PROCESS FOR PRODUCING FUEL, BASE OILS, AND/OR CHEMICALS FROM RENEWABLE FEEDSTOCKS

FIELD OF THE INVENTION

[0001] The present invention relates to the field of producing fuel and/or chemicals from renewable feedstocks.

BACKGROUND OF THE INVENTION

[0002] The increased demand for energy resulting from worldwide economic growth and development have 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. For example, energy conservation, improvements in energy efficiency and electrification may play a role, but also 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) are 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] The metals used for hydrotreating catalysts are often produced as, and loaded in the reactors as, metal oxides. The sulphur content of renewable feeds like vegetable oil, animal fats, or wood is generally well below 1 wt.% and therefore the sulphur content in these feeds is generally too low for sulphiding the hydrotreating catalyst.

[0007] H_2S is a poisonous gas raising health concerns. Further, the gas must be compressed before it can be used in higher pressure hydroprocessing units or stored in high pressure vessels/cylinders. Storage of H_2S also represents a risk of leakage to the surrounding environment. Accordingly, sulphur additives are typically added to the feed. In the reactor, the additives are converted into hydrogen sulphide, which in turn converts the metal oxide into a metal sulphide. Sulphur additives, such as dimethyl sulphide (DMS), dimethyl disulphide (DMDS), di-tertiary nonyl polysulfide (TNPS), and SULFRZOL® are often expensive. Moreover, the additives are often produced using fossil feedstocks.

[0008] Effluent from the hydrotreating step includes hydrotreated liquid and a gas phase containing hydrogen, carbon dioxide, hydrogen sulphide, carbon monoxide, and light hydrocarbons. The effluent is then separated into liquid and offgas streams by a number of different methods. Both from an economic standpoint and an environmental view, the offgas is preferably recycled to the reaction zone. However, without treatment, the concentration of CO_2 and/or carbon monoxide will build-up, thereby reducing the hydrogen partial pressure, negatively impacting the hydrotreating reactions. It is possible to recover hydrogen by conventional separation steps, while H_2S, CO_2 and/or carbon monoxide are typically recovered together.

[0009] Offgas containing H_2S from conventional refineries is most commonly treated in a Claus unit. A Claus unit produces elemental sulphur from gaseous H_2S by first reacting with oxygen to produce sulphur dioxide and water. The sulphur dioxide then reacts with H_2S to produced elemental sulphur and water.

[00010] A challenge with using a Claus unit to react with H_2S in an offgas from a hydrotreating reactor used for treating renewable feedstocks is that there is a higher content of CO_2 in the offgas as compared to conventional petroleum feedstocks due to the oxygen content of the renewable feedstocks. With excess amounts of CO_2, the required temperatures for reaction to occur are not reached and/or excess by-products, for example carbonyl sulphide (COS), are produced. Accordingly, there is a need to find an alternative to Claus units for managing offgas streams from hydrotreating renewable feedstocks.

[00011] Janssen (US20230416614A1, 28 Dec 2023) describes a process for treating offgas from hydrotreating of renewable feedstocks. An effluent from the hydrotreating zone is separated into a liquid stream and an offgas stream. The offgas stream comprising carbon dioxide and hydrogen sulphide is passed to a biological desulfurization unit, where the hydrogen sulphide is converted to elemental sulphur. Janssen suggests that the elemental sulphur may be used to produce fungicides, fertilizers, pesticides, medicines, cosmetics, rubber products, sulphiding agent for hydrotreating, and sulphuric acid.

[00012] Marker et al. (US2009/77864A1, 26 Mar 2009) relates to an integrated process for producing diesel boiling point range fuel from renewable feedstocks and for cultivating algae and greenhouse plants. Carbon dioxide is separated from the vapour stream that was separated from the deoxygenation reaction zone. The separated carbon dioxide is passed to an algae cultivation operation. Hydrogen produced from the algae may be employed in the reaction zone for producing diesel fuel. Hydrogen sulphide may also be separated from the vapour stream and recycled to the deoxygenation reaction zone.

[00013] US7,999,143B2 (Marker et al.) describes a process for producing diesel fuel from renewable feedstocks with reduced hydrogen consumption. The process involves hydrogenating and deoxygenating a renewable feedstock. Water is added to the deoxygenation reaction to drive carbon monoxide and water to react to form hydrogen and CO_2. A gaseous effluent from an isomerization reactor is directed to a system of at least two amine absorbers to separate CO_2 carbon dioxide and H_2S from the effluent. Amine in the first amine absorber is regenerated to release CO_2 and H_2S. The released CO_2 and H_2S is passed to the second amine scrubber that contains an amine selective to H_2S, but not selective to CO_2. H_2S is recycled to the deoxygenation zone.

[00014] One challenge of relying on two amine scrubbers in series is that the H_2S released from the second amine scrubber is in a low-pressure gas stream, requiring significant compression, adding to the operating cost of the process.

[00015] There remains a need for a process for sulphiding catalysts for hydrotreating of renewable fuels in a cost-effective manner.

SUMMARY OF THE INVENTION

[00016] According to one aspect of the present invention, there is provided a process for fuel, base oil, and/or chemicals from a renewable feedstock, comprising the steps of:

pretreating a renewable feedstock to produce a pretreated feedstock; hydrotreating the pretreated feedstock to produce an effluent comprising a hydrotreated liquid and a vapour phase comprising hydrogen sulphide; separating the effluent into one or more liquid streams and one or more offgas streams, wherein at least one of the offgas streams comprises hydrogen sulphide; directing the at least one of the one or more offgas streams to a biological desulfurization unit; converting a majority of the hydrogen sulphide in the biological desulfurization unit to bio-sulphur; and recycling at least a portion of the bio-sulphur to the pretreating step.

BRIEF DESCRIPTION OF THE DRAWINGS

[00017] 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:

[00018] Figs. 1 to 3 are flow diagrams illustrating embodiments of the process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[00019] The present invention provides a process for producing fuel, base oil, and/or chemicals from a renewable feedstock. A renewable feedstock is pretreated to produce a pretreated feedstock, which is then hydrotreated. An effluent produced from the hydrotreating step includes a hydrotreated liquid and a vapour phase comprising hydrogen sulphide. The effluent is separated into one or more liquid steams and one or more offgas streams. At least one of the offgas streams comprising H_2S is directed to a biological desulphurization unit. In the biological desulfurization unit, H_2S is converted to bio-sulphur. In accordance with the present invention, at least a portion of the bio-sulphur is recycled to the pretreating step.

[00020] The bio-sulphur produced from a biological desulfurization unit is often viewed as a low- to negative-value product. Often the bio-sulphur is sent to landfill or used for producing fertilizers. Often there is an associated cost for transporting the sulphur to the landfill or to the fertilizer plant. Alternatively, bio-sulphur has been used for producing liquid sulphur by melting and purifying the sulphur in the bio-sulphur.

[00021] As noted above, there is a challenge in using a conventional Claus unit to treat off-gas from a process for producing fuels and chemicals from a renewable feedstock. In addition, the type of elemental sulphur produced in a Claus process suffers from not mixing

well with the renewable feedstock causing it to drop out of the mixture and melt. The inventors have surprisingly discovered that the bio-sulphur produced from a biological desulfurization unit is better dissolved and utilized in a renewable feedstock.

[00022] Furthermore, the process of the present invention provides an integrated process for managing a by-product of the process and reusing it.

[00023] The process of the present invention is important for the energy transition and can improve the environment by producing energy and/or chemicals from renewable sources, and in particular from degradable waste sources. By recovering the bio-sulphur from the biological desulfurization unit and reusing it in the hydrotreating step, the impact of waste sulphur on the environment is reduced. Further, by reducing or eliminating the need for conventional desulfurizing agents, the environmental impact caused by production of those desulfurizing agents is reduced. In a preferred embodiment, the CO_2-rich gas stream is produced, captured and stored and/or sequestered, thereby lowering the carbon intensity of processes for producing fuel and/or chemicals from renewable sources.

[00024] 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, base oils, 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.

[00025] 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, camelina oil, 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.

[00026] 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.

[00027] 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. The types and relative amounts of impurities will be dependent on the type of feedstock and quality thereof. Certain of the impurities, for example, unsaponifiable compounds, may be tolerated in the processing thereof. However, as required, these impurities are removed from the renewable feedstock before being introduced to the process of the present invention. Examples of impurities that tend to be targeted for removal from renewable feedstocks include nitrogen, inorganic and organic chlorides, metals, and phosphorous.

[00028] The process of the present invention is particularly advantageous in the processing of 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 petroleum-derived hydrocarbons typically have a sulphur content such that the addition of a sulphur additive is not needed. It will be understood by those skilled in the art that the sulphur content of petroleum-derived hydrocarbons will be dependent on the source. The process of the present invention may be advantageous when the combined renewable and petroleum-derived feedstock has a sulphur content less than 0.3 wt.% S, preferably less than 0.2 wt.% S.

[00029] Referring now to Fig. 1, the renewable feedstock 12 is fed to a pretreating unit 14. The pretreating unit 14 is selected from the group consisting of washing units, adsorption units, filtration units, nanofiltration units, evaporators, and combinations thereof.

[00030] One example of a suitable pretreating unit 14 is described in Toukoniitty et al. (US11,427,782B2, 30 Aug 2022), which uses a silica-based adsorbent, a metal chloride adsorbent or a metal oxide adsorbent to adsorb chloride from a renewable feed. An example of a nanofiltration pretreating unit 14 using is disclosed by den Boestert et al. (WO2022/129335A1, 23 Jun 2022).

[00031] Suitable washing fluids include, without limitation, water, chelating agents, acids, preferably weak acids, caustics, and combinations thereof. A preferred acid is citric acid. A preferred chelating agent is EDTA. Suitable adsorbents include, without limitation, silicates, silica hydrogels, treated and/or activated clays (e.g., acid-washed clays, bleaching earth, and the like), diatomaceous earth, and combinations thereof. In a preferred embodiment, the washing unit is followed by an adsorption unit. In a preferred embodiment, the adsorption unit preferentially adsorbs water-soluble polar contaminants over fat-soluble lipophilic species.

[00032] The pretreated feedstock is sent to a hydrotreating zone 16, where the pretreated feedstock 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. The reactions in the hydrotreating zone 16 are catalytic reactions. The hydrotreating zone 16 may be single-stage or multi-stage, and may be operated in a slurry, moving bed, fluidized bed, and/or fixed bed operation. In the case of a fixed bed operation, a reactor in the hydrotreating zone 16 may have a single catalyst bed or multiple catalyst beds. The hydrotreating zone 16 may be comprised of a single reactor or multiple reactors. The hydrotreating zone 16 may be operated in a co-current flow, counter-current flow, or a combination thereof. Preferably, the hydrotreating zone 16 is operated in a co-current flow.

[00033] The catalyst may be the same or different throughout the hydrotreating zone 16. The hydrotreating zone 16 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.

[00034] In one embodiment, the hydrotreating zone 16 further comprises 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.

[00035] The hydrotreating zone 16 may also include one or more guard beds (not shown) for capturing and/or reacting with remaining contaminants in the feed 12. The hydrotreating zone 16 may also include one or more catalyst beds for hydroisomerization, selective cracking and/or hydrodearomatization.

[00036] 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 are activated by sulphiding the metal oxide. Preferably, the hydrotreating catalyst comprises catalytically active metals of Group VIII and/or Group VIB, including, without limitation, Ni, Co, Mo, W, and combinations thereof.

[00037] As discussed above, hydrotreating catalysts are generally more active in a sulphided form as compared to an oxide form of the catalyst. Because renewable feedstocks generally have a low sulphur content, a sulphiding agent is typically added to the feed or hydrotreating zone to maintain the catalyst in a sulphided form.

[00038] In accordance with the present invention, the catalyst in the hydrotreating zone 16 is sulphided by the addition of recycled bio-sulphur 26 from a biological desulfurization unit 18, as will be discussed in more detail below.

[00039] At start-up, bio-sulphur 26 produced in a biological desulfurization unit from another process, or an earlier process may be used in the manner described herein. Alternatively, the catalyst may be initially sulfided with a conventional sulphiding agent such as such as DMS, DMDS, TNPS, and SULFRZOL®. Where a conventional sulphiding agent is used to initially sulphide the catalyst, feed of the conventional sulphiding agent would then be discontinued when the recycled bio-sulphur stream is used.

[00040] 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.

[00041] The hydrotreating metals may be used in bulk metal form, or the metals may be supported on a carrier. 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.

[00042] Operating conditions in the reactors of the hydrotreating zone 16 include pressures in a range of from 1.0 MPa to 20 MPa, temperatures in a range of from 200 to 410°C and liquid hourly space velocities in a range of from 0.3 $m^3/m^3.h$ to 5 $m^3/m^3.h$ based on fresh feed. Preferably, the pressure is selected from 2.0 MPa to 15 MPa. Preferably, the temperature is in the range of from 200 to 400°C, more preferably from 240 to 390°C, most preferably from 260 to 385°C.

[00043] The ratio of hydrogen to feed supplied in the hydrotreating zone 16 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, preferably from 500 to 8,000 NL/kg, more preferably from 800 to 3,000 NL/kg. Reference herein to feed is the total of fresh feedstock excluding diluent.

[00044] The hydrotreating step produces an effluent comprising a hydrotreated liquid and a vapour phase comprising hydrogen sulphide. Other components may be present in the vapour phase including, without limitation, hydrogen, carbon oxides (e.g., CO_2 and/or CO), water, nitrogen, NH_3, NO_2, C1 – C10 compounds, and combinations thereof. Depending at least on the catalyst, feed and operating conditions, the relative amounts of components in the vapour phase may be different or change over time. Typically, the vapour phase will include H_2S and CO_2.

[00045] The effluent from the hydrotreating zone 16 is directed to one or more separation units 20 to separate the product into one or more offgas streams 22 and one or more liquid streams 24. Examples of suitable embodiments of the separation units, without limitation, are disclosed in Janssen (US20230416614A1, 28 Dec 2023).

[00046] A portion of the one or more liquid streams 24 may be recycled to be used as a diluent and/or a quench stream between catalyst beds in a reactor of the hydrotreating zone 16, for example as depicted in Fig. 3. Where the one or more separation units 20 includes a hot-separator, an advantage of recycling a portion of a liquid stream from the hot-separator is that operating costs associated with pumping and/or heating can be reduced. Alternatively, or in addition, feedstock and/or hydrogen feed streams to a reactor in the hydrotreating zone 16 may be staged to two or more injection ports in each of one or more reactors of the hydrotreating zone 16.

[00047] At least one of the one or more offgas streams 22 containing H_2S is directed to a biological desulfurization unit 18. Other treated gas streams (not shown) may be generated in the separation unit 20 of the process of Fig. 1, including, for example, a hydrogen-enriched stream, a fuel-gas enriched stream, carbon monoxide, and combinations thereof.

[00048] Where the offgas stream 22 containing H_2S contains CO_2, the relative concentrations of H_2S and CO_2 in the offgas stream are dependent on the feedstock and the process conditions selected for a desired product. Where the offgas stream 22 containing H_2S does not contain CO_2, CO_2 may be added to the offgas stream 22 or directly to the biological desulfurization unit 18. Preferably, the concentration of H_2S in the offgas stream is in a range from 50 to 5000 ppmv, more preferably in a range from 100 to 3000 ppmv, most preferably from 500 to 2000 ppmv. Preferably, the concentration of CO_2 in the offgas stream is in a range from 0.05 to 15 vol.%, more preferably from 0.2 to 10 vol.%, most preferably from 1 to 5 vol.%. The volumetric ratio of CO_2:H_2S in the offgas stream is in a range of from 500:1 to 1:1, preferably in a range from 200:1 to 3:1, more preferably in a range from 100:1 to 5:1, even more preferably in a range from 50:1 to 7:1.

[00049] The biological desulfurization unit 18 includes one or more bioreactors having sulphur-oxidizing microorganisms. Suitable microorganisms include, without limitation, sulphide-oxidizing bacteria selected from *Halothiobacillus*, *Thioalkalimicrobium*, *Thioalkalispira*, *Thioalkalibacter*, *Thioalkalivibrio*, genetically modified bacteria, and combinations thereof. The one or more bioreactors may be operated in an anaerobic mode, an aerobic mode, or a combination thereof. The microorganisms may be provided in suspension, immobilized on a suitable support, provided as a sludge blanket or film, and combinations thereof.

[00050] The biological desulfurization unit 18 may be a THIOPAQ® O&G unit, available from Paqell B.V. (Utrecht, NL). Examples of suitable desulfurization units are described, for example, in US 10,543,458B2 (Klok et al.) and US9,902,975B2 (Klok et al.).

[00051] The biological desulfurization unit 18 converts a majority of the H_2S to bio-sulphur 26 and yields one or more treated gas streams 28. Preferably, from 90 to 100 mol% of the H_2S is converted to bio-sulphur. More preferably, from 95 to 100 mol% of the H_2S is converted to bio-sulphur. Preferably, less than 5 mol% of the H_2S is converted to other sulphur compounds such as sulphates and thiosulfates. Treated gas streams may include, for example, a CO_2 stream, a fuel gas stream, and/or a hydrogen-rich gas stream. The CO_2 stream is preferably further processed for storage and/or sequestration.

[00052] One embodiment of the bio-sulphur 26 produced in the biological desulfurization unit 18 is described in a Safety Data Sheet for THIOPAQ® Sulphur dated 2008-10-09 (revised 2018-01-17). It will be understood by those skilled in the art that the water content of the bio-sulphur 26 will be affected by the components of the biological desulfurization unit 18 and the operating conditions, which may also be impacted by the environmental conditions, especially temperature, under which the biological desulfurization unit 18 is operated. For example, if the biological desulfurization unit 18 includes a decanter centrifuge for separating the bio-sulphur 26 from the effluent of the bioreactor, the resulting bio-sulphur 26 may have a solids content of about 60 wt.%. However, if the biological desulfurization unit 18 includes a settling tank for separating the bio-sulphur 26 from the effluent of the bioreactor, the resulting bio-sulphur 26 may have a solids content of about 40 wt.%.

[00053] The bio-sulphur 26 has a morphology that is different from a conventional sulphur produced by a Claus process. In the Claus process, sulphur is recovered as a liquid, which is then solidified. The solidified sulphur is then crushed into particles for use. The crushed particles have a relatively low surface area compared to the bio-sulphur 26 recovered in a biological desulfurization unit 18. The bio-sulphur 26 has been found to dissolve more effectively in the feedstock 12 as compared to Claus sulphur. Without being bound by theory, it is believed that the bio-sulphur 26 dissolves and/or is suspended more effectively in the feedstock 12 because of the relatively higher surface area, improved wetting of the bio-sulphur surface, a morphology having a higher surface area (e.g., crystal structure having a high aspect ratio), and/or a lower packing density as compared to Claus sulphur.

[00054] In addition, the bio-sulphur 26 is more easily transported pneumatically, as compared to Claus sulphur, because it does not clog piping and related equipment because there is little static charge build-up, loosely packed particles, and reduced bridge-building in storage vessels.

[00055] The bio-sulphur 26 has a density in a range of from 1.3 to 1.5 g/cm^3. In contrast, sulphur produced via a Claus process has a density of about 2 g/cm^3. The density will be understood to mean density as measured at SATP (Standard Ambient Temperature and Pressure), namely 25°C, 101 kPa.

[00056] The bio-sulphur 26 has an alkali-metal content in a range of from 0.5 to 4.0 wt.% (calculated as elemental alkali metal on a dry weight basis). The alkali-metal may be present as an ionic species, a salt, a complex, and combinations thereof. The alkali-metals of

particular interest are sodium and potassium. The recited alkali-metal content in a range of from 0.5 to 4.0 wt.% is a total of all the alkali metals, including sodium, potassium, and/or other alkali metals.

[00057] When the renewable feedstock 12 is mixed with the bio-sulphur 26 before the pretreating is treated in the pretreating unit 14, the alkali metal is removed to an acceptable level. The acceptable level of alkali metal will be determined for a particular process, pretreatment unit, feedstock composition, dilution of feedstock, catalyst type(s), guard bed(s), and the like. An example of an acceptable level is a maximum of 5 ppmw, preferably a maximum of 2 ppmw, based on the feedstock including any diluting agent and calculated as elemental alkali metal on a dry weight basis.

[00058] The hydrogen-rich gas stream from the biological desulfurization unit 18 is preferably recycled to the hydrotreating zone 16 and/or a separation unit 20.

[00059] The one or more separation units 20 include, 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, 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, and 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 pressure of a hydrotreating reactor in the hydrotreating zone 16, 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 the hydrotreating reactor in the hydrotreating zone 16 pressure or 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 lower than a preceding reactor in the hydrotreating zone 16 temperature, suitably sufficiently above water dew point (e.g., ≥10°C, preferably ≥20°C, above the water dew point) and sufficiently greater than salt deposition temperatures (e.g., ≥10°C, preferably ≥20°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 16. 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.

[00060] In addition, the one or more separation units 20 may include, for example, without limitation, an amine scrubber, a pressure swing adsorption unit, a caustic wash, and combinations thereof.

[00061] In one embodiment, the liquid effluent 24 from the one or more separation units 20 is fractionated into two or more product streams for components or as starting materials of fuels, base oils, and/or chemicals. In another embodiment, the liquid effluent 24 is further processed, for example by hydroisomerization, hydrocracking, selective cracking, steam cracking, hydrodearomatization, and combinations thereof to produce components or as starting materials of fuels, base oils, and/or chemicals. In a preferred embodiment, offgas from these further processing reactors/zones may be combined with the offgas stream 22 from the one or more separation units 20.

[00062] Fig. 2 illustrates several embodiments of the present invention 10. It will be understood that each alternative embodiment presented therein may be used independently or in combination with another alternative embodiment in the present invention 10 presented herein.

[00063] In a preferred embodiment, the renewable feedstock 12 is heated with heater 32 prior to being directed to the pretreating unit 14. The renewable feedstock 12 is preferably heated to a temperature in a range of from 100 to 130°C.

[00064] In a preferred embodiment, the bio-sulphur 26 is mixed with renewable feedstock 12 before pretreating the feedstock 12. The mixing may be accomplished in a manner known to those skilled in the art. An example of a suitable mixer is a static inline mixer. Preferably, the bio-sulphur 26 is mixed with the renewable feedstock 12 that has been heated.

[00065] The amount of bio-sulphur 26 to be added to the renewable feedstock 12 is selected to achieve a sulphur concentration in the renewable feedstock 12 in a range of from 50 to 7,500 ppmw. The amount of bio-sulphur 26 added to the renewable feedstock is in an amount in a range of from 100 to 10,000 ppmw, preferably from 1,000 to 3,000 ppmw.

[00066] Fig. 2 also illustrates an embodiment for integrating a steam cracker 34 for the production of olefins. A portion of the pretreated feedstock with recycled bio-sulphur 26 may be directed to the steam cracker 34 as a source of sulphur. Alternatively, or in addition, a portion of the one or more liquid streams 24 from the separation units 20 may be directed to the steam cracker 34. In this embodiment, as one example, a portion of the one or more liquid streams 24 may be fractionated (not shown) to separate an ultra-low sulphur diesel

product for use as a fuel, with the remainder of the one or more liquid streams 24 being directed to the steam cracker 34 to produce olefins.

[00067] An advantage of providing a portion of the pretreated feedstock to the steam cracker 34 is that the sulphur in the pretreated feedstock is converted to H_2S in the steam cracker 34 to protect the metal components of the steam cracker 34 and associated piping, valves, and the like from corrosion.

[00068] With respect to the biological desulfurization unit 18, Fig. 2 illustrates one embodiment having an adsorption column 36 and a bioreactor 38. One or more of the offgas streams 22 is fed to the absorption column 36. Preferably, the liquid sorbent 42 is fed to the absorption column 36 in a counter-current flow relative to the offgas stream 22.

[00069] The liquid sorbent 42 is preferably a liquid alkaline sorbent capable of absorbing H_2S and, preferably, CO_2. More preferably, the liquid sorbent 42 is selected from sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, and combinations thereof. A hydrogen-containing offgas stream 28′, depleted in H_2S and CO_2 is obtained from the adsorption column 36. In one or more embodiments, the hydrogen is compressed and recycled to the hydrotreating zone 16, the separation units 20 (e.g., stripper, integrated stripper, and/or hot high-pressure separator), and/or reactor for further processing (e.g., hydroisomerization reactor 54 (illustrated in Fig. 3), hydrocracker, selective cracking bed/zone, hydrodearomatization bed/zone, and combinations thereof). In other embodiments, the hydrogen-containing offgas stream 28′ is directed to a reforming unit.

[00070] A stream from the absorption column 36 containing the liquid sorbent 42, now loaded with H_2S and, preferably, CO_2 from the offgas stream 22, is directed to one or more bioreactors 38. Microorganisms in the bioreactor 38 convert sulphides into bio-sulphur 26.

[00071] A liquid product stream from the bioreactor 38 is passed to a separator 44 to separate precipitated solid bio-sulphur 26. The separator 44 may be a settling tank, a decanter centrifuge, a filter press, or a combination thereof. As mentioned above, it will be understood by those skilled in the art that the water content of the bio-sulphur 26 will be affected by the components of the biological desulfurization unit 18 and the operating conditions, which may also be impacted by the environmental conditions, especially temperature, under which the biological desulfurization unit 18 is operated.

[00072] Fig. 3 illustrates several embodiments of the present invention 10. It will be understood that each alternative embodiment presented therein may be used independently

or in combination with another alternative embodiment of the present invention 10 as presented herein.

[00073] In one embodiment of Fig. 3, the bio-sulphur 26 is passed to a dryer 46 before being combined with the renewable feedstock 12. Preferably, the bio-sulphur 26 is dried to a solids content in a range of from 60 to 90 wt.%. More preferably, the bio-sulphur 26 is dried to a solids content in a range of from 70 to 90 wt.%.

[00074] Fig. 3 illustrates an embodiment of the biological desulfurization unit 18 having an adsorption column 36, an anaerobic bioreactor 38′, an aerobic bioreactor 38″, and a separator 44. In an anaerobic mode of operation, H_2S is selectively converted to bio-sulphur 26 with little to no production of sulphates. In the embodiment of Fig. 3, microorganisms from the anaerobic bioreactor 38′ are regenerated in the aerobic bioreactor 38″. An oxygen-containing stream 48, for example air, is sparged into the aerobic bioreactor 38″.

[00075] Fig. 3 also illustrates an embodiment of the present invention 10 having a pressure swing adsorption (PSA) unit 20′ in the one or more separation units 20. The offgas stream from another separation unit 20 is directed to the PSA unit 20′ to separate a hydrogen-enriched stream from an offgas stream 22 containing CO_2 and H_2S. The hydrogen-enriched stream is preferably compressed in compressor 52 to recycle hydrogen to the hydrotreating zone 16 and/or another processing unit.

[00076] Fig. 3 further illustrates an embodiment showing integration of the hydrotreating zone 16 with a hydroisomerization reactor 54. At least a portion of the one or more liquid streams 24 from the separation units 20 is fed to the hydroisomerization reactor 54.

[00077] Paraffinic hydrocarbons in the hydrotreated liquid are isomerized in the hydroisomerization reactor 54 using a suitable isomerization catalyst including, without limitation, Group VIII metals, especially platinum and/or palladium, supported on a refractory oxide and/or a molecular sieve.

[00078] The isomerized liquid product is passed to a work-up section 56 that preferably includes a separator and one or more product strippers and/or fractionators to remove an offgas stream from the isomerized liquid product and further products having different boiling point ranges, including, diesel, naphtha, and jet fuels.

[00079] In the embodiments of Figs. 1 – 3, the feed 12 is illustrated as being fed to the top of a reactor in the hydrotreating zone 16. However, the feed 12 may be divided and fed

to the hydrotreating zone 16 at two or more inputs at the top and/or at multiple points (not shown), for example, between catalyst beds, along the length of a reactor in the hydrotreating zone 16.

[00080] Fig. 3 also illustrates two optional embodiments wherein a portion of the one or more liquid streams 24 is recycled to the feed 12 as a diluent. The volumetric ratio of diluent to fresh feed 12 is preferably in a range of from 1:1 to 30:1. In another optional embodiment, a portion of the one or more liquid streams 24 is provided as one or more quench streams to a reactor in the hydrotreating zone 16. The quench stream is used to control temperature in the hydrotreating zone 16 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 a reactor of the hydrotreating zone 16.

EXAMPLES

[00081] The following non-limiting examples of embodiments of the process of the present invention as claimed herein are provided for illustrative purposes only.

EXAMPLE 1

[00082] The purpose of this example was to determine whether the bio-sulphur from biological desulfurization is soluble in soybean oil. Soybean oil was selected as being representative of the range of renewable feedstocks mentioned above.

[00083] Bio-sulphur was added at a concentration of 5 wt.% to a beaker holding 300 g soybean oil. The oil mixture was heated to 100°C and stirred. The mixture was then allowed to cool to ambient temperature. The test was repeated with 5 wt.% bio-sulphur in 300 g soybean oil at a temperature of 120°C. Once cooled, the clear top layer of the mixture was sampled and tested for sulphur concentration.

[00084] It was observed that a layer of sediment was present in the cooled beaker. Accordingly, the example was repeated with 0.5 wt.% bio-sulphur in soybean oil. There was no noticeable sediment in the beaker after the mixture was cooled to ambient temperature.

[00085] A comparative test was conducted with 0.5 wt.% Claus sulphur. It was observed that the Claus sulphur sank to the bottom of the beaker and melted.

[00086] The results are shown in Table 1.

TABLE 1

Sample	S Concentration (ppmw)
Soybean Oil	8
5 wt.% bio-sulphur in soybean oil heated to 100°C	8
5 wt.% bio-sulphur in soybean oil heated to 120°C	7500
0.5 wt.% bio-sulphur in soybean oil heated to 120°C for 2 hours	4460
0.5 wt.% bio-sulphur in soybean oil heated to 120°C for 8 hours	4490

[00087] Without being bound by theory, it is believed that the structure of the bio-sulphur provided the improved result as compared to Claus sulphur. It is believed that the S8 structure of the bio-sulphur was opened at 120°C, as compared to Claus sulphur melting and dropping out of solution.

EXAMPLE 2

[00088] Autoclave experiments were conducted with soybean oil doped with bio-sulphur to test the efficacy of sulphiding the catalyst.

[00089] 3 grams of soybean oil and 0.5 wt.% bio-sulphur were added to the autoclave together with 3 grams of non-sulphided NiMo catalyst (tests 1 – 4). Test 6 was conducted to provide a comparison with no catalyst added. Tests 5 and 7 were conducted to provide a comparison with conventional SULFRAZOL® as sulphiding agent. The temperature of the autoclave was increased from ambient temperature in the laboratory to a temperature in a range of 200°C to 320°C, as shown in Table 2, in stages to simulate a catalyst sulphiding step in a hydrotreating reactor. The temperature was maintained at the temperature indicated in Table 2 for 12 hours at a hydrogen partial pressure of 70 bar.

[00090] The temperatures were selected in view of known decomposition temperatures for DMDS and SULFRZOL®, specifically 200°C and 160°C, respectively. The decomposition temperatures indicate the temperature at which the sulphiding agent activates the catalyst. The results in Table 2 demonstrate that bio-sulphur is expected to have the same decomposition mechanism as conventional sulphiding agents.

[00091] During the test, the hydrogen partial pressure was observed to drop. After each test, the amount of sulphur remaining in the oil was measured, as shown in Table 2. No measurable sulphur was found and no H_2S was found to be generated in Tests 1 – 4, indicating that the bio-sulphur was consumed by catalyst sulphiding. Likely, the hydrogen partial pressure was not high enough to create H_2S. Tests 6 and 7 without catalyst show

sulphur remained in the oil, further providing evidence that the catalyst was sulphided in Tests 1 – 4.

TABLE 2

Test	Isothermal Temperature (°C)	Catalyst	Sulphur	Sulphur in oil after test
1	200	3g NiMo	Bio-Sulphur	
2	240	3g NiMo	Bio-Sulphur	
3	280	3g NiMo	Bio-Sulphur	
4	320	3g NiMo	Bio-Sulphur	
5	320	3g NiMo	SULFRAZOL®	1000
6	320	-	Bio-Sulphur	3650
7	320	-	SULFRAZOL®	4860

[00092] 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.

CLAIMS

1. A process for producing fuel, base oil, and/or chemicals from a renewable feedstock, comprising the steps of:

pretreating a renewable feedstock to produce a pretreated feedstock;

hydrotreating the pretreated feedstock to produce an effluent comprising a hydrotreated liquid and a vapour phase comprising hydrogen sulphide;

separating the effluent into one or more liquid streams and one or more offgas streams, wherein at least one of the offgas streams comprises hydrogen sulphide;

directing the at least one of the one or more offgas streams to a biological desulfurization unit;

converting a majority of the hydrogen sulphide in the biological desulfurization unit to bio-sulphur; and

recycling at least a portion of the bio-sulphur to the pretreating step.

2. The process of claim 1, wherein the bio-sulphur is dried prior to the recycling step.

3. The process of claim 2, wherein the bio-sulphur is dried to a solids content in a range of from 60 to 90 wt.%.

4. The process of claim 1, wherein the bio-sulphur has a density in a range of from 1.3 to 1.5 g/cm^3.

5. The process of claim 1, wherein the bio-sulphur has an alkali-metal content in a range of from 0.5 to 4.0 wt.% (calculated as elemental alkali metal content on a dry weight basis).

6. The process of claims 1 or 2, wherein the pretreating step further comprises the steps of heating the renewable feedstock and mixing the bio-sulphur with the heated renewable feedstock.

7. The process of claim 6, wherein the renewable feedstock is heated to a temperature in a range of from 100 to 130°C.

8. The process of claim 1, wherein the bio-sulphur is added to the renewable feedstock in an amount in a range of from 100 to 10,000 ppmw S, preferably in a range of from 1,000 to 3,000 ppmw S.

9. The process of claim 1, wherein the hydrotreating step is conducted with a catalyst comprising a catalytically active amount of a metal, or metal sulphides, selected from the group consisting of Group VIII, Group VIB and combinations thereof.

10. The process of claim 1, wherein from 90 to 100 mol% of the hydrogen sulphide is converted to bio-sulphur.

11. The process of claim 1, wherein the biological desulfurization unit comprises an absorption column, a bioreactor, and a separator.

12. The process of claim 1, wherein the pretreating step comprises a pretreater selected from the group consisting of washing units, adsorption units, filtration units, nanofiltration units, ultrafiltration units, evaporators, and combinations thereof.

13. The process of claim 1, wherein the separating step comprises directing the effluent to one or more separator units, the separator unit selected from the group consisting of a hot high-pressure separator, a hot low-pressure separator, an intermediate high-pressure separator, an intermediate low-pressure separator, a cold high-pressure separator, a cold low-pressure separator, a stripper, an integrated stripper, and combinations thereof, and optionally an amine separator, a pressure swing adsorption unit, a caustic wash, and combinations thereof.

14. The process of claim 1, further comprising the step of directing a portion of the one or more liquid streams to a steam cracker for the production of olefins.

15. The process of claim 1, further comprising the step of directing a portion of the pretreated feedstock having the recycled bio-sulphur to a steam cracker for the production of olefins.