

REMOVAL OF FLUORINE IN RENEWABLE FUEL PRODUCTION

TECHNICAL FIELD

The present invention relates to the removal of fluorine in the processing of renewable feedstocks.

5 BACKGROUND

Renewable feedstocks derived from pyrolysis and hydrothermal liquefaction (HTL) of solid biomass waste (e.g. sludge, plastic waste, municipal solid waste) can have a significant content of fluorine. Some fluorine compounds have very high chemical and thermal stability and may be hard to remove, and are therefore sometimes known as "forever chemicals".

- 10 Upgrading of renewable feedstock to transportation fuel such as jet fuel and diesel fuel requires removal of sulfur, nitrogen, and oxygen to very low levels as well as reduction of other unwanted elements like fluorine to meet the relevant product specifications for use as transportation fuel. It has been found that it is hard to produce a jet fuel or a jet fuel component with a low fluorine level e.g. below 2 wt ppm or 1 wt ppm. It has turned out that
15 this can be difficult to achieve by hydroprocessing alone even at very severe conditions in the reactor.

- From upgrading of fossil oil by hydroprocessing it is known that removal of heteroatoms such as sulfur and nitrogen from organic sulfur and nitrogen compounds to form sulfur and nitrogen free compounds is more difficult with increasing carbon number. Therefore, it is
20 expected that the most refractory heteroatomic compounds will be present in the fraction with the highest carbon number. It has surprisingly been found that the most refractory fluorine compounds after hydroprocessing do not concentrate with increasing carbon number, but instead are found in the naphtha and light jet fractions. Fluorine removal is not such an issue in fossil fuel-based refining processes, as the fluorine content of the feed in fossil fuels
25 is typically significantly lower.

SUMMARY

It has surprisingly been discovered that the fluorine content in the jet boiling range is higher than that of the diesel boiling range and higher boiling ranges. By eliminating the lightest part of product boiling in the jet range the resulting heavier part of the jet boiling range has a

significantly lower fluorine content than the full boiling range. As the upgraded product boiling above the jet range has a significantly lower content of fluorine hydrocracking of this material into jet range boiling material will result in jet range product with a low fluorine content. This will result in increased production of jet fuel with a reduced fluorine content.

- 5 The standard solution is to hydroprocess the renewables, but it has turned out that even at very severe conditions (one or more of high activity catalyst, high pressure and high temperature in the reactor) it is very difficult to reduce the fluorine in the jet range to below 2 wt ppm.

10 So, in a first aspect the present invention relates to a process for providing a jet fuel fraction with a low content of fluorine from a solid renewable feedstock, said process comprising the steps of:

- feeding a liquid oil stream comprising at least 5 ppm_{wt} fluorine, 25 ppm_{wt} fluorine, or 50 ppm_{wt} fluorine, said liquid oil stream being derived from said solid renewable feedstock to a fractionation section, and subjecting it to fractionation, to provide at
15 least a light jet fuel fraction and a heavy jet fuel fraction, wherein the fluorine content in the heavy fraction is lower than the fluorine content in the liquid oil stream.

Additional aspects of the invention are presented in the following description text, figures and claims.

LEGENDS TO THE FIGURE

- 20 The technology is illustrated by means of the following schematic illustrations, in which:

Figure 1 shows the product fluorine content from experiment 1

Figure 2 shows the product fluorine content from experiment 2

Figure 3 shows the product fluorine content from experiment 4

Figures 4 and 8 show a conventional layout.

- 25 Figures 5-7 and 9-11 show various layouts according to the invention.

DETAILED DISCLOSURE

The term "fluorine" is used in the present invention to mean inorganic and organic molecules containing F. A "low content" of fluorine means a content of less than 5 wt ppm fluorine. Fluorine content is measured by ASTM D7359.

- 5 The invention concerns – in general terms – a process for providing a jet fuel fraction with a low content of fluorine from a solid renewable feedstock, said process comprising the steps of:
- feeding a liquid oil stream comprising at least 5 ppm_{wt} fluorine, 25 ppm_{wt} fluorine, or 50 ppm_{wt} fluorine, said liquid oil stream being derived from said solid renewable
 - 10 feedstock to a fractionation section, and subjecting it to fractionation, to provide at least a light jet fuel fraction and a heavy jet fuel fraction, wherein the fluorine content in the heavy fraction is lower than the fluorine content in liquid oil stream.

The new feature is to eliminate the lightest fraction of the jet cut originating from the hydroprocessing of the renewable feedstock by distillation. The resulting heavier jet cut will

15 then have a reduced fluorine content. In cases where hydrocracking is used both the lightest and heavier fraction of the jet will have a reduced content of fluorine. The amount of light jet that can be added to the heavier jet fraction will then be higher.

Renewable feedstock

The process comprises a liquid oil stream derived from a solid renewable feedstock. In one

20 aspect, said renewable feedstock comprises one or more of:

- a lignocellulosic biomass such as wood products, algae, grass, forestry waste and/or agricultural residue;
- recycled solid waste, in particular the organic portion thereof, where the recycled solid waste is defined as a feedstock containing materials of items discarded by the public,
- 25 such as mixed recycled solid waste given in EU Directive 2018/2001 (RED II), Annex IX, part A; or
- nitrogen-rich renewable feedstock such as manure or sewage sludge.

In an embodiment, the portion of the solid renewable feedstock originating from a renewable source is 5-60 wt%, such as 10 or 50 wt%. In another embodiment, the portion of the

30 feedstock originating from a renewable source is higher than 60 wt%, for instance 70-90 wt%.

Deriving the liquid oil feed

Said solid renewable feedstock needs to be decomposed to produce the liquid oil stream. Therefore, in one aspect, said process further comprises a step of thermal decomposition of the renewable feedstock to produce said liquid oil stream, preferably wherein said thermal decomposition comprises a pyrolysis step and/or a hydrothermal liquefaction step. While specific process conditions are mentioned for specific processes below, similar thermal decomposition processes may be realized, involving conditions from 300°C to 700°C, pressures from 1 atm to 400 atm and residence time from 1 second to 1 hour, with different benefits.

- 10 The pyrolysis step may include the use of a pyrolysis unit such as fluidized bed, transported bed, or circulating fluid bed, as is well known in the art. Generally, this takes place at 350-650°C at around 1atm. For instance, the pyrolysis step may comprise the use of a pyrolysis unit (also referred herein as pyrolysis reactor), cyclone(s) to remove particulate solids such as char, and a cooling unit for thereby producing an off-gas stream (i.e., pyrolysis off-gas)
- 15 and said liquid oil stream, i.e. condensed pyrolysis oil. The off-gas stream comprises light hydrocarbons e.g., C1-C4 hydrocarbons, CO and CO₂. The liquid oil stream is also referred to as pyrolysis oil or bio-oil and is a liquid substance rich in blends of molecules usually consisting of more than two hundred different compounds including aldehydes, ketones and/or other compounds such as furfural having a carbonyl group, resulting from the
- 20 depolymerisation of products treated in pyrolysis. In this way, the liquid oil feed derived from a renewable feedstock may be pyrolysis oil or bio-oil.

- In an embodiment, the pyrolysis step comprises fast pyrolysis, also referred to in the art as flash pyrolysis. Fast pyrolysis means the thermal decomposition of a solid renewable feedstock in the absence of oxygen, at temperatures in the range 350-650°C e.g. about
- 25 500°C and reaction times of 10 seconds or less, e.g. below 10 seconds, such as 5 seconds or less, e.g. about 2 seconds; i.e. the vapor residence time is 10 seconds or below, such as 2 seconds or less e.g. about 2 seconds. The pressure is usually 1 atm. In this way, the reaction is provided with sufficient heat to at least partly decompose larger organic compounds such as polymers present in the renewable feedstock. The elevated temperature will not cause the
- 30 renewable feedstock to combust because the reaction occurs under oxygen-poor conditions.

- Traditionally, fast pyrolysis may for instance also be conducted by autothermal operation e.g., in a fluidized bed reactor. The latter is also referred as autothermal pyrolysis and is characterized by employing air, optionally with an inert gas or recycle gas, as the fluidizing gas, or by using a mixture of air and inert gas or recycle gas. Thereby, the partial oxidation
- 35 of pyrolysis compounds being produced in the pyrolysis reactor (autothermal reactor)

provides the energy for pyrolysis while at the same time improving heat transfer. For details about autothermal pyrolysis, reference is given to e.g. "Heterodoxy in Fast Pyrolysis of Biomass" by Robert Brown: <https://dx.doi.org/10.1021/acs.energyfuels.0c03512>. In an embodiment, the pyrolysis step comprises autothermal pyrolysis.

- 5 In embodiments, the pyrolysis step comprises catalytic fast pyrolysis (CFP). Such a catalytic fast pyrolysis step comprises using a catalyst e.g. an acid catalyst, such as a zeolite catalyst. Catalytic fast pyrolysis can both be operated in an in-situ mode, where the catalyst is located inside a pyrolysis unit, and in an ex-situ mode, where the catalyst is placed in a separate reactor.
- 10 The pyrolysis step may comprise in-situ catalytic fast pyrolysis. In one embodiment, the catalyst is located inside the pyrolysis unit and deoxygenation (DO) (through e.g. decarbonylation, decarboxylation by an acid-based catalyst such as a zeolite catalyst) takes place inside the pyrolysis reactor immediately after the pyrolysis vapours are formed. Suitable catalysts for CFP include alumina and all the types of zeolite catalysts that are
- 15 normally used for hydrocracking (HCR) and cracking in refinery processes, such as HZSM-5. Alternatively, in one embodiment, hydrogen is added and a hydrotreating catalyst such as a hydrodeoxygenating catalyst is located in the pyrolysis unit, and the pyrolysis vapours are hydrodeoxygenated immediately in the pyrolysis reactor after they are formed, typically resulting in 50% to 99 % or even complete oxygen removal. Said process is referred to as in-
- 20 situ HDO (also called reactive catalytic fast pyrolysis, RCFP, which normally operate at 1.5 barg H_2), but a combination of in-situ HDO and ex-situ HDO may also be used, resulting in more than 95 % or even complete oxygen removal. Suitably catalysts for HDO are metal-based catalysts, including reduced Ni, Mo, Co, Pt, Pd, Re, Ru, Fe, such as CoMo or NiMo catalysts, suitably also in sulfide form: CoMoS, NiS, NiMoS, NiWS, RuS. The catalyst
- 25 supports may be the same in conventional HDO in refinery processes, typically a refractory support such as alumina, silica or titania, or combinations thereof.

If operated in in-situ mode, H_2 is added to the pyrolysis reactor. If operated in ex-situ mode the H_2 can both be added to the pyrolysis reactor or to the HDO reactor. The H_2 pressure is normally between 1 barg to 40 barg.

- 30 The use of a catalyst in the pyrolysis reactor can in some cases reduce the required temperature for conducting the pyrolysis. In addition, increased selectivity towards desired pyrolysis oil compounds may be achieved.

In an embodiment the pyrolysis step is fast pyrolysis, in which the vapor residence time is 10 seconds or less, e.g. below 10 seconds, such as 5 seconds or less, e.g. about 2 seconds, or 1

second, or in the range 1-5 seconds, and which is selected from: simple fast pyrolysis; in-situ catalytic fast pyrolysis (in-situ CFP); ex-situ catalytic fast pyrolysis (ex-situ CFP); reactive catalytic fast pyrolysis (RCFP); hydrolysis (HP); catalytic fast hydrolysis (CHP).

5 As an alternative to fast pyrolysis, intermediate and/or slow pyrolysis may also be used and may – in some instances – be preferred.

In an embodiment, the pyrolysis step is intermediate pyrolysis, in which the vapor residence time is in the range of 10 seconds – 5 minutes, such as 11 seconds – 3 minutes. As for fast pyrolysis, the temperature is also in the range 350-650°C e.g. about 500°C. Often this pyrolysis is conducted in pyrolysis reactors handling different types of waste, where the vapor
10 is burned after the pyrolysis reactor. Typical reactors are: Herreshoff furnace, rotary drums, amaron, CHOREN paddle pyrolysis kiln, auger reactor, and vacuum pyrolysis reactor.

In another embodiment, the pyrolysis step is slow pyrolysis, in which the solid residence time is in the range of 5 minutes – 2 hours, such as 10 min – 1 hour. The temperature is suitably about 300°C. This pyrolysis gives a high char yield and the char can be used as a fertilizer or
15 as char coal; the pyrolysis still produces some gas and biocrude and if the carbon is used a fertilizer the final bio-oil can have a GHG above 100 %, thus being carbon negative. Typical reactors are auger reactor – yet with a different residence time than for intermediate pyrolysis – fixed bed reactor, kiln, lambiotte SIFIC/CISR retort, Lurgi process, wagon reactor, and carbo twin resort.

20 Accordingly, said liquid oil feed comprises compounds formed under moderately elevated temperatures (>80 °C) but below the temperatures resulting in substantially complete hydrotreatment. Said liquid oil feed may comprise i) a feed rich in conjugated diolefins or styrene and its homologs resulting from thermochemical decomposition of plastic waste, municipal solid waste, refuse derived fuel and solid recovered fuel, ii) a feed rich in carbonyls
25 and sugars resulting from thermochemical decomposition of lignocellulosic biomass and/or iii) a feed rich in nitrogen resulting from thermochemical decomposition of nitrogen-rich renewable feedstock, such as manure and sewage sludge, and/or similar compositions from other sources. In embodiments, said liquid oil feed may comprise larger compounds as the compounds resulting from thermochemical decomposition (e.g. compounds of i)-iii)) may
30 subsequently react i.e. reactive functional groups may react with either the same functional group (e.g. diolefin with diolefin) or across functional groups (e.g. aldehyde with phenol) to provide larger compounds. Said larger compounds may potentially result in full or partial blockage of reactors, tubes, heaters, heat exchangers and catalysts comprised in later process steps.

35

Accordingly, the process of the invention may further comprise a step of thermal decomposition of the renewable feedstock to produce said liquid oil stream, preferably wherein said thermal decomposition comprises a pyrolysis step and/or a hydrothermal liquefaction step.

- 5 In an embodiment, the thermal decomposition is hydrothermal liquefaction. Hydrothermal liquefaction means the thermochemical conversion of biomass into liquid fuels by processing in a hot, pressurized water environment for sufficient time to break down the solid polymeric or bio-polymeric structure to mainly liquid components. Typical hydrothermal processing conditions are temperatures in the range of 250-400°C and operating pressures in the range of 40-400 bar. This technology offers the advantage of operation of a lower temperature, higher energy efficiency and lower tar yield compared to pyrolysis, e.g. fast pyrolysis. For details on hydrothermal liquefaction of biomass, reference is given to e.g. Golakota et al., "A review of hydrothermal liquefaction of biomass", Renewable and Sustainable Energy Reviews, vol. 81, Part 1, Jan. 2018, p. 1378-1392.
- 10
- 15 In an embodiment, the thermal decomposition is liquefaction. Liquefaction means the thermochemical conversion of biomass into liquid fuels by processing in the absence of water. Typical conditions are temperatures in the range of 250-375°C and operating pressures in the range of 40-220 bar. For instance, also as described in WO21209555 A1.
- 20 The liquid oil stream fed to the plant suitably comprises more than 5 wt ppm fluorine, such as more than 25 wt ppm fluorine, more than 50 wt ppm fluorine, or more than 75 wt ppm fluorine.

Stabilization

- The process – in one aspect – comprises a step of subjecting the liquid oil stream to a stabilization step in a stabilization section, prior to the fractionation step.
- 25

- The purpose of said process step is to provide a stabilized liquid oil stream, which may be characterised as a stream comprising a lower content of reactive compounds than the liquid oil stream from which it is derived. This may be achieved by modification of the chemical composition of the liquid oil and/or by removal of destabilization components from the liquid oil. Said stabilized liquid oil stream may have a lower vapor pressure than the liquid oil stream from which it is derived. In this way, said process step provides a less reactive liquid oil stream i.e. a stabilized liquid oil stream, which may be fed into subsequent process steps.
- 30

In one aspect, said process comprises reacting said liquid oil stream with hydrogen within the stabilization reactor in the presence of a catalyst where said catalyst comprises at least one metal selected from Ni, Co, Mo, W, Cu, Pt, Pd, Ru such as nickel-molybdenum molybdenum (Ni-Mo), cobalt-molybdenum (Co-Mo), nickel-tungsten (NiW), nickel-copper (NiCu), Pt, Pd, or
5 Ru to provide at least one stabilized liquid oil stream. The catalyst may be S-passivated.

In one aspect, said process comprises operating the stabilization reactor at a temperature of 80-230°C and at a pressure of 20-200 barg. Said temperature encompasses the inlet temperature of the liquid oil stream and the outlet temperature of stabilized liquid oil stream.
10 The unit barg denotes pressure above atmospheric (atmospheric pressure is about 1 bar), where said pressure may also be referred to as "hydrogen pressure". Said process may be conducted at a hydrogen to liquid oil ratio of 500- 10000 NL/L, such as 2000-5000 NL/L, for instance 2500, 3000, 3500, 4000 or 4500 NL/L. As used herein, the term "hydrogen to liquid oil ratio" or "H₂/oil ratio" means the volume ratio of hydrogen to the flow of the liquid oil
15 stream. It would be understood, that the unit NL means "normal" liter, i.e. the amount of gas taken up this volume at 0°C and 1 atmosphere. The volume of liquid is taken as standard volume at 15°C and 1 atmosphere. Where H₂/oil ratio is mentioned, the values are exemplary, and if a specific reaction step has an exceptionally high or low consumption of hydrogen, the H₂/oil ratio may be adjusted accordingly. Commonly a safety factor of 6 is
20 multiplied with the observed or the theoretical consumption of hydrogen, but a safety factor from 3 to 8 may be observed in practice. Where H₂/oil ratio is considered, an adjustment for the concentration of hydrogen in the gas phase may also be included, such that a hydrogen concentration of 80 % vol/vol results in an increase in the required gas to oil ratio by 100/80, compared to the H₂/oil ratio requirements for 100 % vol/vol hydrogen.

25 In this way, said process step may result in the modification of the liquid oil stream through hydrogenation to remove destabilizing components, thus said process converts reactive compounds present in the liquid oil stream to less reactive compounds under low temperature conditions. In one aspect, the liquid oil stream – at the inlet of the stabilisation section – comprises at least 0.5 wt% oxygen (O), such as at least 4 wt% O, such as at least
30 20 wt% O, such as at least 30 wt% O, or at least 45 wt% O. Pyrolysis oil from recycled plastic typically contains 0.5-4 wt% O, while pyrolysis oil from biological materials typically contains 5-50 wt% O. The oxygen may be present as reactive compounds such as furfural, furans, aldehydes, ketones and acids, which may be converted into alcohols, for instance by
35 efficiently converting carbonyls into alcohols. Conversion of carbonyls into alcohols occurs at a temperature of approx. 100-200°C (temperature within the reactor). The alcohols can further be converted to saturated organic compounds during the stabilization, and/or in a subsequent hydroprocessing process step such as hydrodeoxygenation (HDO).

In one specific embodiment, said process step comprises hydrotreating a liquid oil stream by, in a continuous operation in a fixed bed reactor, reacting the liquid oil stream with hydrogen in the presence of a nickel-molybdenum (Ni-Mo) based catalyst at a temperature, e.g. inlet temperature, of 80-230°C, a pressure of 100-200 barg, a liquid hourly space velocity (LHSV) of 0.1 -1.1 h⁻¹, and a hydrogen to liquid oil ratio, defined as the volume ratio of hydrogen to the flow of the liquid oil stream, of 500-10000 NL/L, such as 2000-5000 NL/L, thereby forming a stabilized liquid oil stream. Commonly the amount of hydrogen is calculated from a theoretical consumption of hydrogen, multiplied by a factor. As an example a feedstock with 6.3 wt% O, and 8.7 wt% N, may have a theoretical hydrogen consumption of about 300 NL/L (ignoring hydrogen consumption by removal of other heteroatoms, saturation of double bonds, hydrocracking etc.), which by application of a safety factor of 6, requires a volume ratio of hydrogen to oil of 1800 NL/L.

The combination of features i.e. low temperatures, high pressure, low LHSV and high H₂-to liquid oil ratio, as recited above, enables stabilization of the liquid oil by i.e. converting carbonyls to alcohols and thereby increase operation time before plugging issues - if any - arise, while at the same time suppressing coking of the catalyst and attendant catalyst deactivation, as well as avoiding hydrogen starvation.

The temperature range 80-230°C encompasses the inlet temperature of the liquid oil stream and the outlet temperature of stabilized liquid oil stream. For instance, the inlet temperature can be 80, 100, 110, 120 or 130°C. The higher the inlet temperature e.g. 130°C, the easier the ignition of the process to initiate the exotherm. The outlet temperature can for instance be 200 or 215 or 230°C. More generally, the temperature in a given step or reactor (unit) thereof, means the inlet temperature in an adiabatic step, or the reaction temperature in an isothermal step. Accordingly, suitably said temperature of 80-230°C means inlet temperature. The term continuous operation, as is well known in the art, means that the incoming stream of liquid oil during a given production cycle is constant, as also is the stabilized liquid oil stream being withdrawn as the outcoming product. This contrasts a batch operation i.e. discontinuous operation, as is also well known in the art, in which the total amount of liquid oil and catalyst is introduced at the beginning of the process, and the outcoming product is withdrawn after a certain period of time.

Hence, low temperature (80-230°C) operation result in stabilization of a liquid oil stream and avoids plugging problems, but also allows for stabilization without deactivating the catalyst and without risk of hydrogen starvation.

Guard unit

If required, the hydroprocessing section comprises a guard unit. The guard unit is present upstream the first hydroprocessing unit, and captures one or more heteroatom(s) in the guard material. Typically, the heteroatom(s) captured is/are selected from one or more of arsenic (As), phosphorus (P), silicon (Si), iron (Fe), nickel (Ni), vanadium (V), potassium (K), sodium (Na), zinc (Zn), magnesium (Mg), chromium (Cr) or molybdenum (Mo), halides or combinations thereof. Said heteroatoms may be advantageously captured as they can solidify as sulfides or other solid compounds in said guard material.

Commonly the guard conditions are similar to the downstream hydrotreating conditions, which typically involves a temperature in the interval 250-420°C, a pressure in the interval 30-200 bar, and a liquid hourly space velocity (LHSV) in the interval 0.01-2. Commonly the hydrogen to oil ratio will include the hydrogen required for downstream hydrotreatment, and may be in the range 500-4500 NL/L.

The guard material may be a metal guard bed. A metal guard bed means a bed i.e. a fixed bed which comprises a material active in hydrometallation (HDM) and/or hydrodeoxygenation (HDO). The process of hydrodemetallation (HDM) is meant to cover a pre-treatment, by which free metals are generated and then converted into metal sulfides. Hydrodemetallation hereby differ from e.g. hydrodesulfurization (HDS) as, the heteroatom (S) in HDS is removed in gas form. In addition to removing heteroatoms such as those mentioned above, the guard material may also be provided with deoxygenation activity.

A suitable guard bed may be a porous material comprising alumina, the alumina comprising alpha-alumina. The alumina may further comprise theta-alumina such as 0-50 wt% and optionally smaller amounts gamma-alumina such as 0-10 wt% as determined by XRD. Said porous material may have a BET-surface area of 1-110 m²/g measured according to ASTM D4567-19 (i.e. single-point determination of surface area by the BET equation), suitably also having a total pore volume of 0.50-0.80 ml/g, as measured by mercury intrusion porosimetry according to ASTM D4284. The pore size distribution (PSD) of said porous material may be of at least 30 vol% of the total pore volume being in pores with a radius > 400 Å, suitably pores with a radius > 500 Å, such as pores with a radius up to 5000 Å; as for instance disclosed in Applicant's co-pending patent application PCT/EP2021/068656. The porous material may further comprise one or more metals selected from Co, Mo, Ni, W and combinations thereof, preferably Ni. Combinations of Ni with at least one other metal are possible. The content of the one or more metals is 0.25-20 wt%, such as 0.25-15 wt%, 0.25-10 wt%, or 0.25-5 wt%. In one embodiment, at least one metal is in the form of oxides or sulfides.

Catalytic hydroprocessing

In one aspect, the process comprises subjecting the liquid oil stream to a catalytic hydroprocessing step in a hydroprocessing section, prior to the fractionation step, and preferably after the stabilization step. This results in one or more hydroprocessed product stream(s). In this way, the process encompasses at least one catalytic hydroprocessing step.

- 5 In one aspect, said process comprises one or more catalytic hydroprocessing steps selected from hydrodeoxygenation (HDO), hydrotreating, hydrodenitrogenation (HDN), hydrodesulfurization (HDS), saturation of aromatic rings (HDA), hydrocracking and/or isomerisation, performed within one or more hydroprocessing reactors. Hydrodeoxygenation (HDO) refers to the process where oxygen is removed from the liquid oil feed mainly as H₂O,
10 but possibly also as CO and CO₂.

- In the following, reference may be made to a first and a second hydroprocessing step. As the oxygen-compounds typically are more reactive than nitrogen-compounds, the first hydroprocessing step may also be referred to as the HDO step and the second
15 hydroprocessing step may also be referred to as the HDN step in the following, even though multiple hydrotreatment reactions take place in parallel.

- The material catalytically active in hydrotreating typically comprises an active metal (sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum, but possibly also either
20 elemental noble metals such as platinum and/or palladium) and a refractory support (such as alumina, silica or titania, or combinations thereof). Hydrotreating typically involves a temperature in the interval 250-420°C or even 425°C, a pressure in the interval 30-200 bar, and a liquid hourly space velocity (LHSV) in the interval 0.1-2 or even 5 hr⁻¹ and a GOR (gas to oil ratio) of 300-5000 NL/L optionally together with intermediate cooling by quenching with
25 cold hydrogen, feed or product.

- Hydrodearomatization (HDA) refers to a hydrotreating process in which hydrogen is used in the presence of heat, pressure, and catalysts to saturate aromatic hydrocarbons to produce low-aromatic hydrocarbon content in the product stream. The material catalytically active in hydrodearomatization typically comprises an active metal (typically elemental noble metals
30 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 conditions involve a temperature in the interval 200-350°C, a pressure in the interval 20-200 bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8.0 and a GOR (gas to oil ratio) of 300-
35 1500 NL/L.

- Hydrocracking refers to a bi-functional catalytic process combining catalytic cracking and hydrogenation, thus wherein the liquid oil feed undergo cracking in the presence of hydrogen. The material catalytically active in hydrocracking is of similar nature to the material catalytically active in isomerization, and it typically comprises an active metal (either
- 5 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) and a refractory support (such as alumina, silica or titania, or combinations thereof). The difference to material catalytically active isomerization is typically the nature of the acidic support,
- 10 which may be of a different structure (even amorphous silica-alumina) or have a different acidity e.g. due to silica:alumina ratio. Hydrocracking conditions involve a temperature in the interval 250-400°C, a pressure in the interval 30-200 bar, a liquid hourly space velocity (LHSV) in the interval 0.5-8.0 and a GOR (gas to oil ratio) of 300-2500 NL/L, optionally together with intermediate cooling by quenching with cold hydrogen, feed or product.
- 15 Isomerization process (including hydrodewaxing) is intended to improve flow indexes of the liquid oil stream. 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
- 20 MOR, FER, MRE, MWW, AEL, TON and MTT) and a refractory support (such as alumina, silica or titania, or combinations thereof). Isomerization conditions involve a temperature in the interval 250-400°C, a pressure in the interval 20-200 bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8.0 and a GOR (gas to oil ratio) of 300-5000 NL/L.

Fractionation

- 25 The liquid oil stream derived from the solid renewable feedstock is fed to a fractionation section, and subjected to fractionation by distillation, to provide at least a light jet fuel fraction and a heavy jet fuel fraction. Following this separation of the jet fraction into light and heavy jet fractions, the fluorine content in the heavy fraction is lower than the fluorine content in the light jet fraction. Fractionation may be a 1-step or a multi-step process.
- 30 Typically jet fuel has a boiling range from 149 to 300°C. The fractionation cut point between light and heavy jet will be selected according to the fluorine distribution and will be selected in the range from 175 to 225°C. With a given fractionation cut point, the light jet fuel fraction will contain at least 75% of material boiling below the specified cut point (determined by simulated distillation) and the heavy jet fraction will contain at least 75% of material boiling
- 35 above the cut point (determined by simulated distillation).

As the optimal cut point between a light fluorine rich jet fuel fraction and a heavier fluorine lean jet fuel fraction may depend on the method of thermochemical decomposition and the renewable feedstock, and it may be preferred to determine the cut point experimentally, instead of using a pre-defined value. A proposed process for determination involves

- 5 fractionating a representative sample of product by boiling point, e.g. in intervals of 10°C, and defining the boiling point limits of light jet fuel according to this distribution, e.g. to withdraw the range where the fluorine content is above 5 wt ppm.

- The light jet fuel fraction may be distinguished from the heavy jet fuel fraction by the boiling points of the fractions. The light jet fuel fraction suitably has a boiling point in the range 149–
10 200°C, preferably in the range 149–190°C. The heavy jet fuel fraction suitably has a boiling point in the range 175–300°C, preferably in the range 200–300°C. Heavy jet fuel fraction shall be construed as a stream being suitable for use as a jet fuel component, fulfilling boiling point specifications for jet fuel, having an initial boiling point being higher than 175°C, but
15 the term shall not be construed as implying any jet fuel specifications other than boiling point. Such other specifications, including cold flow properties, flash point, density, aromatics content, H content, smoke point etc. may beneficially be used individually or collectively be used to specify the heavy fuel fraction more narrowly in accordance with ASTM D7566, to define an even more suited jet fuel component.

- The heavy jet fuel fraction obtained by the process suitably comprises less than 2 wt ppm,
20 such as less than 1 wt ppm fluorine, and therefore meets the required specification.

In addition to the jet fuel fractionation step further provides one or more streams selected from: a gas stream, a naphtha stream, a diesel stream and a fuel oil stream.

- In one aspect of the invention, the hydroprocessing section comprises: a guard unit, a first hydroprocessing unit, and a second hydroprocessing unit, wherein said liquid oil product
25 stream is passed through said guard unit, said first hydroprocessing unit and said second hydroprocessing unit in order. Optionally, a stabilisation unit is located upstream the guard unit.

- The first hydroprocessing unit suitably involves a temperature in the interval 250–420°C, a pressure in the interval 30–200 barg, a liquid hourly space velocity (LHSV) in the interval 0.1–
30 2, and a hydrogen to oil ratio of 500–10000 NL/L. The same parameters may be used for the second hydroprocessing unit. Suitably, the second unit can e.g. operate with lower LHSV and higher pressure than the first unit. The second unit is typically also operated with a more hydrogen rich treat gas.

The amount of jet fuel can be further increased by hydrocracking the product boiling above the jet range into a product boiling in the jet range. In one aspect, therefore, the process may further comprising a step of feeding at least a portion of the diesel stream and/or at least a portion of the fuel oil stream to a hydrocracking section so as to provide a cracked stream, and optionally feeding at least a portion of said cracked stream to a second hydroprocessing unit, e.g. a hydrodenitrogenation (HDN) unit. In this case the heavy product from the fractionator (i.e. a combination of diesel and fuel oil) is routed to a hydrocracking reactor HC, being a third reactor section, where the heavy product primarily is converted into jet boiling range material with a reduced fluorine content. One scenario is full recycle of the diesel stream and the fuel stream. The reactor effluent from the HC reactor is routed to the HDN unit, but may also bypass the HDN unit and be fed directly to the fractionation section. This aspect increases the output from the process, by recycling and cracking heavy product from the fractionation section.

In another scenario, the HC reactor can also be downstream the second (HDN) unit. Therefore, hydroprocessing section may comprise a hydrocracking section downstream said second hydroprocessing unit, said process comprising a step of cracking the liquid oil product stream from the second hydroprocessing unit.

In another application the renewable feedstock can be distilled prior to the deep hydrotreating (i.e. second) stage to produce a heavy naphtha stream. This distillation is carried out in such a way that naphtha and part of the light jet containing a relative high amount of fluorine is removed. In this way the heavy product from the distillation process routed to the hydrotreating stage has a lower fluorine content and the amount of light jet material with a "high" fluorine content will be reduced.

As noted, the light jet fraction has a higher content of fluorine than the heavy jet fraction. The resulting heavy jet fraction may be mixed with an amount of light jet fraction to obtain a combined jet fuel fraction with an acceptable amount of fluorine. The process according to the invention may therefore, further comprise a step of mixing at least a portion of the heavy jet fuel fraction with at least a portion of the light jet fuel fraction to provide a combined jet fuel fraction.

A water wash of the liquid oil stream is able to remove halogens, ammonia, hydrogen sulfide and salts. In one aspect, the process therefore further comprises a step of washing the stabilized liquid oil stream with water between the first and second hydroprocessing units. Alternatively or additionally, the process further comprises a step of washing the stabilized liquid oil stream with water between the second hydroprocessing unit and the fractionation section.

In a further preferred aspect, the hydroprocessing section comprises a stripper column arranged between the first hydroprocessing unit and the second hydroprocessing unit. The stripper column is arranged to receive a liquid oil product stream from the first hydroprocessing unit, and fractionate it to a first gas stream, a light oil product stream and a partly hydrotreated bottom product, wherein at least a portion of the partly hydrotreated bottom product is arranged to be fed to the second hydroprocessing unit. The stripper separates the liquid oil stream into an overhead gas stream and a light oil product stream containing naphtha and a light jet cut. The bottom product is then further hydrotreated in the second hydroprocessing unit. The heavy product may be recycled to a hydrocracking reactor for conversion into jet range products.

Specific embodiments of the invention

Figure 4 shows a simple layout of a conventional system/process for renewable fuel production. Liquid oil feed (1) is mixed with a hydrogen rich treat gas before it is routed to a stabilization section (10) for stabilization of the feedstock, and thus to provide a stabilized liquid oil stream (11). This stabilized liquid oil stream (11) is fed to a hydroprocessing section (30) comprising a guard unit (30a), a first hydroprocessing unit (30b) and a second hydroprocessing unit (30c). In guard unit (30a), contaminants such as As, P, Si and other metals are captured. After the guard unit (30a), the reactor effluent is routed to a first hydroprocessing unit (30b) where removal of oxygen, sulfur and nitrogen takes place.

The stabilized liquid oil stream (11) is washed with water between the first hydroprocessing unit (30b) and the second hydroprocessing unit (30c). As shown, the effluent from the first unit (30b) is mixed with water in front of a high pressure three phase separator (30e) where the hydrogen rich treat gas (39) is separated from the liquid oil and the spent water phase. The treat gas (39) is recycled back to the reactor system after addition of make-up hydrogen. Part of the hydrogen rich treat gas (39) can be purged prior to addition of make-up hydrogen. Part of the liquid oil can optionally be recycled back to the reactor system. The liquid oil from the first hydroprocessing unit (30b) is routed to a second hydroprocessing unit (30c) for additional removal of nitrogen and sulfur.

The stabilized liquid oil stream (11) is subjected to at least one step of catalytic hydroprocessing, to provide hydroprocessed product stream (31). The hydroprocessed liquid oil stream (31) is fed to a fractionation section (40), and subjected to fractionation, to provide a gas stream (43), a naphtha stream (44), a diesel stream (45), a fuel oil stream (46) and a (single) jet fuel fraction (41+42). Figure 4 also shows a step of washing the hydroprocessed liquid oil stream (31) with water between the second hydroprocessing unit

(30c) and the fractionation section (40). This washing step takes place in a similar manner to that between the first and second hydroprocessing steps, described above.

The layout of Figure 8 is a conventional layout, similar to that of Figure 4. In this layout all the treatment is carried out in a single-stage configuration (compared to Fig. 4-7 in which a two-stage configuration is used). The single-stage layout can be used in cases where the feedstock is relatively easy to upgrade. Therefore, the layout of Figure 8 shows stabilisation section (10), guard unit (30a), the first hydroprocessing unit (30b) but no separate second hydroprocessing unit (30c). The hydroprocessed product stream(s) (31) is fed to a fractionation section (40), and subjected to fractionation, to provide a gas stream (43), a naphtha stream (44), a diesel stream (45), a fuel oil stream (46) and a (single) jet fuel fraction (41+42).

In cases where the amount of nitrogen present in the feedstock is higher than about 0.5 wt% it is attractive to use a two-stage configuration (e.g. Figures 4-7) where the amount of ammonia in the treat gas is significantly reduced in the second stage as compared to the amount of ammonia in the treat gas in the first stage.

Figure 5 is based on the layout of Figure 4. In the fractionation section (40) of Figure 5, fractionation takes place to separate a light jet fuel fraction (41) and a heavy jet fuel fraction (42). The fluorine content in the heavy fraction is lower than the fluorine content in the light jet fraction. Optionally, in the layout of Figure 5, at least a portion of the heavy jet fuel fraction (42) is mixed with at least a portion of the light jet fuel fraction (41) to provide a combined jet fuel fraction (49), to meet specification.

Figure 6 is based on the layout of Figure 5. According to Figure 6, at least a portion of the fuel oil stream (46) is fed to a hydrocracking section (50) so as to provide a cracked stream (51). Alternatively or additionally, at least a portion of the diesel stream (45) may be fed to the hydrocracking section (50). At least a portion of the cracked stream (51) output from the hydrocracking section (50) is fed to the hydrodenitrogenation (HDN) unit (30c).

In the embodiment of Figure 7, a stripper column (30d) is present after the high pressure separator. The stripper separates the liquid oil product into a first gas stream (35), a light oil product stream (36) and a partly hydrotreated bottom product (37). The partly hydrotreated bottom product (37) is fed to the hydrodenitrogenation (HDN) unit (30c).

The layout in Figure 9 is a single-stage layout where the jet fraction is divided into a light and heavy jet fraction, in a similar manner to the layout in Figure 5 to reduce the fluorine content of the resulting jet fraction.

In the layout of Figure 10, a hydrocracking reactor (50) is introduced to the layout of Figure 9. The heavy product from fractionator (40) is routed to a hydrocracking reactor (50), which is positioned in a so-called “reverse staging configuration” downstream the second hydroprocessing reactor and upstream the first hydroprocessing reactor where the product is cracked to jet range product with a reduced fluorine content. The effluent from the hydrocracker reactor is routed back to guard unit (30a). It can also be routed back to any point before the water wash. For some feedstocks, it may also be possible to locate the hydrocracking reactor after the unit 30b.

In the layout of Figure 11 (a development of Fig. 7) a deep HDF step (catalytic removal of fluorine) has been added. The idea is to treat stream 36 over a noble metal catalyst in reactor (60) and reduce the content of fluorine compound down to a significantly lower level. The “deep HDF” step can in included at other locations as well.

EXAMPLES

A pilot test was carried out to produce a first stage product from a pyrolysis oil derived from sewage sludge. The product from this test was further processed in a pilot plant unit by use of a commercially available hydrotreating catalyst with a very high HDN activity.

The properties of the first stage product are shown in Table 1.

Feed properties		
SG	ASTM D 7359	0.8537
Nitrogen, wt ppm	ASTM D 4629	6443
Fluorine, wt ppm	ASTM D 7359	25.8

Table 1: Feed properties

The feed was processed in a pilot unit equipped with one reactor followed by a gas liquid separation section. In the test 20 ml of a commercially available high activity Ni-Mo based catalyst designed for removal of nitrogen was loaded. The test was conducted using a liquid hourly feed flow in the range from 0.52 to 0.61 h⁻¹ using a hydrogen to oil ratio of about 2500 NI/I at pressures of 122 barg and 71 barg, respectively.

Liquid product was collected during the test at stable reactor conditions at different reactor temperatures and reactor pressures as shown in Table 2. The amounts of nitrogen and fluorine were measured in the liquid product sampled during each experiment.

Experiment	Run hour	LHSV, h ⁻¹	P, barg	Reactor T, °C	N, wt ppm _{wt} (ASTM D 4629)	F, ppm _{wt} (ASTM D 7359)
1	163-306	0.53	122	360	25.8	18.7
2	331-404	0.53	122	380	0.5	10.5
3	493	0.61	122	400	0.1	5.1
4	619-740	0.52	71	400	15.1	7.6

Table 2: Experiment 1-4.

It was found that the amounts of nitrogen and fluorine decrease with increasing reactor temperature and with increasing reactor pressure.

The liquid products collected for experiment 1, 2 and 4 were fractionated in a batch distillation unit into various boiling ranges representing naphtha, jet, diesel and unconverted oil cuts. The distillation was carried out according to ASTM D 2892. The fluorine content of each boiling range was determined according to ASTM D 7359. The results of the fractionation are shown in Figure 1-3.

It was surprisingly found that the amount of fluorine is significantly higher in the lower boiling ranges than in the higher boiling ranges. The first cut (<150°C) is representing a naphtha product and the next cut is representing a light jet range product (150-175°C or 150-250°C). The boiling range for jet fuel is typically from 150 to 300°C so by excluding the lower boiling range material in the jet range a jet fuel with a low fluorine content can be produced.

The boiling range for jet fuel is typically from 150 to 300°C. By converting material boiling higher than 300°C having a very low fluorine content by hydrocracking to jet range material it will be possible to produce jet range material with a very low fluorine content and increase the amount of jet fuel with a low fluorine content.

The present invention has been described with reference to a number of embodiments and examples. The skilled person may combine these embodiments and examples within the scope of the invention, which is defined by the claims. All references cited here are incorporated by reference.

CLAIMS

1. A process for providing a jet fuel fraction with a low content of fluorine from a solid renewable feedstock, said process comprising the steps of:

- 5
- feeding a liquid oil stream (31) comprising at least 5 ppm_{wt} fluorine, 25 ppm_{wt} fluorine, or 50 ppm_{wt} fluorine, said liquid oil stream being derived from said solid renewable feedstock to a fractionation section (40), and subjecting it to fractionation by distillation, to provide at least a light jet fuel fraction (41) and a heavy jet fuel fraction (42), wherein the fluorine content in the heavy fraction is lower than the fluorine content in the liquid oil stream.

10

2. The process according to claim 1, further comprising the step of:

- subjecting the liquid oil stream (31) to a stabilization step in a stabilization section (10), prior to the fractionation step.

15

3. The process according to any one of the preceding claims, further comprising the step of:

- subjecting the liquid oil stream (31) to a catalytic hydroprocessing step in a hydroprocessing section (30), prior to the fractionation step, and preferably after the stabilization step.

20

4. The process according to any one of the preceding claims, wherein the renewable feedstock comprises one or more of:

- a lignocellulosic biomass such as wood products, algae, grass, forestry waste and/or agricultural residue;
- 25 - recycled solid waste, in particular the organic portion thereof, where the recycled solid waste is defined as a feedstock containing materials of items discarded by the public, such as mixed recycled solid waste given in EU Directive 2018/2001 (RED II), Annex IX, part A; or
- nitrogen-rich renewable feedstock such as manure or sewage sludge.

30

5. The process according to any one of the preceding claims, wherein the fractionation cut point between light and heavy jet fuel fractions is in the range from 175 to 225°C, and wherein, with a given fractionation cut point, the light jet fuel fraction will contain at least 75% of material boiling below the specified cut point and the heavy jet fraction will contain at least 75% of material boiling above the cut point.

35

6. The process according to any one of the preceding claims, wherein the heavy jet fuel fraction (42) comprises less than 2 wt ppm, such as less than 1 wt ppm fluorine.

7. The process according to any one of claims 2-6, wherein the liquid oil stream (31) – at the inlet of the stabilization section (10) – comprises more than 5 wt ppm fluorine, such as more than 25 wt ppm fluorine, more than 50 wt ppm fluorine, or more than 75 wt ppm fluorine.

8. The process according to any one of the preceding claims, wherein said hydroprocessing section (30) comprises:

- a guard unit (30a)
- a first hydroprocessing unit (30b)
- a second hydroprocessing unit (30c)

and wherein said liquid oil product stream (31) is passed through said guard unit (30a), said first hydroprocessing unit (30b) and said second hydroprocessing unit (30c) in order.

9. The process according to claim 8 wherein said process further comprises a step of washing the liquid oil product stream (31) with water between the first (30b) and the second (30c) hydroprocessing units.

10. The process according to any one of claims 8-9, wherein said process further comprises a step of washing the liquid oil product stream (31) with water between the second hydroprocessing unit (30c) and the fractionation section (40).

11. The process according to any one of the preceding claims, wherein the fractionation step further provides one or more streams selected from: a gas stream (43), a naphtha stream (44), a diesel stream (45) and a fuel oil stream (46).

12. The process according to claim 11, further comprising a step of feeding at least a portion of the diesel stream (45) and/or at least a portion of the fuel oil stream (46) to a hydrocracking section (50) so as to provide a cracked stream (51), and optionally feeding at least a portion of said cracked stream (51) to the second hydroprocessing unit (30c).

13. The process according to any one of claims 8-12, wherein said hydroprocessing section (30) comprises a hydrocracking section downstream said second hydroprocessing unit

(30c), said process comprising a step of cracking the liquid oil product stream (31) from the second hydroprocessing unit (30c).

14. The process according to any one of the preceding claims, wherein said
5 hydroprocessing section (30) comprises a stripper column (30d) arranged between the first hydroprocessing unit (30b) and the second hydroprocessing unit (30c), said stripper column (30d) being arranged to receive a liquid oil product stream (31) from the first hydroprocessing unit (30b) and fractionate it to a first gas stream (35), a light oil product stream (36) and a partly hydrotreated bottom product (37), wherein at least a portion of the
10 partly hydrotreated bottom product (37) is arranged to be fed to the second hydroprocessing unit (30c).

15. The process according to any one of the preceding claims, wherein said process further comprises a step of thermal decomposition of the solid renewable feedstock to
15 produce said liquid oil stream (31), preferably wherein said thermal decomposition comprises a pyrolysis step and/or a hydrothermal liquefaction step.

16. The process according to any one of the preceding claims, further comprising a step of mixing at least a portion of the heavy jet fuel fraction (42) with at least a portion of the light
20 jet fuel fraction (41) to provide a combined jet fuel fraction (49).