

5 **Title: Method for production of aviation fuel**

Conversion of 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
10 320°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 or 310°C, which means that the heavy part of a paraffins from renewable feedstocks needs to be converted into lighter materials to produce only jet fuel. A further challenge in the production of jet fuel from renewables is the discovery of a surprisingly high production of aromatics, during hydro-
15 drotreatment of renewable feedstocks. The present disclosure relates to a process having a high yield of renewable jet fuel meeting typical product requirements by converting the heavy material to lighter material and by limiting the amount of aromatics in the product.

20 It is known to produce jet fuel from renewable feedstocks by co-producing some jet fuel in a unit designed for making diesel. However, there is an interest in making a full conversion from renewable feedstocks boiling mainly in the diesel range to jet fuel products, which requires significant conversion.

25 The standard controlling the quality of jet fuel originating from hydroprocessed oxygenates such as 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
30 0.5wt%. In addition, the standard requires an amount of low boiling product by requiring T₁₀, i.e. the temperatures at which 10% has been distilled according to ASTM D86, to be below 205°C. The final boiling point (FBP) is specified as 300°C, according to ASTM D86, which means that all material distilling above 300°C according to ASTM D86 needs to be converted into lighter components to fall into the jet fuel range.

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Summary

In one 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 less than 1 wt/wt% aromatics, comprising the steps of

- 5 a. combining the feedstock with a diluent hydrocarbon stream to form a hydrotreatment feed stream to contact a material catalytically active in hydrotreatment comprising one or more sulfided metals taken from the group of nickel, cobalt, molybdenum or tungsten, supported on a carrier comprising an amorphous refractory oxides, under hydrotreating conditions to provide a hydrotreated intermediate product,
- 10 b. directing said hydrotreated intermediate product to contact a material catalytically active in hydrocracking comprising one or more sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum, an acidic support and a refractory support, under hydrocracking conditions to provide a hydrocracked intermediate product,
- c. separating the hydrocracked intermediate product in a hydrocracked intermediate liquid fraction and a gaseous fraction,
- 15 d. directing at least an amount of said hydrocracked intermediate liquid fraction to contact a material catalytically active in hydrodearomatization comprising 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 and a refractory support, preferably amorphous silica-alumina, alumina, silica or
- 20 titania, or combinations thereof, under hydrodearomatization conditions sufficient to provide a treated product comprising less than 1 wt/wt%, aromatics, calculated by total mass of aromatic molecules relative to all hydrocarbons in the stream and comprising the hydrocarbon fraction suitable for use as jet fuel.

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In another aspect of the present disclosure, there is provided a process plant for production of a hydrocarbon suitable for use as a jet fuel from a feedstock comprising less than 1 wt/wt% aromatics being a renewable feedstock or an oxygenate feedstock, comprising a hydrotreatment section containing a material catalytically active in hydrodeoxygenation comprising one or more sulfided metals taken from the group of nickel, cobalt, molybdenum or tungsten, supported on a carrier comprising an amorphous refractory

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- oxides, a hydrocracking section containing a material catalytically active in hydrocracking, comprising one or more sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum, an acidic support and a refractory support and a hydrodearomatization section containing a material catalytically active in hydrodearomatization comprising 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 and a refractory support, preferably amorphous silica-alumina, alumina, silica or titania, or combinations thereof, said process plant being configured for
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- 10 a. directing the feedstock to the hydrotreatment section to provide a hydrotreated intermediate product,
- b. directing the hydrotreated intermediate product to the hydrocracking section to provide a hydrocracked intermediate product,
- c. directing at least an amount of said hydrocracked intermediate product to a hydrodearomatization section to provide a treated product comprising the hydrocarbon
- 15 fraction suitable for use as a jet fuel wherein said treated product comprises less than 1 wt/wt% aromatics, calculated by total mass of aromatic molecules relative to all hydrocarbons in the stream.

Description

Now according to the present disclosure it is proposed to carry out jet fuel production in a two-stage configuration, where the feed is hydrotreated, hydrocracked and optionally isomerized in the first stage, and after removal of sour gases hydro-dearomatized and optionally isomerized in the second stage. Between the two stages, a full fractionation section may be used to separate out a kerosene feedstock for the second stage and to produce a stream heavier than kerosene that is recycled to extinction in the first stage. Isomerization to improve the freezing point of the jet fuel can be done in first stage, second stage or both stages.

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 ppmw shall be used to signify parts per million weight, i.e. mg/kg.

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 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.

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.

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A broad aspect of the present disclosure relates to a process for production of a hydrocarbon fraction suitable for use as jet fuel from an oxygenate feedstock, which may be a feedstock being a renewable feedstock, comprising the steps of

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a. combining the feedstock with a diluent hydrocarbon stream to form a hydrotreatment feed stream to contact a material catalytically active in hydrotreatment under hydrotreating conditions to provide a hydrotreated intermediate product,

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b. directing at least an amount of said hydrotreated intermediate product to contact a material catalytically active in hydrocracking under hydrocracking conditions to provide a hydrocracked intermediate product,

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c. separating the hydrocracked intermediate product in a hydrocracked intermediate liquid fraction and a gaseous fraction,

d. directing at least an amount of said hydrocracked intermediate liquid fraction to contact a material catalytically active in hydrodearomatization under hydrodearomatization conditions to provide a treated product comprising the hydrocarbon fraction suitable for use as jet fuel,

with the associated benefit of producing a hydrocarbon fraction suitable for use as jet fuel with a high yield from an oxygenate feedstock.

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In a further embodiment an amount of said hydrocracked intermediate liquid fraction is directed as said diluent hydrocarbon stream, with the associated benefit of providing a diluent hydrocarbon stream as heat sink and for moderating polymerization reactions by dilution, while avoiding or reducing the required amount of an external stream, potentially fully avoiding the use of fossil feedstock in the operation.

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In a further embodiment step c comprises separating the liquid hydrocracked intermediate product according to ASTM D86 being less than 310°C, with the associated benefit of withdrawing the product fraction being heavier than the hydrocarbon fraction suitable for use as jet fuel.

In a further embodiment step c comprises separating the liquid hydrocracked intermediate product according to boiling point, to provide a hydrocracked intermediate jet product having T5 above 120°C and final boiling point below 310°C according to ASTM D86
5 which constitutes the hydrocracked intermediate liquid fraction of step d, with the associated benefit of enabling hydrodearomatization to take place on a material catalytically active comprising elemental noble metals and allowing for maximum jet yield in spite of hydrocracking side reactions over the material catalytically active in isomerization.

10 In a further embodiment step b or d further comprises directing a stream for isomerization being either said hydrotreated intermediate product, said hydrocracked intermediate product or said treated product to contact a material catalytically active in isomerization providing an isomerized stream being used in step b or d as said hydrotreated intermediate product, said hydrocracked intermediate product or said treated product
15 respectively, with the associated benefit of providing a product having a freezing point in compliance with jet fuel specification ASTM D7566.

In a further embodiment an amount of the hydrocracked intermediate product optionally after separation according to boiling point, and at least comprising a hydrocarbon fraction boiling above 310°C, is directed to be combined with either said feedstock or said
20 hydrotreated intermediate product with the associated benefit of further hydrocracking the hydrocracked intermediate product, to ensure a high degree of conversion to a product boiling in the jet fuel range, and optionally if directed to the material catalytically active in hydrotreatment to provide a diluent which may control the temperature of the
25 material catalytically active in hydrotreatment.

In a further embodiment step b comprises separating the hydrotreated intermediate product in a liquid hydrotreated intermediate product and a gaseous fraction, and optionally the further step of separating the liquid hydrotreated intermediate product according to boiling point, providing a hydrotreated intermediate jet product having T10
30 above 120°C and final boiling point below 310°C according to ASTM D86, with the associated benefit of removing sour gases upstream hydrocracking, to allow for hydrocracking to be carried out in the presence of a catalytically active material comprising elemental noble metals, and if including the further step of separation minimizing

the volume required for hydrodearomatization as well as the potential yield loss of e.g. naphtha.

5 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 the material catalytically active in hydrotreatment 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 ensuring stable operation of a material catalytically active in hydrotreatment comprising a sulfided base metal, if the
10 feedstock comprises an insufficient amount of sulfur.

In a further embodiment said feedstock comprises at least 50%wt triglycerides or fatty acids, with the associated benefit of providing a feedstock yielding a highly paraffinic hydrotreated intermediate product

15 In a further embodiment the process conditions are selected such that the conversion, defined as the difference in the amount of material boiling above 310°C in said hydrocracked intermediate product and the amount of material boiling above 310°C in said second fraction, relative to the amount of material boiling above 310°C in said second fraction, is above 20%, 50% or 80%, with the associated benefit of providing a process with full or substantially full overall conversion, while avoiding excessive conditions and excessive yield loss.

25 In a further embodiment said treated product comprises 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, with the associated benefit of providing a jet fuel in compliance with fulfilling jet fuel specification ASTM D7566.

30 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, and wherein if the hydrocracked intermediate product is separated in a liquid fraction and a gaseous fraction an amount of said gaseous fraction is optionally purified and directed to contact the material catalytically active in hydrotreatment, with the associated benefit

of an efficient use of hydrogen in the process, as the gas stream from hydrodearomatization does not require further purification before being directed to hydrotreatment and hydrocracking.

5 In a further embodiment the treated product is directed to a gas/liquid separator to provide a second stage gaseous fraction and a treated intermediate jet product, which is directed to a further means of separation, such as a stripper, to provide said hydrocarbon fraction suitable for use as jet fuel and a treated product off gas, with the associated benefit of providing a stable jet fuel product, while requiring a minimum of equipment for separation.
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In a further embodiment the hydrotreatment 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 hydrotreatment 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.
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20 In a further embodiment hydrocracking 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 0.5-8, 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 adjusting the boiling point of a product to match the kerosene boiling point range.
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In a further embodiment at least an amount of said first fraction or said hydrodearomatized product is directed to contact a material catalytically active in isomerization

(ISOM) under isomerization conditions, with the associated benefit of such a process providing a product complying with the requirements to cold flow properties for jet fuels.

5 In a further embodiment 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
10 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, with the associated benefit of such conditions and materials being a cost effective and selective process for adjusting the cold flow properties of product.

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 elemental noble metals such as platinum or palladium and a refractory support, preferably
20 amorphous silica-alumina, alumina, silica or titania, or combinations thereof, with the associated benefit of such process conditions being suitable for hydrogenation of aromates. Said material catalytically active in hydrodearomatization under hydrodearomatization conditions may be a material catalytically active in hydrocracking or material
25 catalytically active isomerization operating at moderate temperatures favoring hydrodearomatization. Hydrodearomatization conditions preferably involve at least 50% or 80% conversion of aromatics.

30 A further aspect of the present disclosure relates to a process plant for production of a hydrocarbon suitable for use as a jet fuel from a feedstock being a renewable feedstock or an oxygenate feedstock, comprising a hydrotreatment section, a hydrocracking section and a hydrodearomatization section, said process plant being configured for di-

- recting the feedstock to the hydrotreatment section to provide a hydrotreated intermediate product, directing at least an amount of the hydrotreated intermediate product to the hydrocracking section to provide a hydrocracked intermediate product, directing at least an amount of said hydrocracked intermediate product to a hydrodearomatization
- 5 section to provide a treated product comprising the hydrocarbon fraction suitable for use as a jet fuel, with the associated benefit of such a process plant being able to produce a jet fuel having a boiling point and a content of aromatics in compliance with jet fuel specification ASTM D7566, A2.1.
- 10 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-
- 15 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
- 20 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%.
- 25 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 feed-
- 30 stock. 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, which will form an undesired heavy fraction in the product. The resulting product stream will be a hydrotreated 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. Especially at elevated temperatures the catalytic hydrodeoxygenation process may result in side reactions forming aromatics. If the feedstocks comprises nitrogen, ammonia may be formed, which can have an effect of deactivating the catalytically active material, thus requiring such elevated temperatures, with consequential formation of aromatics, in amounts above the limit of ASTM D7566 defining jet fuel specification.

The material catalytically active in hydrotreatment, typically comprises an active metal (one or more sulfided base metals such as nickel, cobalt, tungsten or molybdenum, but possibly also elemental noble metals such as platinum and/or palladium) and a refractory support (such as alumina, silica or titania, or combinations thereof).

Typical hydrotreatment involves directing the feedstock to contact a catalytically active material typically comprising one or more sulfided base metals such as nickel, cobalt, tungsten or molybdenum, but possibly also elemental noble metals such as platinum and/or palladium, 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. Hydrotreatment is typically exothermic, 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 hydrotreated intermediate product will mainly be of same structure as the carbon skeleton of the feedstock oxygenates, or if the feedstock comprises triglycerides, n-paraffins, but possibly of a shorter length than the fatty acids. Typically, the hydrotreated 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 hydrotreatment step if the unsaturated fatty acids polymerizes and form aromatic structures.

For the hydrotreated 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 hydrotreated intermediate product to contact a material catalytically active in isomerization

The material catalytically active in isomerization typically comprises an active metal (either elemental noble metals such as platinum and/or palladium or sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum), 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 hydrotreated feedstock to contact a material catalytically active in isomerization. The conditions are typically 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. 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 section. When the active metal on the material catalytically active in isomerization is a noble metal, the hydrotreated 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}. When the active metal is a base metal the intermediate hydrotreated feedstock preferably contains at least 50 ppm_v sulfur.

For the hydrotreated intermediate product stream to be used as a kerosene fraction, the boiling point range must be adjusted. The boiling point is adjusted by hydrocracking of long paraffins to shorter paraffins, by directing the hydrotreated intermediate product to contact a material catalytically active in hydrocracking.

The material catalytically active in hydrocracking is of a nature similar to that of the material catalytically active in isomerization, and it typically comprises an active metal (either elemental noble metals such as platinum and/or palladium or 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 difference to a material catalytically active in isomerization is typically the nature of the acidic support, which may be of a different structure (even amorphous silica-alumina) or have a different acidity e.g. due to silica:alumina ratio. 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.

Typically hydrocracking involves directing the intermediate hydrotreated feedstock to contact a material catalytically active in hydrocracking. 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 exothermic, the process may involve intermediate cooling e.g. by quenching with cold hydrogen, feed or product. When the active metal on the material catalytically active in isomerization is a noble metal, the hydrotreated 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}. When the active metal is a base metal the intermediate hydrotreated feedstock preferably contains at least 50 ppm_v sulfur.

Hydrodeoxygenation of unsaturated fatty acids and hydrocracking may also produce aromatics as a side reaction, especially if the temperature and/or the conversion is

high. Therefore, a low conversion during hydrocracking has typically been desired, hindering full conversion to a kerosene fraction. One consideration in increasing conversion has been to recycle hydrocracked intermediate product for additional contact with the material catalytically active in hydrocracking, but even this may produce an extensive amount of aromatics.

Therefore, it may be further necessary even for an oxygenate feedstock comprising less than 1% aromatics, to direct the hydrocracked intermediate product to contact a material catalytically active in hydrodearomatization, which is surprising, as the renewable feedstocks contain no or little aromatics. In some instances, hydrodearomatization may be satisfactorily carried out in the presence of the material catalytically active in hydroisomerization, but it may also be necessary to have a separate reactor or reactor bed with material catalytically active in hydrodearomatization.

The material catalytically active in hydrodearomatization typically comprises an active metal (typically elemental noble metals such as platinum and/or palladium but possibly also sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum) 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. As the preferred active metal on the material catalytically active in hydrodearomatization is a noble metal, the hydrocracked intermediate product is typically purified by gas/liquid separation to reduce the content of sulfur to below 1-10 ppm.

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.

In one aspect of the disclosure the boiling point is adjusted by hydrocracking in the same stage as hydrodeoxygenation, both operating under sour conditions, with a catalytically active material comprising sulfided base metals.

The hydrodearomatization will typically require sweet conditions, as the catalyst typically comprises a noble metal, which operates at lower temperatures, thus employing the fact that the equilibrium of the hydrodearomatization reaction is shifted away from aromatics at low temperatures. Therefore, a separation of gases may be carried out prior to hydrodearomatization, and optionally also a separation of intermediate hydrocracked product according to boiling point, such that only intermediate hydrocracked product boiling in the kerosene range contacts the material catalytically active in hydrodearomatization. Isomerization may be carried out either in connection with hydrocracking or in connection with hydrodearomatization. In both cases the material catalytically active in isomerization may be positioned either upstream or downstream the material catalytically active in hydrocracking or hydrodearomatization respectively.

In another aspect the boiling point is adjusted by hydrocracking in the same stage as hydrodearomatization, both operating under sweet conditions, with a catalytically active material comprising elemental noble metals. Therefore, a separation of gases may be carried out prior to hydrocracking, and optionally also a separation of intermediate hydrotreated product according to boiling point, such that only intermediate hydrotreated product boiling in the jet fuel range and above contacts the materials catalytically active in hydrocracking and hydrodearomatization. Isomerization may be carried out by contact with a material catalytically active in isomerization comprising an elemental noble metal either upstream the material catalytically active in hydrocracking, downstream the material catalytically active hydrodearomatization or between the two. Isomerization

may also be carried out by contacting the intermediate hydrotreated product with a material catalytically active in isomerization comprising a sulfided base metal before the separation of gases.

- 5 Operating the material catalytically active in hydrocracking with recycle allows full conversion at moderate temperatures, thus maintaining a high yield of kerosene and minimized over-cracking to naphtha and lighter. 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
- 10 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 are known to produce aromatics in small amounts in typical hydroprocessing conditions, since these aromatics will be saturated in the second
- 15 stage.

- One embodiment according to the present disclosure corresponds to a process in which a stream comprising oxygenates and diluent hydrocarbons, and comprising an amount of sulfur is directed to a hydrodeoxygenation reactor containing a catalytically
- 20 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 as a heat sink, absorbing the released heat of reaction from the hydrodeoxygenation, thus maintaining a moderate temperature in the hydrodeoxygenation reactor. This step
- 25 provides a stream comprising a high amount of saturated linear alkanes, in combination with an amount of water, hydrogen sulfide and ammonia.

- The hydrotreated stream is directed to a hydrocracking reactor containing a catalytically active material comprising one or more base metals and a refractory support with
- 30 high acidity. Such a material is active in hydrocracking, and this step provides a stream in which higher boiling hydrocarbons are converted to lower boiling hydrocarbons. As the material catalytically active in hydrocracking comprises base metals it is not neces-

sary to remove hydrogen sulfide, and furthermore the presence of ammonia may contribute to regulation of the hydrocracking activity. The lower cost of base metals compared to noble metals is also a benefit.

5 The hydrocracked stream is directed to a separation section comprising a means of separation, such as a stripper or a fractionator, and at least a gas fraction, an intermediate fraction and a bottoms fraction are withdrawn. All streams out of the fractionator have a very low level of hydrogen sulfide and ammonia. The bottoms fraction of the hydrocracked stream will be too heavy for being used as jet product, and is recycled to
10 the hydrodeoxygenation reactor. The intermediate fraction has a boiling range which often is suitable for use as jet fuel, but the content of aromatics and the freezing point may not be within specification.

Therefore, the intermediate fraction is directed to an isomerization reactor containing a
15 material catalytically active in isomerization and a material catalytically active in 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, e.g. a zeolite, to provide a selective isomerization, rearranging linear alkanes to branched alkanes, with minimal production
20 of lighter hydrocarbons. For hydrodearomatization, an acidic support also contributes to 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.
25 Hydrodearomatization may even take place on the material catalytically active in isomerization, which often will have some hydrodearomatization activity. An amount of hydrocracking may occur in the isomerization reactor, and therefore it may be preferred that the hydrocracked stream is slightly heavier than jet specifications.

30 The layout therefore provides a full conversion of feedstock to jet range or lighter product, as all heavy product is recycled and hydrocracked. Furthermore, the adjustment of freezing point is made selectively by isomerization on a noble metal catalyst, inde-

pendently of hydrocracking conditions, and finally hydrodearomatization may be efficiently carried out at moderate temperatures in the same reactor and possibly even the same catalytically active material as isomerization.

- 5 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.

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Figures

Figure 1 shows a process according to the present disclosure.

Figure 2 shows a simplified illustration of a process according to the present disclosure.

Figure 3 shows a simplified illustration of a process according to the prior art.

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- Figure 1 shows a process layout for production of a hydrocarbon suitable for use as jet fuel (106) from a renewable feedstock (2) added stepwise (2a, 2b and 2c) to a hydrotreatment section (8). A first amount of the renewable feedstock (2c) is combined with a diluent (6) and directed to a hydrotreatment section (8) where it contacts a material catalytically active in hydrotreatment (10a). Further amounts of renewable feedstock (2b, 2c) and an amount of hydrogen rich gas (12a) are directed to contact individual beds of catalytically active material (10b, 10c, 10d) under hydrotreating conditions. This provides a hydrotreated intermediate product (14). The hydrotreated intermediate product (14) is directed to a hydrocracking section (16) to contact a material catalytically active in hydrocracking comprising a base metal (18a, 18b) under hydrocracking conditions, as well as a material catalytically active in isomerization comprising a base metal (20) providing a hydrocracked intermediate product (22). In a gas/liquid separator (24) the hydrocracked intermediate product (22) is separated into a gaseous fraction (26) and a liquid fraction (34). The gaseous fraction (26) is split in an optional purge (28) and a recycle gas (30) which is pressurized (32) and directed as quench hydrogen supply of the hydrotreatment section (12a) in one or more positions between reactor beds as well as to the hydrocracking section (12b, 12c). The liquid hydrocracked intermediate product (34) is directed to a stripper (36), which also receives a stripping medium (38) and optionally a stripper overhead recycle (40). From the stripper a gaseous
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- 25
- 30

stripper product (42) is directed to a gas/liquid separator (44), from which an off-gas (46) and a light naphtha fraction (48) are withdrawn. An amount of the light naphtha is withdrawn as product (50), an amount (52) may optionally be directed as feed (102) to a kerosene stabilizer (100) and an amount is directed as overhead recycle (40) to the

5 stripper (36). The liquid stripper product (54) is directed to fractionator (56), from which a light overhead stream (58) is directed to an overhead vessel (60), from which a heavy naphtha (62) is withdrawn. An amount of heavy naphtha (64) is withdrawn as product and a further amount (66) is directed as fractionator recycle (66). A bottom fraction (68) is split in to a recycle stream (72) and a reboiled stream (74). From a side column (78)

10 a hydrocracked intermediate jet product (80) is combined with a of hydrogen rich stream (84c) and directed as feed (82) to a hydrodearomatization and hydrodewaxing section (86), where it contacts a material catalytically active in isomerization (88) and a material catalytically active in hydrodearomatization (90a, 90b) under hydrodearomatization conditions, receiving further hydrogen rich streams (84a, 84b), providing a

15 treated product (92), which is directed to a product gas/liquid separator (94) from which a second gaseous fraction (96) is withdrawn and combined with the recycle stream (72) and provided as make-up hydrogen in the diluent (76) to the hydrotreatment section (8). An intermediate jet product (98) is withdrawn from the product separator, and directed to a further means of separation (100), such as a kerosene stabilizer, optionally

20 also receiving an amount of light naphtha (102), from which a liquid product (104) is withdrawn and split in a hydrocarbon fraction suitable for use as jet fuel (106) and a re-boiler liquid (110). The gaseous overhead from the kerosene stabilizer (108) is combined with the gaseous stripper product (42) and directed to a gas/liquid separator (44).

25 In a further embodiment (not shown) the second gaseous fraction (96) is not directed as make-up gas for the hydrotreatment section, but instead directed to the a hydrodearomatization and hydrodewaxing section (86), possibly requiring an additional compressor, but also resulting in added simplicity. In this case make-up hydrogen is then added separately to the hydrotreatment section.

30 In a further embodiment the gaseous overhead from the kerosene stabilizer (92) may be handled in a separate overhead circuit with the benefit of simplicity and independence, but at the cost of extra equipment items for cooling, separation and reflux pumps.

In a further embodiment the separator, fractionation and light ends recovery sections can be configured in multiple ways as it is known to the skilled person. If light materials like LPG or propane are valuable, the recovery of these can be improved by using a sponge oil absorption system e.g. using the heavy naphtha from the fractionator overhead as lean oil and returning the rich oil to the stripper.

Figure 2 is a simplified figure showing a layout similar to that of Figure 1, omitting supply of gaseous streams and details of separation for simplicity. A renewable feedstock (202) is combined with a diluent (226) and directed as a hydrotreatment feed stream (204) together with an amount of a hydrogen rich stream (not shown) to a hydrotreatment section (HDO) where it contacts a material catalytically active in hydrogenation under hydrotreating conditions. This provides a hydrotreated intermediate product (206). The hydrotreated intermediate product (206) is directed to a hydrocracking section (HDC) operating under hydrocracking conditions, providing a hydrocracked intermediate product (212), which is directed to a fractionation section (FRAC) shown for simplicity as a single unit, separating the hydrocracked intermediate product in a light overhead stream (220), a naphtha stream (222), a hydrotreated intermediate jet product (224) and a bottom fraction (226). The bottom fraction (226) is directed as a recycle stream, which, as mentioned, is combined with the renewable feedstock (202). The hydrotreated intermediate jet product (224) is directed as feed to a post treat section (PT), where it contacts a material catalytically active in isomerization (ISOM) and a material catalytically active in hydrodearomatization (HDA) under hydrodearomatization conditions, providing a treated jet fuel product (218).

Figure 3 shows an example of the prior art, in a level of detail similar to Figure 2, omitting supply of gaseous streams and details of separation for simplicity. A renewable feedstock (302) is combined with a recycle diluent stream (310) and directed as a hydrotreatment feed stream (304) together with an amount of a hydrogen rich stream (not shown) to a hydrotreatment section (HDO) where it contacts a material catalytically active in hydrogenation under hydrotreating conditions. This provides a hydrotreated intermediate product (306), from which gases are separated e.g. in a stripper (SEP), providing a sweet hydrotreated intermediate product (308), which is split into said recycle diluent stream (310) and an isomerization feed (312) which is directed to a hydroisomerization section (ISOM) where it contacts a material catalytically active in isomerization under isomerization conditions, providing a dewaxed intermediate product (314).

The dewaxed intermediate product (314) is directed to a hydrocracking section (HDC) where it contacts a material catalytically active in hydrocracking under hydrocracking conditions, providing a hydrocracked product (316). The hydrocracked product (316) 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 2 and 3 have been compared, based on two similar feedstocks, and process conditions optimized for maximum jet yield.

Table 1 shows the characteristics of a renewable feedstock which is a mixture of 50% used cooking oil and 50% animal fat. The feedstock comprises 6% aromatics and 80% boils above 500°C; mainly due to the presence of high boiling triglycerides.

Feedstock A was treated in a process in accordance with Figure 2 and 3, and the results of this treatment is shown in Table 2.

In the hydrotreatment a significant conversion of boiling point is seen due to triglycerides being converted to alkanes. In addition, an amount of conversion is observed in the hydrocracking reactor and the isomerization reactor. The true conversion per pass is however quite low, since the amount of recycle is high.

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/wt%). The example according to the present disclosure (Figure 2) has a jet yield of 63 wt/wt%, whereas the Example according to the prior art (Figure 3) has a jet yield of 58 wt/wt%. In addition, naphtha is produced in both scenarios. In a process designed for production of jet, the yield difference of 5% is of course valuable.

The configuration of Figure 2, where the product of hydrodeoxygenation and hydrocracking is split in a light and a heavy fraction and the heavy fraction is recycled, results in a full conversion of heavy feedstock to jet product, and thus a higher yield of jet product compared to the configuration of Figure 3.

Table 1

SG	0.9209
Aromatics in feed, wt/wt%	6
destillation:	
SimDist, wt/wt %	
IBP	340
5%	365
10%	398
20%	533
30%	582
40%	597
50%	601
60%	602
70%	608
80%	610
90%	611
95%	612
FBP	695

Table 2

Example	Figure 2	Figure 3
P	70 barg	70 barg
T(HDO)	320°C	320°C
T(HDC)	380°C	310
T(DWX)	325°C	320
LHSV (DWX)	1	2
LHSV HDC	0.8	1
Freezing pt Jet	-40°C	-40°C
Aromatics content in jet boiling range	<0.5 wt/wt%	<0.5 wt/wt%
Naphtha boiling range yield (bp.30-110°C), wt/wt%	15	11
Jet boiling range yield (bp.110-310°C), wt/wt%	63	58
Heavier than jet yield (bp.310-370°C), wt/wt%	-	11

Claims:

1. A process for production of a hydrocarbon fraction suitable for use as jet fuel from an oxygenate feedstock comprising less than 1 wt/wt% aromatics, comprising the steps of
 - 5 a. combining the feedstock with a diluent hydrocarbon stream to form a hydrotreatment feed stream to contact a material catalytically active in hydrotreatment comprising one or more sulfided metals taken from the group of nickel, cobalt, molybdenum or tungsten, supported on a carrier comprising an amorphous refractory oxides, under hydrotreating conditions
 - 10 to provide a hydrotreated intermediate product,
 - b. directing said hydrotreated intermediate product to contact a material catalytically active in hydrocracking comprising one or more sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum, an acidic support and a refractory support, under hydrocracking conditions to provide
 - 15 a hydrocracked intermediate product,
 - c. separating the hydrocracked intermediate product in a hydrocracked intermediate liquid fraction and a gaseous fraction,
 - d. directing at least an amount of said hydrocracked intermediate liquid fraction
 - 20 to contact a material catalytically active in hydrodearomatization comprising 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 and a refractory support, preferably amorphous silica-alumina, alumina, silica or titania, or combinations thereof, under hydrodearomatization conditions sufficient to provide a treated
 - 25 product comprising less than 1 wt/wt%, aromatics, calculated by total mass of aromatic molecules relative to all hydrocarbons in the stream and comprising the hydrocarbon fraction suitable for use as jet fuel.
2. The process according to claim 1, wherein an amount of said hydrocracked
- 30 intermediate liquid fraction is directed as said diluent hydrocarbon stream.
3. The process according to claim 1 or 2 wherein step c comprises separating the hydrocracked intermediate product according to boiling point, providing a

hydrocracked intermediate jet product having T10 above 205°C and final boiling point below 310°C according to ASTM D86.

4. The process according to claim 1, 2 or 3 wherein step b or d further comprises
5 directing a stream for isomerization being either said hydrotreated intermediate product, said hydrocracked intermediate product or said treated product to contact a material catalytically active in isomerization under isomerization conditions, to provide an isomerized stream being used in step b or d as said hydrotreated
10 intermediate product, said hydrocracked intermediate product or said treated product respectively.
5. The process according to claim 1, 2, 3 or 4 wherein an amount of the hydrocracked
intermediate product optionally after separation according to boiling point, and at
15 least comprising a hydrocarbon fraction boiling above 310°C, is directed to be combined with either said feedstock or said hydrotreated intermediate product.
6. The process according to claim 1, 2, 3, 4 or 5 wherein step b comprises separating
the hydrotreated intermediate product in a liquid hydrotreated intermediate product
and a gaseous fraction, and optionally the further step of separating the liquid
20 hydrotreated intermediate product according to boiling point, providing a hydrotreated intermediate jet product having T10 above 120°C and final boiling point below 310°C according to ASTM D86.
7. The process according to claim 1, 2, 3, 4, 5 or 6 wherein the process conditions are
25 selected such that the conversion, defined as the difference in the amount of material boiling above 310°C in said hydrocracked intermediate product and the amount of material boiling above 310°C in said hydrotreated intermediate product, relative to the amount of material boiling above 310°C in said hydrotreated
intermediate product, is above 20%, 50% or 80%.
8. The process according to claim 1, 2, 3, 4, 5, 6, or 7 wherein said treated product
30 comprises less than 0.5 wt/wt% or 0.1 wt/wt% aromatics, calculated by total mass of aromatic molecules relative to all hydrocarbons in the stream.

9. The process according to claim 1, 2, 3, 4, 5, 6, 7, or 8 wherein a hydrogen rich stream comprising at least 90 vol/vol% hydrogen is directed to contact the material catalytically active in hydrodearomatization, and wherein an amount of said gaseous fraction is optionally purified and directed to contact the material catalytically active in hydrotreatment.
10. The process according to claim 1, 2, 3, 4, 5, 6, 7, 8 or 9 wherein the treated product is directed to a gas/liquid separator to provide a second stage gaseous fraction and a treated intermediate jet product which is directed to a further means of separation, such as a stripper, to provide said hydrocarbon fraction suitable for use as jet fuel and a treated product off gas.
11. The process according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10, wherein hydrotreatment 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 hydrotreatment 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.
12. The process according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11, wherein hydrocracking 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 0.5-4, 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).
13. The process according to claim 4 or a claim dependent thereon, 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.

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14. The process according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13, wherein hydrodearomatization conditions involve a temperature in the interval 200-350°C, a pressure in the interval 20-100 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 elemental noble metals such as platinum or palladium and a refractory support, preferably amorphous silica-alumina, alumina, silica or titania, or combinations thereof.

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15. A process plant for production of a hydrocarbon suitable for use as a jet fuel from a feedstock comprising less than 1 wt/wt% aromatics being a renewable feedstock or an oxygenate feedstock, comprising a hydrotreatment section containing a material catalytically active in hydrodeoxygenation comprising one or more sulfided metals taken from the group of nickel, cobalt, molybdenum or tungsten, supported on a carrier comprising an amorphous refractory oxides, a hydrocracking section containing a material catalytically active in hydrocracking, comprising one or more sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum, an acidic support and a refractory support and a hydrodearomatization section containing a material catalytically active in hydrodearomatization comprising 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

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palladium and a refractory support, preferably amorphous silica-alumina, alumina, silica or titania, or combinations thereof, said process plant being configured for

- a. directing the feedstock to the hydrotreatment section to provide a hydrotreated intermediate product,
- 5 b. directing the hydrotreated intermediate product to the hydrocracking section to provide a hydrocracked intermediate product,
- c. directing at least an amount of said hydrocracked intermediate product to a hydrodearomatization section to provide a treated product comprising the hydrocarbon fraction suitable for use as a jet fuel wherein said treated
- 10 product comprises less than 1 wt/wt% aromatics, calculated by total mass of aromatic molecules relative to all hydrocarbons in the stream.