

Title: Method for co-production of aviation fuel and diesel

Conversion of oxygenates such as renewables in hydroprocessing has so far been focused on making diesel, since the paraffins corresponding to the typical fatty acids of biological materials such as vegetable oils and animal fats (C14, C16 and C18) typical boil from 250°C to 320°C, corresponding well with typical diesel products boiling from 150°C to 380°C. Jet fuel products require a boiling range of 120°C to 300°C, which means that an amount of the heavy part of paraffins from renewable feedstocks needs to be converted into lighter materials to produce only jet fuel. The present disclosure relates to a process having a high yield of a mix of liquid transportation fuels, especially renewable diesel and renewable jet fuel meeting typical product requirements by selectively converting the heavy material to lighter material.

Summary

In an aspect of the present disclosure, there is provided a process for production of a hydrocarbon fraction suitable for use as jet fuel from an oxygenate feedstock, comprising the steps of

- a. combining the feedstock with an amount of a liquid diluent to form a combined feedstock, directing said combined feedstock to contact a material catalytically active in hydrodeoxygenation (HDO) under hydrotreating conditions to provide a hydrodeoxygenated intermediate product,
- b. separating said hydrodeoxygenated intermediate product in at least two fractions including a vapor fraction and a liquid fraction,
- c. optionally providing at least an amount of said liquid fraction as said liquid diluent,
- d. directing at least an amount of said liquid fraction to contact a material catalytically active in isomerization (ISOM) under isomerization conditions to provide an isomerized intermediate product,
- e. directing at least an amount of said isomerized intermediate product and a stream comprising sulfur to contact a material catalytically active in hydrocracking (HDC) under hydrocracking conditions to provide a hydrocracked intermediate product, and

f. fractionating said hydrocracked intermediate product providing at least said hydrocarbon fraction suitable for use as jet fuel.

In another aspect of the present disclosure, there is provided a process plant for production of a hydrocarbon fraction suitable for use as jet fuel from a feedstock being a renewable feedstock or an oxygenate feedstock, said process plant comprising a hydrodeoxygenation section (HDO), a separation section (SEP), an isomerization section (ISOM), a hydrocracking section (HDC) and a fractionation section (FRAC), said process plant being configured for

a. directing the feedstock and a liquid diluent to the hydrodeoxygenation section (HDO) to provide a hydrodeoxygenated intermediate product,

b. separating said hydrodeoxygenated intermediate product in a vapor fraction and a liquid fraction in said separation section (SEP),

c. directing at least an amount of said hydrodeoxygenated intermediate product to contact a material catalytically active in isomerization (ISOM) under isomerization conditions providing an isomerized intermediate product, and

d. directing at least an amount of said isomerized intermediate product in a stream comprising sulfur to contact a material catalytically active in hydrocracking (HDC) under hydrocracking conditions to provide the hydrocracked intermediate product,

e. fractionating said isomerized intermediate product in said fractionation section (FRAC) to provide at least a hydrocarbon fraction suitable for use as jet fuel.

Description

During hydrotreatment of renewable feedstocks in a unit designed for making diesel, an amount of jet fuel is often also produced. However, there is an interest in making a flexible and well controlled conversion from the intermediate products of renewable feedstocks boiling mainly in the diesel range to jet fuel products, which requires significant conversion.

The standard controlling the quality of jet fuel originating from hydroprocessed esters and fatty acids is ASTM D7566, A2.1, which inter alia specifies the boiling point curve

and composition. Most of these properties can be easily met by hydrotreating and fractionation. However, special care need to be taken to meet the freezing point (FP) requirement of max -40°C and the total aromatics content of max 0.5%wt. In addition, the standard requires an amount of low boiling product by requiring T_{10} , i.e. the temperatures below which 10% boils, to be below 205°C. The final boiling point (FBP) is specified as 300°C, according to ASTM D86, which means that all material boiling above 300°C needs to be converted into lighter components to fall into the jet fuel range.

Now according to the present disclosure it is proposed to carry out combined production of diesel and jet fuel in a two-stage configuration, where the feed is hydrodeoxygenated in the first stage, and after removal of sour gases the product is isomerized in the presence of a noble metal isomerization catalyst and after addition of a sulfur donor hydrocracked in the presence of a sulfided base metal isomerization catalyst and finally

fractionated. By this process, isomerization may be carried out on a selective noble metal catalyst, resulting in specific reduction of freezing point, while hydrocracking may be carried out on the isomerized product with a less expensive base metal catalyst, which may also function as a hydrodearomatization catalyst. If the amount of aromatics is too high, a hydrodearomatization catalyst may also be provided for this purpose.

In the following the term stage shall be used for a section of the process, in which no separation is performed.

In the following the abbreviation ppm_{molar} shall be used to signify atomic parts per million.

In the following the abbreviation ppm_v shall be used to signify volumetric parts per million, e.g. molar gas concentration.

In the following the abbreviation wt/wt% shall be used to signify weight percentage.

In the following the abbreviation vol/vol% shall be used to signify volume percentage for a gas.

In the following the term renewable feedstock or hydrocarbon shall be used to indicate a feedstock or hydrocarbon originating from biological sources or waste recycle. Recycled waste of fossil origin such as plastic shall also be construed as renewable.

In the following the term hydrodeoxygenation shall be used to signify removal of oxygen from oxygenates by formation of water in the presence of hydrogen, as well as removal of oxygen from oxygenates by formation of carbon oxides in the presence of hydrogen.

In the following, the term topology of a molecular sieve is used in the sense described in the "Atlas of Zeolite Framework Types," Sixth Revised Edition, Elsevier, 2007, and three letter framework type codes are used in accordance herewith.

- A broad aspect of the present disclosure relates to a process for production of a hydrocarbon fraction suitable for use as jet fuel from a feedstock being oxygenate feedstock, comprising the steps of combining the feedstock with an amount of a liquid diluent, to form a combined feedstock (104), directing said combined feedstock (104) to contact a material catalytically active in hydrodeoxygenation under hydrotreating conditions to provide a hydrodeoxygenated intermediate product, separating said hydrodeoxygenated intermediate product in at least two fractions including a vapor fraction and a liquid fraction, optionally providing at least an amount of said liquid fraction as said liquid diluent, directing at least an amount of said liquid fraction to contact a material catalytically active in isomerization under isomerization conditions to provide an isomerized intermediate product, directing at least an amount of said isomerized intermediate product and a stream comprising sulfur to contact a material catalytically active in hydrocracking under hydrocracking conditions to provide a hydrocracked intermediate product, and fractionating said hydrocracked intermediate product providing at least said hydrocarbon fraction suitable for use as jet fuel, with the associated benefit of such a process being well suited for efficiently converting the upper-boiling point of a renewable feedstocks to a lower boiling product, such as non-fossil kerosene. In addition to said jet fuel, diesel and other hydrocarbons may also be produced.
- 20 In a further embodiment said hydrocarbon fraction suitable for use as jet fuel has a final boiling point according to ASTM D86 being less than 300°C, with the associated benefit of the product of such a process fulfilling boiling point specifications of the renewable jet fuel specification ASTM D7566.
- 25 In a further embodiment the total volume of hydrogen sulfide relative to the volume of molecular hydrogen in the gas phase of the combined feedstock directed to contact the material catalytically active in hydrodeoxygenation is at least 50 ppm_v, 100 ppm_v or 200 ppm_v, possibly originating from an added stream comprising one or more sulfur compounds, such as dimethyl disulfide or fossil fuels, with the associated benefit of such a process operating efficiently with a low cost material catalytically active in hydrodeoxygenation comprising sulfided base metal.
- 30

In a further embodiment the total volume of hydrogen sulfide relative to the volume of molecular hydrogen in the gas phase of the total stream directed to contact directed to

contact the material catalytically active in hydrocracking is at least 50 ppm_v, 100 ppm_v or 200 ppm_v, optionally by adding a stream comprising one or more sulfur compounds, such as dimethyl disulfide or fossil fuels, with the associated benefit of enabling the use of an inexpensive material catalytically active in hydrocracking comprising sulfided
5 base metal(s).

In a further embodiment said feedstock comprises at least 50wt/wt% triglycerides or fatty acids, with the associated benefit of such a feedstock being highly suited for providing a jet fuel with excellent properties.

10

In a further embodiment hydrodeoxygenation conditions involve a temperature in the interval 250-400°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.1-2 and wherein the material catalytically active in hydrodeoxygenation comprises one or more metals taken from the group of nickel, cobalt, molybdenum or tungsten, supported on a carrier comprising one or more refractory oxides, such as alumina, silica or titania, with the associated benefit of such process conditions being well suited for cost effective removal of heteroatoms, especially oxygen from a renewable feedstock.

15

20 In a further embodiment hydrocracking conditions involve a temperature in the interval 250-425°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-4, optionally together with intermediate cooling by quenching with cold hydrogen, feed or product and wherein the material catalytically active in hydrocracking comprises (a) one or more active metals taken from the group platinum, palladium, nickel, cobalt, tungsten and molybdenum, (b) an acidic support taken from the group of a molecular sieve showing high cracking activity, and having a topology such as MFI, BEA and FAU and amorphous acidic oxides such as silica-alumina and (c) a refractory support, such as alumina, silica or titania, or combinations thereof, with the associated benefit of such process conditions being highly suited for reducing the
25 boiling point of a product to match the kerosene boiling point range.
30

In a further embodiment the amount of material boiling above 300°C in said hydrocracked intermediate product is reduced by at least 20%wt, 50%wt or 80%wt or more compared to said isomerized intermediate product, with the associated benefit of

the high conversion being a minimization of product boiling above 300°C, as a result of a high process severity.

5 In a further embodiment at least an amount of said isomerized intermediate product or said hydrocracked intermediate product is directed to contact a material catalytically active in hydrodearomatization under hydrodearomatization conditions to provide a hydrodearomatized product comprising less than 1 wt/wt%, 0.5 wt/wt% or 0.1 wt/wt% aromatics, calculated by total mass of the aromatic molecules relative to all hydrocarbons in the stream, where said hydrodearomatized product is fractionated in place of said
10 hydrocracked intermediate product in step (f), with the associated benefit of the product of such a process fulfilling jet fuel specification ASTM D7566. Said material catalytically active in hydrodearomatization under hydrodearomatization conditions may be the material catalytically active in hydrocracking or material catalytically active isomerization operating at moderate temperatures favoring hydrodearomatization. Hydrodearomatization conditions preferably involve at least 50% or 80% conversion of aromatics.
15

In a further embodiment hydrodearomatization conditions involve a temperature in the interval 200-350°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8 and wherein said material catalytically active in hydrodearomatization comprises an active metal taken from the group comprising platinum, palladium, nickel, cobalt, tungsten and molybdenum, preferably one or more sulfided base metals such as nickel, cobalt, tungsten and molybdenum and a refractory support, preferably amorphous silica-alumina, alumina, silica or titania, or combinations thereof, with the associated benefit of such process conditions being suitable for hydrogenation of aromatics.
20
25

In a further embodiment a hydrogen rich stream comprising at least 90 vol/vol% hydrogen is directed to contact the material catalytically active in hydrodearomatization, with the associated benefit of directing high purity hydrogen required by the overall process to the hydrodearomatization step contributing to shifting the equilibrium away from aromatics.
30

In a further embodiment isomerization conditions involves a temperature in the interval 250-400°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity

(LHSV) in the interval 0.5-8 and wherein the material catalytically active in isomerization comprises an active metal taken from the group comprising platinum, palladium, nickel, cobalt, tungsten and molybdenum, preferably one or more elemental noble metals such as platinum or palladium, an acidic support preferably a molecular sieve, more preferably having a topology taken from the group comprising MOR, FER, MRE, MWW, AEL, TON and MTT and an amorphous refractory support comprising one or more oxides taken from the group comprising alumina, silica and titania, or combinations thereof, with the associated benefit of such conditions and materials being a cost effective and selective process for adjusting the cold flow properties of product.

A further aspect of the present disclosure relates to a process plant for production of a hydrocarbon fraction suitable for use as jet fuel from a feedstock being a renewable feedstock or an oxygenate feedstock, said process plant comprising a hydrodeoxygenation section, a separation section, an isomerization section, a hydrocracking section and a fractionation section, said process plant being configured for directing the feedstock and a liquid diluent to the hydrodeoxygenation section to provide a hydrodeoxygenated intermediate product, configured for separating said hydrodeoxygenated intermediate product in a vapor fraction and a liquid fraction in said separation section, configured for directing at least an amount of said hydrodeoxygenated intermediate product to contact a material catalytically active in isomerization under isomerization conditions to provide an isomerized intermediate product, and configured for directing at least an amount of said isomerized intermediate product and a stream comprising sulfur to contact a material catalytically active in hydrocracking under hydrocracking conditions to provide the hydrocracked intermediate product, and configured for fractionating said hydrocracked intermediate product in said fractionation section, providing at least a hydrocarbon suitable for use as jet fuel, with the associated benefit of such a process plant being suited for carrying out the disclosed process for cost effective and selective production of jet fuel.

In a further embodiment the process plant comprises a recycle connection configured for providing an amount of said liquid hydrodeoxygenated product as liquid diluent, with the associated benefit of controlling the temperature in the hydrodeoxygenation reactor, without adding a diluent, such as a fossil feedstock.

The processes described in the present disclosure receives a renewable feedstock and/or an oxygenate feedstock which comprises one or more oxygenates taken from the group consisting of triglycerides, fatty acids, resin acids, ketones, aldehydes, alcohols, phenols and aromatic carboxylic acids where said oxygenates originate from one or more of a biological source, a gasification process, a pyrolysis process, Fischer-Tropsch synthesis, methanol based synthesis or a further synthesis process, especially obtained from a raw material of renewable origin, such as originating from plants, algae, animals, fish, vegetable oil refining, domestic waste, used cooking oil, plastic waste, rubber waste or industrial organic waste like tall oil or black liquor. Some of these feedstocks may contain aromatics; especially products derived by pyrolysis or other processes from e.g. lignin and wood or waste products from e.g. frying oil. Depending on source, the oxygenate feedstock may comprise from 1 wt/wt% to 40 wt/wt%. Biological sources will typically comprise around 10 wt/wt%, and derivation products from 1 wt/wt% to 20 wt/wt% or even 40 wt/wt%.

For the conversion of renewable feedstocks and/or oxygenate feedstocks into hydrocarbon transportation fuels, the feedstocks are together with hydrogen directed to contact a material catalytically active in hydrotreatment, especially hydrodeoxygenation. Especially at elevated temperatures the catalytic hydrodeoxygenation process may have side reactions forming a heavy product e.g. from olefinic molecules in the feedstock. To moderate the release of heat, a liquid hydrocarbon may be added, e.g. a liquid recycle stream or an external diluent feed. If the process is designed for co-processing of fossil feedstock and renewable feedstock, it is convenient to use the fossil feedstock as diluent, since less heat is released during processing of fossil feedstock, as fewer heteroatoms are released and less olefins are saturated. In addition to moderating the temperature, the recycle or diluent also has the effect of reducing the potential of olefinic material to polymerize. The resulting product stream will be a hydrodeoxygenated intermediate product stream comprising hydrocarbons, typically n-paraffins, and sour gases such as CO, CO₂, H₂O, H₂S, NH₃ as well as light hydrocarbons, especially C₃ and methane.

Typically, hydrodeoxygenation involves directing the feedstock to contact a catalytically active material typically comprising one or more sulfided metals taken from the group of nickel, cobalt, molybdenum or tungsten, supported on a carrier comprising one or more

refractory oxides, typically alumina, but possibly silica or titania. The support is typically amorphous. The catalytically active material may comprise further components, such as boron or phosphorous. The conditions are typically a temperature in the interval 250-400°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.1-2. Hydrodeoxygenation is typically exothermal, and with the presence of a high amount of oxygen, the process may involve intermediate cooling e.g. by quenching with cold hydrogen, feed or product. The feedstock may preferably contain an amount of sulfur to ensure sulfidation of the metals, in order to maintain their activity. If the gas phase comprises less than 10, 50 or 100 ppm_v sulfur, a sulfide donor, such as dimethyldisulfide (DMDS) may be added to the feed.

The hydrodeoxygenated intermediate product will mainly be linear hydrocarbons, like the feedstock, or if the feedstock comprises triglycerides, n-paraffins, but possibly of a shorter length than the fatty acids. Typically, the hydrodeoxygenated intermediate product will be dominated by linear alkanes having boiling point range (250°C to 320°C) and a freezing point (0°C to 30°C) unsuited for use as jet fuel. Some heavy components and aromatics may also be formed in the hydrodeoxygenation step if the unsaturated fatty acids polymerizes.

For the hydrodeoxygenated intermediate product to be used as a fuel in practice, the freezing point must be adjusted. The freezing point is adjusted by isomerization of n-paraffins to i-paraffins, by directing the hydrodeoxygenated intermediate product to contact a material catalytically active in isomerization

The material catalytically active in isomerization typically comprises an active metal (which according to the present disclosure is one or more elemental noble metals such as platinum and/or palladium), an acidic support (typically a molecular sieve showing high shape selectivity, and having a topology such as MOR, FER, MRE, MWW, AEL, TON and MTT) and a typically amorphous refractory support (such as alumina, silica or titania, or combinations thereof). The catalytically active material may comprise further components, such as boron or phosphorous. Preferred isomerization catalysts comprise molecular sieves such as EU-2, ZSM-48, beta zeolite and combined beta zeolite and zeolite Y.

Typically, isomerization involves directing the intermediate hydrodeoxygenated feedstock to contact a material catalytically active in isomerization. The conditions are typically a temperature in the interval 250-400°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8. Isomerization is substantially thermally neutral and consumes only hydrogen in hydrocracking side reactions so only a moderate amount of hydrogen is added in the isomerization reactor. As the active metal on the most selective materials catalytically active in isomerization is a noble metal, the hydrodeoxygenated feedstock is typically purified by gas/liquid separation to reduce the content of potential catalyst poisons to low levels such as levels of sulfur, nitrogen and carbon oxides to below 1-10 ppm_{molar}.

For the isomerized intermediate product stream to be used as a kerosene fraction, the boiling point range must be adjusted. A boiling point adjustment may also be required if an amount of heavy product is present in the isomerized intermediate product. The boiling point is adjusted by hydrocracking of long paraffins to shorter paraffins, by directing the hydrodeoxygenated intermediate product to contact a material catalytically active in hydrocracking.

Hydrocracking involves directing the isomerized intermediate feedstock to contact a material catalytically active in hydrocracking. The material catalytically active in hydrocracking typically comprises an active metal (which in the present disclosure is one or more sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum), an acidic support (typically a molecular sieve showing high cracking activity, and having a topology such as MFI, BEA and FAU, but amorphous acidic oxides such as silica-alumina may also be used) and a refractory support (such as alumina, silica or titania, or combinations thereof). The catalytically active material may comprise further components, such as boron or phosphorous. Preferred hydrocracking catalysts comprise molecular sieves such as ZSM-5, zeolite Y or beta zeolite.

According to the present disclosure, the material catalytically active in hydrocracking is a base metal positioned downstream the material catalytically active in hydroisomerization, and thus addition of a sulfur donor is required to maintain sulfidation, and thus activity, of the sulfided active metal.

The conditions are typically a temperature in the interval 250-400°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-4. As hydrocracking is exothermal, the process may involve intermediate cooling e.g. by quenching with cold hydrogen, feed or product. The active metal(s) on the material catalytically active in hydrocracking is a base metal, so the intermediate hydroisomerized feedstock including the gas phase is typically directed to contact the material catalytically active in hydrocracking without further purification. The gas phase mixture should preferably contain at least 50 ppm_v sulfur.

- Hydrodeoxygenation of unsaturated fatty acids may produce aromatics as a side reaction. Therefore, even for an oxygenate feedstock comprising less than 1% aromatics, it may be further necessary to direct the isomerized product to contact a material catalytically active in hydrodearomatization. It has now been identified that a hydrocracking catalyst may also fulfil this role, if positioned downstream the isomerization catalyst, and operating at a lower temperature, such as below 350°C.

- In some instances, hydrodearomatization may be satisfactorily carried out in the presence of the material catalytically active in hydroisomerization or hydrocracking, but it may also be necessary to have a separate reactor or reactor bed with material catalytically active in hydrodearomatization.

- Such a material catalytically active in hydrodearomatization typically comprises an active metal (preferably sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum but possibly – after purification - noble metals such as platinum and/or palladium) and a refractory support (such as amorphous silica-alumina, alumina, silica or titania, or combinations thereof). Hydrodearomatization is equilibrium controlled, with high temperatures favoring aromatics, noble metals are preferred as the active metal, since they are active at lower temperatures, compared to base metals.

- Typically, hydrodearomatization involves directing an intermediate product to contact a material catalytically active in hydrodearomatization. As the equilibrium between aromatics and saturation molecules shifts towards aromatics at elevated temperatures, it is preferred that the temperature is moderate. The conditions are typically a temperature in the interval 200-350°C, a pressure in the interval 30-150 Bar, and a liquid hourly

space velocity (LHSV) in the interval 0.5-8. Base metal catalysts may be used, and in this case the gas phase associated with intermediate hydroisomerized feedstock preferably contains at least 50 ppm_v sulfur. Often a hydroisomerization catalyst operating at temperatures below 350°C will be able to catalyze moderate hydrodearomatization, e.g. reducing 10%wt aromatics to below 0.5%wt aromatics. Alternatively the active metal(s) on the material catalytically active in hydrodearomatization may be noble metal(s), since noble metal catalysts in general are active at lower temperatures than comparable base metal catalysts.

This necessity to combine 3 or 4 catalytically active materials for conversion of renewable feedstocks into jet fuel naturally complicates the process layout, and the sequence of the materials must be considered carefully. In addition, recycle may be used for three different purposes; gas recycle for efficient use of hydrogen, liquid recycle around the material catalytically active in hydrocracking to maximize the yield of the kerosene fraction and liquid recycle around the material catalytically active in hydrodeoxygenation to limit the temperature increase due to exothermal hydrodeoxygenation reactions.

As isomerization is carried out using a catalytically active material comprising noble metals, "sour gases", including hydrogen sulfide and ammonia, are removed prior to this reaction. An amount of the intermediate product of hydrocracking and/or hydrodearomatization may also be recycled to the inlet of the hydrodeoxygenation reactor.

The use of an isomerization catalyst to improve freezing point of the jet fuel, allows increasing the distillation endpoint of the jet fuel while still meeting freezing point requirement. Finally, since the second stage will saturate aromatics, it is not required for the first stage to meet any aromatics requirements, which allows the first stage to treat heavier and/or more aromatic, naphthenic or unsaturated feedstocks as well as feedstocks such as used cooking oil, pyrolysis products or tall oil pitch, which contain aromatics or unsaturated feedstock which may produce aromatics in small amounts in typical hydroprocessing conditions, since these aromatics will be saturated in the second stage.

One embodiment according to the present disclosure corresponds to a process in which a stream comprising oxygenates and recycled hydrocarbons, comprising an

amount of sulfur is directed to a hydrodeoxygenation reactor containing a catalytically active material comprising one or more base metals and a refractory support, with low acidity. Such a material is active in hydrodeoxygenation and other hydrotreatment reactions removing heteroatoms and double bonds. The recycled hydrocarbons contribute
5 as a heat sink, absorbing the released heat of reaction from the hydrodeoxygenation, thus maintaining a moderate temperature in the hydrodeoxygenation reactor. This step provides a stream comprising a high amount of saturated linear alkanes, in combination with an amount of water, CO, CO₂, methane, hydrogen sulfide and ammonia.

10 The hydrodeoxygenated hydrocarbon stream is directed to a separation section, withdrawing water, hydrogen sulfide and ammonia, and providing a sweet hydrocarbon stream. An amount of the sweet hydrocarbon stream is recycled as recycled hydrocarbons and an amount is directed as feed to an isomerization reactor containing a material catalytically active in isomerization and optionally a material catalytically active in
15 hydrodearomatization. Both materials are based on a noble metal catalyst, such as platinum, palladium or a combination, in combination with an acidic support. For isomerization the acidic support is preferably shape selective, to provide a selective isomerization, rearranging linear alkanes to branched alkanes, with minimal production of lighter hydrocarbons. For hydrodearomatization, an acidic support also contributes to
20 the reaction, and in addition as the activity of noble metals is higher than that of base metals, the reaction will take place at lower temperatures. As the equilibrium between aromatic and non-aromatic compounds is shifted away from aromatics at low temperatures, noble metals provide the benefit that the lower temperature matches the equilibrium. Hydrodearomatization may even take place on the material catalytically active in
25 isomerization, which often will have some hydrodearomatization activity.

As the sweet hydrocarbon stream does not contain hydrogen sulfide or ammonia, both the noble metal function and the acidic function of the material catalytically active in isomerization are undisturbed, and a branched hydrocarbon stream is produced with
30 high selectivity.

The isomerized stream is then directed to a hydrocracking reactor to contact a catalytically active material comprising one or more base metals and a refractory support with high acidity, being catalytically active in hydrocracking. When this catalytically active

material comprises base metals a presence of sulfur is required, and therefore a source of sulfur is provided. As the material is active in hydrocracking, this step provides a hydrocracked stream in which higher boiling hydrocarbons are converted to lower boiling hydrocarbons. The severity of the hydrocracking process will define the boiling point characteristics of the product, and it will typically be operated with full conversion of the fraction boiling above the diesel range. If hydrocracking severity is selected for full conversion of the fraction boiling above the jet range the yield loss to gases and naphtha will typically be too high.

10 The hydrocracked stream is directed to a fractionator (after appropriate removal of the gas phase in a separator train), and at least a gas fraction, an intermediate fraction and a bottoms fraction are withdrawn.

15 The layout provides a conversion of feedstock to diesel, jet range or lighter product, as some or even all heavy hydrodeoxygenated hydrocarbons may be hydrocracked to yield lighter products. Jet/diesel co-production or only diesel production is possible, and the conversion of boiling point is mainly carried out in a hydrodeoxygenation section and hydrocracking section employing inexpensive base metal catalysts only. Furthermore, the adjustment of freezing point is made selectively by isomerization on a noble metal catalyst, independently of hydrocracking conditions.

20 Should it be desired to produce only diesel and no jet fuel, hydrocracking is not desired. In this case, it may be preferred to either by-pass the hydrocracking reactor or alternatively cool the product prior to this reactor, such that it is inactive. The process plant may be configured for allowing such a configuration with short notice, e.g. by setting up appropriate equipment and control in the control room.

Figures

Figure 1 shows a simplified illustration of a process according to the present disclosure.
30 Figure 2 shows a simplified illustration of a process according to the prior art.
Figure 3 shows a simplified illustration of a process according to the prior art.

Figure 1 is a simplified figure showing a layout according to the present disclosure, omitting supply of gaseous streams and details of separation for simplicity. A renewable feedstock (102) is combined with a recycle diluent stream (128) and directed as a hydrodeoxygenation feed stream (104) together with an amount of a hydrogen rich stream (not shown) to a hydrodeoxygenation reactor (HDO) where it contacts a material catalytically active in hydrogenation under hydrotreating conditions. This provides a hydrodeoxygenated intermediate product (106). The hydrodeoxygenated intermediate product (106) is directed to separation section (SEP), shown for simplicity as a single unit, separating the hydrodeoxygenated intermediate product in a gas stream which may be used for recycle or for other purposes and a liquid intermediate product stream (108). The liquid intermediate product stream (108) is split in a recycle diluent stream (128) and an isomerization reactor feed stream (110) is together with a substantially sulfur free stream of hydrogen (not shown) directed as feed to an isomerization reactor (ISOM), where it contacts a material catalytically active in isomerization under isomerization conditions and provides an intermediate isomerized product stream (112) which is directed as a hydrocracker feed to a hydrocracking reactor (HDC) operating under hydrocracking conditions, optionally in the presence of an added sulfur donor (114), providing a hydrocracked intermediate product (118), which is directed to a fractionation section (FRAC) shown for simplicity as a single unit, separating the isomerized product in a light overhead stream (120), a naphtha product (122), a jet product (124) and a bottom diesel fraction (126).

The hydrocracked intermediate product (118) may optionally contact a further material catalytically active in hydrodearomatization (not shown) under hydrodearomatization conditions, providing an isomerized product.

Figure 2 shows an example of the prior art, in a level of detail similar to Figure 1, omitting supply of gaseous streams and details of separation for simplicity. A renewable feedstock (202) is combined with a recycle diluent stream (228) and directed as a hydrodeoxygenation feed stream (204) together with an amount of a hydrogen rich stream (not shown) to a hydrodeoxygenation reactor (HDO) where it contacts a material catalytically active in hydrogenation under hydrotreating conditions. This provides a hydrodeoxygenated intermediate product (214), which is directed to a hydroisomeriza-

tion reactor (ISOM) where it contacts a material catalytically active in isomerization under isomerization conditions, providing a dewaxed intermediate product (216). The dewaxed intermediate product (216) is directed to a fractionation section (FRAC) shown for simplicity as a single unit, separating the hydrocracked product in a light overhead stream (220), a naphtha stream (222), a jet product (224) and a bottom diesel fraction which is split in a recycle diluent stream (228) and a diesel product stream (226).

Figure 3 shows a further example of the prior art, omitting supply of gaseous streams and details of separation for simplicity. A renewable feedstock (302) is combined with a recycle diluent stream (328) and directed as a hydrodeoxygenation feed stream (304) together with an amount of a hydrogen rich stream (not shown) to a hydrodeoxygenation reactor (HDO) where it contacts a material catalytically active in hydrogenation under hydrotreating conditions. This provides a hydrodeoxygenated intermediate product (306), which is directed to a separator (SEP), from which a purified hydrodeoxygenated intermediate product (308) is retrieved, and split in a recycle diluent stream (328) and an isomerization feed stream (310), which is combined with a sulfur free hydrogen stream (not shown) and to a hydroisomerization reactor (ISOM). In this reactor the combined feed stream contacts a noble metal based material catalytically active in isomerization under isomerization conditions, providing a dewaxed intermediate product (312). The dewaxed intermediate product (312) is directed to a fractionation section (FRAC) shown for simplicity as a single unit, separating the hydrocracked product in a light overhead stream (320), a naphtha stream (322), a jet product (324) and a bottom diesel fraction (326).

Examples

The performance of the process layouts shown in Figures 1 and 3 have been compared.

Table 1 shows the characteristics of a renewable feedstock which is a combination of animal fat and cooking oil and the intermediate products after hydrotreatment. The intermediate product is dominated by C16 and C18 alkanes, has a high freezing point (24°C) and contains more than 1.5 wt/wt% aromatics. The feedstock was treated in two

processes in accordance with Figure 1 and 3 respectively, and the results of this treatment are shown in Table 2 where "Example 1" corresponds to Figure 1 and "Example 2" corresponds to Figure 2. The values for "net jet make" are calculated as the amount of jet produced in the process, subtracting the amount of jet already present in the feedstock by the formula *net jet make* = *[total jet product] - [native jet present in the feed]*. Yields are presented in this table as wt/wt% of feed to the unit. Eg. a jet yield of 51 wt/wt% indicate that 51 kg of jet fuel is produced for each 100 kg of feed that is processed in the unit.

The results of both examples show a production of a jet fuel with excellent properties, a low freezing point (-40°C) and a low aromatics content (<0.5%wt). Example 1 according to the present disclosure has a jet yield of 51 wt/wt%, whereas Example 2 has a jet yield of 43 wt/wt%, assuming a cut point between jet and diesel of 300°C. In the optimization of a process under the assumption of a higher value of jet fuel, this difference is evidently a highly attractive benefit of Example 1.

The key difference between the performance in the two cases is that Example 1 provides a jet yield of 51 wt/wt%, whereas Example 2 provides a much lower yield of 43 wt/wt%. This is due the conversion of high boiling diesel to jet fuel in the hydrocracking reactor.

Table 1

Feedstock		
	Source	Feedstock A
	Animal fat/used cooking oil	
	C16 fatty acids	20 wt/wt%
	C18 fatty acids	74 wt/wt%
Properties of hydrodeoxygenated intermediate product		
Property	Method of Analysis	
Freezing point	ASTM D 5972	24°C
Aromatics	ASTM D 6591	1.5 wt/wt%
Boiling point (°C)	ASTM D 7213 C	
IBP		200
10 wt/wt%		290
30 wt/wt%		317
50 wt/wt%		321
70 wt/wt%		323
90 wt/wt%		324
FBP		482
Native jet, 110-300°C	%wt	17

	Example 1	Example 2
P	70 barg	70 barg
T(HDO)	320°C	320°C
T(HDC)	300°C	-
LHSV (HDC)	1	-
Conversion per pass (HDC)		
T(ISOM)	320°C	330°C
LHSV (ISOM)	2	2
Net jet make	34 wt/wt%	26 wt/wt%
Freezing pt Jet	-40°C	-40°C
Aromatics Jet	<0.5 wt/wt%	<0.5 wt/wt%
Naphtha Yield (bp. 60°C -110°C)	8 wt/wt%	5 wt/wt%
Jet yield (bp. 110°C -300°C)	51 wt/wt%	43 wt/wt%
Diesel yield (bp. 300°C -370°C)	22 wt/wt%	35 wt/wt%

Claims:

1. A process for production of a hydrocarbon fraction suitable for use as jet fuel from an oxygenate feedstock, comprising the steps of
 - a. combining the feedstock with an amount of a liquid diluent to form a combined feedstock, directing said combined feedstock to contact a material catalytically active in hydrodeoxygenation (HDO) under hydrotreating conditions to provide a hydrodeoxygenated intermediate product,
 - b. separating said hydrodeoxygenated intermediate product in at least two fractions including a vapor fraction and a liquid fraction,
 - c. optionally providing at least an amount of said liquid fraction as said liquid diluent,
 - d. directing at least an amount of said liquid fraction to contact a material catalytically active in isomerization (ISOM) under isomerization conditions to provide an isomerized intermediate product,
 - e. directing at least an amount of said isomerized intermediate product and a stream comprising sulfur to contact a material catalytically active in hydrocracking (HDC) under hydrocracking conditions to provide a hydrocracked intermediate product, and
 - f. fractionating said hydrocracked intermediate product providing at least said hydrocarbon fraction suitable for use as jet fuel.
2. The process according to claim 1, wherein said hydrocarbon fraction suitable for use as jet fuel has a final boiling point according to ASTM D86 being less than 300°C.
3. The process according to claim 1 or 2, wherein the volume of hydrogen sulfide relative to the volume of molecular hydrogen in the gas phase of the combined feedstock directed to contact the material catalytically active in hydrodeoxygenation is at least 50 ppm_v, 100 ppm_v or 200 ppm_v, optionally by adding a stream comprising one or more sulfur compounds, such as dimethyl disulfide or fossil fuels.
4. The process according to claim 1, 2, or 3, wherein the volume of hydrogen sulfide relative to the volume of molecular hydrogen in the gas phase of the total stream directed to contact the material catalytically active in hydrocracking (HDC) is at

least 50 ppm_v, 100 ppm_v or 200 ppm_v, possibly originating from added an stream comprising one or more sulfur compounds, such as dimethyl disulfide or fossil fuels.

- 5 5. The process according to claim 1, 2, 3, or 4, wherein said feedstock comprises at least 50%wt triglycerides or fatty acids.
- 10 6. The process according to claim 1, 2, 3, 4, or 5, wherein hydrodeoxygenation conditions involve a temperature in the interval 250-400°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.1-2 and wherein the material catalytically active in hydrodeoxygenation comprises one or more sulfided metals taken from the group of nickel, cobalt, molybdenum or tungsten, supported on a carrier comprising one or more refractory oxides, such as alumina, silica or titania.
- 15 7. The process according to claim 1, 2, 3, 4, 5, or 6, wherein hydrocracking conditions involve a temperature in the interval 250-425°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-4, optionally together with intermediate cooling by quenching with cold hydrogen, feed or product and wherein the material catalytically active in hydrocracking comprises (a) one or more active metals taken from the group platinum, palladium, nickel, cobalt, tungsten and molybdenum, (b) an acidic support taken from the group of a molecular sieve showing high cracking activity, and having a topology such as MFI, BEA and FAU and amorphous acidic oxides such as silica-alumina and (c) a refractory support such as alumina, silica or titania, or combinations thereof.
- 20 8. The process according to claim 1, 2, 3, 4, 5, 6, or 7, wherein the amount of material boiling above 300°C in said hydrocracked intermediate product is reduced by at least 20%wt, 50%wt or 80%wt or more compared to said isomerized intermediate product.
- 25 9. The process according to claim 1, 2, 3, 4, 5, 6, 7, or 8, wherein at least an amount of said isomerized intermediate product or said hydrocracked intermediate product is directed to contact a material catalytically active in hydrodearomatization (HDA) under hydrodearomatization conditions to provide a hydrodearomatized product
- 30

comprising less than 1 wt/wt%, 0.5 wt/wt% or 0.1 wt/wt%, calculated by total mass of the aromatic molecules relative to all hydrocarbons in the stream, where said hydrodearomatized product is fractionated in place of said hydrocracked intermediate product in step (f).

5

10. The process according to claim 9, wherein hydrodearomatization conditions involve a temperature in the interval 200-350°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8 and wherein said material catalytically active in hydrodearomatization comprises an active metal taken from the group comprising platinum, palladium, nickel, cobalt, tungsten and molybdenum, preferably one or more sulfided base metals such as nickel, cobalt, tungsten and molybdenum and a refractory support, preferably amorphous silica-alumina, alumina, silica or titania, or combinations thereof.
11. The process according to claim 8, 9, or 10, wherein a hydrogen rich stream comprising at least 90 vol/vol% hydrogen is directed to contact the material catalytically active in hydrodearomatization.
12. The process according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11, wherein isomerization conditions involves a temperature in the interval 250-350°C, a pressure in the interval 30-150 Bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8 and wherein the material catalytically active in isomerization comprises an active metal taken from the group comprising platinum, palladium, nickel, cobalt, tungsten and molybdenum, preferably one or more elemental noble metals such as platinum or palladium, an acidic support preferably a molecular sieve, more preferably having a topology taken from the group comprising MOR, FER, MRE, MWW, AEL, TON and MTT and an amorphous refractory support comprising one or more oxides taken from the group comprising alumina, silica and titania or combinations thereof.
13. A process plant for production of a hydrocarbon fraction suitable for use as jet fuel from a feedstock being a renewable feedstock or an oxygenate feedstock, said process plant comprising a hydrodeoxygenation section (HDO), a separation section

(SEP), an isomerization section (ISOM), a hydrocracking section (HDC) and a fractionation section (FRAC), said process plant being configured for

- a. directing the feedstock and a liquid diluent to the hydrodeoxygenation section (HDO) to provide a hydrodeoxygenated intermediate product ,
 - 5 b. separating said hydrodeoxygenated intermediate product in a vapor fraction and a liquid fraction in said separation section (SEP),
 - c. directing at least an amount of said hydrodeoxygenated intermediate product to contact a material catalytically active in isomerization (ISOM) under isomerization conditions providing an isomerized intermediate product, and
 - 10 d. directing at least an amount of said isomerized intermediate product an a stream comprising sulfur to contact a material catalytically active in hydrocracking (HDC) under hydrocracking conditions to provide the hydrocracked intermediate product,
 - e. fractionating said isomerized intermediate product in said fractionation section (FRAC) to provide at least a hydrocarbon fraction suitable for use as jet
 - 15 fuel.
14. A process plant according to claim 13 further comprising a recycle connection being
- configured for providing an amount of said liquid hydrodeoxygenated product as liquid diluent.
- 20