production results in a reduced loss of carbon for desirable paraffins, for example C₁₆ and C₁₈ paraffins, instead of C₁₅ and C₁₇ paraffins.

[0008] An example of a monometallic Group VIB metal catalyst is described by Egeberg et al. (US8,912,375B2, 16 Dec 2014). In Egeberg et al., a fossil-based feedstock is coprocessed with 1 – 35 wt.% renewable feed using an unpromoted Mo catalyst having 0.1 to 20 wt.% Mo. Egeberg et al. found that an unpromoted catalyst being impregnated only with Mo (and not Co or Ni) is effective in converting vegetable oils, animal fats, fatty acids, and fatty acid methyl esters into normal paraffins. As explained therein, the unpromoted catalyst has a somewhat lower activity than traditional NiMo or CoMo catalysts. Accordingly, the potential for forming coke and other deposits that damage catalyst activity and cause increased pressure drop is reduced. By using a carrier with a bimodal pore distribution, the catalyst employed in the process is more resistant to pore plugging and minimizes increases in pressure drop and deactivation rate.

[0009] Bhan (US11,434,431B2, 6 Sept 2022) provide an improved catalyst having 5 – 25 wt.% Mo supported in a silica-alumina support having a mean pore diameter of 40 – 500 Å and a nitrogen surface area from 200 to 500 m²/g. A bio-derived feedstock is contacted with the catalyst to yield a conversion product that has an oxygen content that is reduced below the initial oxygen content of the feedstock.

[0010] A challenge of using a Mo-only catalyst for hydrotreating a renewable feedstock is that the Mo-only catalyst has a low hydrogenation strength.

[0011] Efforts have been made to find a catalyst system that addresses the challenges of the monometallic and bimetallic catalyst systems.

[0012] Abhari et al. (US8,026,401B2, 27 Sept 2011) describes conducting a hydrodeoxygenation process in two selective steps. The first step uses a low-activity catalyst,

such as Haldor Topsoe TK-709, to crack the triglycerides in the feed into a fatty alcohol and a diester. The second step requires a higher-activity catalyst, such as NiMo, to hydrodeoxygenate the fatty alcohol and the diester to paraffins. Hydrotreating of the organic oxygen-containing compounds, namely the fatty alcohol and diester, introduced to the NiMo catalyst step results in the formation of carbon oxides.

[0013] Gomes et al. (US8,507,738B2, 13 Aug 2013) relates to hydrotreating a feedstock containing between 1 and 75 wt.% biomass oil diluted in a refinery stream of petroleum hydrocarbons. The feedstock is contacted with a first monometallic catalytic bed containing only one Group VIB metal oxide, selective for hydroconversion of biomass oil into C₁₂ – C₁₈ n-paraffins, and at least one second bimetallic catalytic bed for hydrogenating unsaturated hydrocarbons and removal of heteroatomic contaminants from a refinery stream of petroleum hydrocarbons. The examples in Gomes et al. show the invention using 50% by volume of a first bed of monometallic Mo catalyst and a second bed with a bimetallic catalyst NiMo.

[0014] There remains a need for improving the catalyst activity and yield of desirable paraffins for fuel and/or chemical production.

SUMMARY OF THE INVENTION

[0015] According to one aspect of the present invention, there is provided a process for hydroprocessing a renewable feedstock, the process comprising the steps of: providing a renewable feedstock; passing the renewable feedstock to a first catalyst zone comprising a monometallic Group VIB catalyst, under hydrodeoxygenation conditions, to produce a first reaction mixture comprising a hydrotreated oil having an olefin content exceeding a thermodynamic equilibrium olefin content by a factor of at least 250 times; and passing the first reaction mixture to a second catalyst zone comprising a bimetallic catalyst having a Group VIII metal and a Group VIB metal, under hydrogenation conditions, to produce an effluent comprising a hydroprocessed oil having an olefin content proximate a thermodynamic equilibrium olefin content.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] 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:

[0017] Figs. 1 – 5 are flow diagrams illustrating embodiments of the process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The present invention provides a process for hydrotreating a renewable feedstock using a catalyst system having a first catalyst zone comprising a monometallic catalyst having a Group VIB metal and a second catalyst zone comprising a bimetallic catalyst having a Group VIII metal and a Group VIB metal.

[0019] The present invention is contrary to conventional wisdom that the hydrotreating/deoxygenation reactions require a catalyst having a sufficiently strong hydrogenation function to conduct the hydrotreating/deoxygenation reactions and, therefore, that a monometallic catalyst would not be suitable. Rather the present invention capitalizes on a conventionally understood to be negative feature of a monometallic catalyst where olefins are produced. The present invention provides for full conversion of organic oxygen in a renewable feed in the first catalyst zone, thereby producing olefins, conventionally deemed to be deleterious. An advantage of the full conversion of organic oxygen in the first catalyst zone is that C₁₆ and C₁₈ hydrocarbons are conserved without producing hardly any C₁₅ and C₁₇ hydrocarbons. The reaction mixture from the first catalyst zone comprises a hydrotreated oil having an olefin content exceeding a thermodynamic equilibrium olefin content by a factor of at least 250 times, preferably at least 500 times, more preferably at least 1000 times. Preferably, the olefin content of the hydrotreated oil has a reference olefin content of at least 125, preferably 250, more preferably 500 ppm-w.

[0020] Hydroprocessing catalysts catalyse both hydrogenation and dehydrogenation reactions. Under typical operating pressure and temperature, thermodynamics dictate that the equilibrium reaction almost completely favours paraffinic components with only a small amount, for example, a few ppm-w or less, of olefinic components in the equilibrium mixture. The strength of the hydrogenation/dehydrogenation function of the hydroprocessing catalyst and the available space velocity determine whether the reaction rates are sufficient to reach the thermodynamic equilibrium between paraffinic and olefinic components.

[0021] The olefins in the hydrotreated oil are formed during the hydrodeoxygenation reaction. As discussed below, any olefins in the renewable feedstock itself are preferably removed with a guard bed before the first catalyst zone. Accordingly, the olefins mentioned in

the oils produced in the first and second catalyst zone are intended to mean formed olefins, rather than olefins contained in the original feedstock.

[0022] The second catalyst zone is operated at conditions favouring hydrogenation. The effluent from the second catalyst zone comprises a hydroprocessed oil having an olefin content proximate the thermodynamic equilibrium olefin content. Preferably, the olefin content of the hydroprocessed oil has a reference olefin content in a range of 0.5 ppm-w to 5 ppm-w.

[0023] As used herein, “reference olefin content” is calculated herein as a ratio of the molecular weight of mercaptan to octadecane. Assuming the organic sulphur-containing molecules (predominantly mercaptans) are formed out of H_2S and olefins, the olefin concentration is estimated from the observed organic sulphur concentration in the collected effluent. As an example of the calculation, for 105 ppm-w sulphur in the effluent. With one sulphur atom in a mercaptan (MW = 32 g/mol) based on octadecene (MW=252 g/mol), the reference olefin content is calculated as 827 ppm-w ($105 \times 252 / 32$).

[0024] In the first catalyst zone, the hydrodeoxygenation of the renewable feedstock results in the formation of olefins, which drives the formation of organic sulphur compounds, namely mercaptans, disulphides and others, by sulphur recombination with the H_2S present in the reactor and the follow-on operations in the process. The inventor surprisingly discovered that substantially full conversion of organic oxygen can be attained with a first mono-metallic Group VIB catalyst and that the olefins formed in the first catalyst zone can effectively be removed in a second catalytic zone of a bimetallic catalyst resulting in a more efficient hydroprocessing step.

[0025] The present invention advantageously avoids the undesirable formation of mercaptans by recombination with the H_2S , for example, in the catalyst bed and/or in a high-pressure separation system. Preferably, the elemental sulphur content of the separated hydroprocessed oil exiting the high-pressure separation is at most 5 ppm-w, preferably at most 2 ppm-w, corresponding to a reference olefin content of at most 40 ppm-w, preferably at most 15 ppm-w. This represents a significant advantage over conventional processes, where the reference olefin content is more than 800 ppm-w.

[0026] 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.

[0027] Embodiments of process units for carrying out the process 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 and/or chemicals 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 effluent 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 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] 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.

[0030] 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 acid (TOFA), tallow, used cooking oil, yellow grease, white grease, and combinations thereof.

[0031] 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.

[0032] The renewable materials to be used as feedstock in the process of the present invention may be pre-treated to remove impurities, such as, for example, without limitation, solids, iron, chloride, phosphorus, alkali metals, alkaline-earth metals, polyethylene, and unsaponifiable compounds. Methods to remove these impurities are known to the person skilled in the art.

[0033] The process of the present invention is most particularly advantageous in the processing of feed streams comprising substantially 100% renewable feedstocks. However, in one embodiment of the present invention, renewable feedstock may be co-processed with petroleum-derived hydrocarbons. Petroleum-derived hydrocarbons include, without limitation, all fractions from petroleum crude oil, natural gas condensate, tar sands, shale oil, synthetic crude, and combinations thereof. The present invention is more particularly advantageous for a combined renewable and petroleum-derived feedstock comprising a renewable feed content in a range of from 5 wt.% to 30 wt.%. In one embodiment, the renewable feedstock is coprocessed with a heavy fraction from a petroleum refinery. For example, the petroleum-derived feedstock may be a heavy fraction from a gas oil unit.

[0034] In accordance with the present invention, the hydrotreating zone 14 has a first catalyst zone 22 and a second catalyst zone 24. The first and second catalyst zones are operated in a co-current flow through fixed bed catalysts. Each catalyst zone 22, 24 may have a single catalyst bed or multiple catalyst beds. The hydrotreating zone 14 may be comprised of a single reactor or multiple reactors. The catalyst zones 22, 24 may have different catalysts in the same catalyst bed.

[0035] In the first catalyst zone 22, the hydrotreating reaction conditions are selected to favour hydrodeoxygenation. In the second catalyst zone 24, the hydrotreating reactions are selected to favour hydrogenation. Other hydrotreating reactions including, without limitation, hydrodenitrogenation, hydrodesulphurization, hydrodearomatization, hydrodemetallization, and combinations thereof, also occur in the hydrotreating zone 14. Hydrodemetallization will be favoured in the first catalyst zone 22, while hydrodenitrogenation, hydrodesulphurization and hydrodearomatization will be favoured in the second catalyst zone 24.

[0036] The catalyst in the first catalyst zone 22 is a monometallic Group VIB catalyst. As used herein, the term “monometallic” is reference to the active metal being from Group VIB,

excluding Group VIII metals, but may include more than one Group VIB metal. Suitable Group VIB metals include Mo, W, and combinations thereof. The monometallic Group VIB catalyst may further comprise promoter metals. The monometallic catalyst may be supported or unsupported. Preferably, the monometallic catalyst is a supported catalyst. The Group VIB metal content is in a range of from 5 to 25 wt.%, preferably from 7 to 22 wt.%, more preferably from 10 to 20 wt.% based on the weight of the catalyst.

[0037] An example of a suitable monometallic Group VIB catalyst for the first catalyst zone is described in Bhan (US11,434,431B2, 6 Sept 2022).

[0038] The catalyst of the first catalyst zone 22 may be supported on a suitable carrier, selected from refractory oxides, molecular sieves, and combinations thereof. Examples of suitable refractory oxides include, without limitation, alumina, amorphous silica-alumina (ASA), 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.

[0039] The catalyst in the second catalyst zone 24 is a bimetallic Group VIII and Group VIB catalyst. As used herein, the term “bimetallic” is reference to there being an active metal from Group VIII and an active metal from Group VIB but may include more than one Group VIII metal and more than one Group VIB metal. The bimetallic catalyst may be supported or unsupported. Preferably, the bimetallic catalyst is a supported catalyst. Suitable Group VIII metals include Pd, Pt, Ni, Co, and combinations thereof. Preferably, the Group VIII metal is selected from Ni and Co. Suitable Group VIB metals include Mo, W, and combinations thereof.

[0040] The catalyst of the second catalyst zone 24 may be supported on a suitable carrier, selected from refractory oxides, molecular sieves, and combinations thereof. Examples of suitable refractory oxides include, without limitation, alumina, ASA, 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.

[0041] The monometallic and bimetallic hydrotreating catalysts are generally more active in a sulphided form as compared to an oxide form of the catalyst. Catalyst metals are often in an oxide state when charged to a reactor and preferably activated by reducing or sulphiding the metal oxide. A sulphiding procedure is used to transform the catalyst from a calcined oxide state to an active sulphided state. The 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.

[0042] The hydrotreating catalyst may be sulphided in-situ or ex-situ. In-situ sulphiding may be achieved by supplying a sulphur source, usually H_2S or an H_2S precursor (i.e., a compound that easily decomposes into H_2S 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.

[0043] Preferably, H_2S is provided to the reactor in an amount in the range of from 50 to 5,000 ppm-v, preferably from 100 to 3,000 ppm-v, more preferably from 500 to 2,000 ppm-v. The amount of H_2S provided is dependent on a number of factors, including, for example, without limitation, type and amount of catalyst metal, operating temperature, other operating conditions, in the hydrotreating step.

[0044] Preferably, the volumetric amount of catalyst of the first catalyst zone 22 is greater than the volumetric amount of catalyst in the second catalyst zone 24. More preferably, the volumetric ratio of monometallic:bimetallic catalyst is in a range of from 60:40 to 95:5, most preferably in a range of from 70:30 to 90:10. The volumetric ratio herein relates to the volume of the supported monometallic and bimetallic catalysts. The volumetric ratio excludes any volume of any guard-bed catalyst or non-catalytic trap material.

[0045] In one embodiment, the hydrotreating zone 14 further comprises a guard bed in advance of the first catalyst zone to demetallize the renewable feedstock and/or to hydrogenate any bulk olefins in the renewable feedstock. The guard bed may be low activity catalysts and/or a non-catalytic trap. 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. The metal content is typically lower in the guard bed, for example from 2.5 to 5 wt.%, and will often have a larger porosity support to trap captured metals from the renewable feedstock. Suitable carriers include refractory oxides, molecular sieves, and combinations thereof. Examples of suitable refractory oxides include, without limitation, alumina, ASA, 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.

[0046] Operating conditions in the hydroprocessing reactor include pressures in a range of from 1.0 MPaG to 20 MPaG, temperatures in a range of from 200 to 410°C and liquid hourly space velocities in a range of from 0.3 m³/m³.h to 5 m³/m³.h based on fresh feed. Preferably, the pressure is selected from a pressure in the range of 2.0 MPaG to 15 MPaG. Preferably, the temperature is in the range of from 200 to 400°C.

[0047] The ratio of hydrogen to feed supplied in the hydrotreating zone 14 is in a range of from 200 to 10,000 normal L (at standard conditions of 0°C and 1 atm (0.101 MPa)) per kg of feed. Reference herein to feed is the total of fresh feedstock excluding any diluent that may be added. Preferably, the hydrogen is added at the top of the hydrotreating zone 14.

[0048] As noted above, the process of the present invention is particularly advantageous for processes requiring a separation zone before a follow-on process. For example, without limitation, where the hydrotreated effluent is passed to a hydroisomerization zone having a noble metal catalyst, the hydrotreated effluent is typically passed to a separation zone prior to the hydroisomerization zone. In conventional processes where there is H₂S in the hydrotreater effluent, a problem arises in the separation zone when the sulphur recombines with olefins to form deleterious mercaptans.

[0049] Accordingly, in a preferred embodiment of the present invention, the hydrotreated oil from the second catalyst zone 24 is directed to a separation zone 30 for separating the product of the hydrotreating reactions into a vapor phase effluent and a liquid hydrotreated effluent 16. Where the catalyst used for hydroisomerization has a noble metal, the separation zone 30 is provided to remove or at least substantially reduce components that poison or otherwise adversely impact the hydroisomerization catalyst. Where a non-noble metal is used for hydroisomerization, the separation zone 30 is optional. Where in the hydrotreated oil is passed to a thermal cracker, such as a steam-cracker, for the production of olefins, it is desirable to separate the light ends from the liquid effluent in a separation zone 30.

[0050] When the separation zone 30 is included, the separation zone 30 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. An intermediate temperature will be understood to mean any temperature between the temperature of a hot- or cold-separator.

[0051] In addition, the separation zone 30 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 H_2S and/or carbon oxides from H_2 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 the hydrotreating zone 14.

[0052] A portion of the hydrotreated effluent 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. Recycle and quench streams may be made in a manner known to those skilled in the art. Preferably, the recycle stream is combined with the renewable feedstock. Alternatively, the recycle stream may be partitioned and added at two or more inlets to the hydrotreating zone 14. One or more quench streams are added in a manner known to those skilled in the art above catalyst beds in the first catalyst zone 22 and/or the second catalyst zone 24.

[0053] The hydrotreated effluent 16 (with or without a separation step) is passed to a hydroisomerization zone 34 under hydroisomerization conditions to cause a hydroisomerization reaction. The hydroisomerization reaction increases branching of the

paraffinic compounds resulting from the hydrotreating zone 14, thereby improving the cold flow properties of the fuel.

[0054] 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 VIB metal, preferably Mo or W.

[0055] 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.

[0056] The catalyst may be the same or different throughout the hydroisomerization zone 34. The hydroisomerization zone 34 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.

[0057] The hydroisomerization zone 34 is operated in the presence of hydrogen at a pressure in a range of from 1 MPaG to 30 MPaG and at a temperature in a range of from 260°C to 400°C. Preferably, the pressure is in a range of from 2 MPaG to 17 MPaG, 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 effluent 16. The ratio of the hydrogen gas to the liquid supplied to the hydroisomerization zone 34 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 liquid.

[0058] 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 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.

[0059] The product from the hydroisomerization zone 34 is directed to a work-up section. Various embodiments for the work-up section may be considered. For example, without limitation, the work-up section may be as described in WO2023/043792 or WO2023/043764 published 2023 March 23, incorporated by reference herein.

[0060] The work-up section includes one or more product recovery zones 36 resulting in desired product streams. For example, the embodiment of Fig. 1 illustrates an off-gas stream 42, a naphtha boiling point range stream 44, a kerosene boiling point range stream 46, a diesel boiling point range stream 48, and a heavy fraction 52. In this embodiment, the off-gas stream 42 suitably comprises C₁-C₅ hydrocarbons, while the naphtha boiling point range 44 suitably comprises C₄-C₁₂ hydrocarbons in a boiling point range of from -12°C to 204°C. The kerosene boiling point range stream 46 is preferably comprised of C₆-C₁₈ hydrocarbons having a boiling point range of from 90°C to 300°C. In one embodiment, the diesel boiling point range stream comprises C₈-C₂₆ hydrocarbons having a boiling point range of from 120°C to 400°C. In this embodiment, the heavy fraction 52 has C₁₇⁺ hydrocarbons having a boiling point greater than 250°C.

[0061] In the embodiment of Fig. 2, the heavy fraction 52 is recycled to the hydroisomerization zone 34. In the embodiments of Figs. 3 and 4, the heavy fraction is recycled to a hydrocracking zone 54 before contacting the hydrotreated effluent 16.

[0062] In a preferred embodiment, the process 10 is directed towards improving the yield of the kerosene boiling point range stream 46. 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.

[0063] In this case, as shown in Figs. 2 and 3, at least a portion of the diesel boiling point range stream 48 is recycled with the heavy fraction 52. Another portion of the diesel boiling point range stream 48 may be drawn off as a bleed stream. The product recovery zone 36 may include a further separation of the diesel boiling point range stream 48 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.

[0064] Additionally, or alternatively, the product recovery zone 36 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.

[0065] In one embodiment, as shown in Fig. 4, the diesel boiling point range hydrocarbons may be part of the heavy fraction 52 and recycled for cracking and isomerization to extinction.

[0066] The product streams and recycle options shown in Figs. 2 – 4 are examples and may be modified and/or used in other of the embodiments of Figs. 2 – 4. For example, the option of diesel boiling point range hydrocarbons being recycled to extinction as shown in Fig. 4 may be implemented in the embodiments of Figs. 2 and 3. Alternatively, a diesel boiling point range stream as shown in Figs. 2 and 3 may be drawn off the product recovery zone in the Fig. 4 embodiment, with or without a bleed stream.

[0067] As noted above, the embodiments of the product recovery zone 36 may be comprised of one or more unit operations. For example, the product recovery zone 36 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.

[0068] In the embodiments of Figs. 3 and 4, 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] 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.

[0070] 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, ASA. 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.

[0071] 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 VIB metal, preferably Mo or W.

[0072] The hydrocracking catalyst may further comprise a binder and/or carrier, such as, without limitation, silica, alumina, silica-alumina, and combinations thereof.

[0073] The hydrocracking zone 54 is operated in the presence of hydrogen at a pressure in a range of from 1 MPaG to 30 MPaG and at a temperature in a range of from 260°C to 400°C. Preferably, the pressure is in a range of from 2 MPaG to 18 MPaG, and the temperature is in a range of from 280°C to 400°C.

[0074] The hydrocracking conditions and catalyst are selected to favour cracking over branching.

[0075] In the embodiment of Fig. 3, the hydrocracking zone 54 is provided in a single-stage configuration above the hydroisomerization zone 34. In this embodiment, the heavy fraction 52 is recycled to a single stage reactor comprising both the hydrocracking zone 54 and a hydroisomerization zone 34. 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 34 where it is combined with the hydrotreated effluent 16 for isomerizing the hydrocracked effluent and the hydrotreated effluent 16 concurrently.

[0076] In the embodiment of Fig. 4, the hydrocracking zone 54 and the hydroisomerization zone 34 are provided in a two-stage configuration. In this embodiment, 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 34 where it is combined with the hydrotreated effluent 16 for isomerizing the hydrocracked effluent and the hydrotreated effluent 16.

[0077] The hydroisomerization zone 34 optionally includes a hydrofinishing zone (not shown). During the hydroisomerization step and/or depending on the feedstock used (for example, cashew oil), some aromatics and/or trace olefins may be present in the effluent of the hydroisomerization zone. In this case, the hydrofinishing step is preferably provided to reduce the aromatic content of the product stream(s).

[0078] 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, ASA, titania, silica, and combinations thereof.

[0079] Another embodiment of the present invention is illustrated in Fig. 5, wherein the hydrotreated effluent 16 is passed to a steam cracker 64 for production of olefins. Optionally, a product stream of ultra-low sulphur diesel 62 is produced with a remainder stream set to the steam cracker 64.

[0080] The hydrotreated effluent 16 and a dilution gas, preferably steam, is preheated to a temperature of 140 – 375°C at a pressure in a range of from 1 – 2 MPaG to produce a gas/liquid mixture. The preheated gas/liquid mixture is separated in a vapor-liquid separator. The separated gas is fed to a convection zone and then a radiant zone of the steam cracker 64 where the gas is pyrolyzed into a product containing olefins.

EXAMPLES

[0081] The following non-limiting examples of embodiments of the process of the present invention as claimed herein are provided for illustrative purposes only.

Comparative Example 1

[0082] In a reactor, a monometallic hydrotreating catalyst was placed. The catalyst bed was 93.75 mL of a hydrotreating catalyst comprising 14.5 wt.% Mo on ASA/alumina. The hydrotreating catalyst bed was 1:1.5 diluted with 0.2 mm silicon carbide particles. The silicon carbide particles were applied to mitigate reactor wall effects which could disturb the uniform liquid distribution over the catalyst bed cross section.

[0083] The temperature of the catalyst bed was controlled by means of an oven to operate at a temperature of 300°C.

[0084] A feedstock consisting of refined tallow was supplied to the catalyst bed at a WHSV of 1.33 g fresh oil per mL catalyst per hour. The feedstock was spiked with 0.34 wt.% SULFRZOL® as a hydrogen sulphide precursor to keep the catalyst sulphided as the sulphur concentration in the tallow was 3.6 ppm-w. The reactor was operated with recycling a liquid fraction of the hydrocarbon effluent at a volumetric ratio of 1:1 compared to the fresh feed. A gas stream comprising 100 vol% hydrogen was supplied at a gas-to-oil ratio of 875 NL/kg on a fresh feed basis. The total pressure at the reactor outlet was 75 bar (gauge).

[0085] The degree of conversion of the tallow feedstock was determined in multiple ways. The hydrocarbon liquid was analysed using pyrolysis and UV fluorescence to determine the concentration of organic oxygen and sulphur. The gaseous effluent was analysed using gas chromatography.

[0086] The conversion of organic oxygen was larger than 99% with a concentration of 900 ppm-w elemental oxygen in the effluent, while the concentration of organic sulphur was 105 ppm-w. The selectivity to the formation of carbon oxides, determined by the gas chromatography analysis of the gaseous effluent, was 3% indicating that almost all C₁₆ and C₁₈ hydrocarbons were preserved. The nature of the sulphur components was determined using two-dimensional gas chromatography with sulphur sensitive detection to confirm that sulphur in the effluent was not present in the form of hydrogen sulphide or unconverted SULFRZOL®.

Example 2

[0087] In an example of one embodiment of the present invention, Comparative Example 1 was repeated with a different catalyst package. In this case, a hydrogenation catalyst bed consisting of 68.75 mL of a hydrogenation catalyst comprising 14.5 wt.% Mo on ASA/alumina was placed above a bed of 25 mL of a conventional hydrotreating catalyst comprising 4 wt.% Ni and 15 wt.% Mo on alumina. The catalyst in the hydrodeoxygenation bed was 1:1.5 diluted with 0.2 mm diameter silicon carbide particles, while the catalyst in the hydrogenation catalyst bed was 1:1.5 diluted with 0.2 mm silicon carbide particles.

[0088] The reactor was operated at a temperature of 300°C.

[0089] In this example, the organic oxygen conversion was again larger than 99% with an elemental oxygen concentration of less than the detection limit of 300 ppm-w in the liquid effluent, while the organic sulphur concentration was 1 ppm-w. The selectivity towards formation of carbon oxides was 12%.

[0090] Surprisingly, the replacement of part of the Mo on ASA/alumina catalyst with a conventional hydrotreating catalyst with a stronger hydrogenation function improves the robustness of the process by eliminating the trace level of olefins that are typically present in the effluent of hydrotreating processes and thus preventing the recombination of hydrogen sulphide with these olefins into organic sulphur compounds like mercaptans.

[0091] 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 hydroprocessing a renewable feedstock, the process comprising the steps of:
 - providing a renewable feedstock;
 - passing the renewable feedstock to a first catalyst zone comprising a monometallic Group VIB catalyst, under hydrodeoxygenation conditions, to produce a first reaction mixture comprising a hydrotreated oil having an olefin content exceeding a thermodynamic equilibrium olefin content by a factor of at least 250 times; and
 - passing the first reaction mixture to a second catalyst zone comprising a bimetallic catalyst having a Group VIII metal and a Group VIB metal, under hydrogenation conditions, to produce an effluent comprising a hydroprocessed oil having an olefin content proximate a thermodynamic equilibrium olefin content.
2. The process of claim 1, wherein the hydrotreated oil has an olefin content exceeding a thermodynamic equilibrium olefin content by a factor of at least 500 times.
3. The process of claim 1, wherein the hydrotreated oil has a reference olefin content of at least 125 ppm-w.
4. The process of claim 1, wherein the hydroprocessed oil has a reference olefin content in a range of from 0.5 ppm-w to 5 ppm-w.
5. The process of claim 1, wherein the volumetric amount of monometallic catalyst is greater than the volumetric amount of bimetallic catalyst.
6. The process of claim 1, wherein the volumetric ratio of monometallic:bimetallic catalysts is in a range of from 60:40 to 95:5, preferably in a range of from 70:30 to 90:10.
7. The process of claim 1, further comprising the step of separating the hydroprocessed oil from vapour phase present in the effluent from the second catalyst zone.
8. The process of claim 7, wherein the separating step comprises a high-pressure separator.

9. The process of claim 7, wherein the mercaptan content of the separated oil has a reference olefin content of at most 40 ppm-w, preferably at most 15 ppm-w.
10. 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.
11. The process of claim 1, further comprising adding a petroleum-derived feedstock for co-processing with the renewable feedstock, preferably in an amount to produce a feed stream comprising from 5 to 30 wt.% renewable feedstock.
12. The process of claim 7, further comprising the step of passing the hydroprocessed oil to a hydroisomerization step.
13. The process of claim 7, further comprising the step of passing the hydroprocessed oil to a steam cracking step.