

METHOD FOR PROCESSING LIQUEFIED MATERIAL

FIELD OF THE INVENTION

The invention relates to the field of hydroprocessing of liquid oils such as pyrolysis oils, more specifically to the stabilization of the liquid oil by hydrotreating prior to being upgraded by further hydroprocessing. More particularly, the invention relates to the stabilization of pyrolysis oil containing polymerisable reactive compounds.

BACKGROUND OF THE INVENTION

The field of renewable feedstocks has been attracting a great deal of attention, not only in Europe, but also US and China. Using renewable feedstocks enables a sustainable approach to the production of hydrocarbon products boiling in the transportation fuel range, in particular any of diesel, jet fuel and naphtha as well as petrochemicals, such as raw materials for steam crackers and plastic production.

The hydroprocessing of renewable feedstocks is a challenging task, due to the variety and complexity of these feedstocks. Currently, it is normally perceived that there are three generations of renewable feedstocks. The first generation are renewable feedstocks which are already liquid and include virgin oils, such as rapeseed oil and soybean oil. The second generation are waste oil and fats, such as used cooking oils, animal fats and crude tall oil (CTO). The third generation is much larger in volume, i.e. is more available, than for instance the second generation. This third generation includes solid renewable feedstocks which encompasses: i) solid renewable feedstock, such as plastic waste, municipal solid waste, agricultural residue and forestry residue, for instance lignocellulosic biomass such as grass; and ii) low indirect land-use change (ILUC) crops such as castor, which offer the benefit of not competing for space with food crops and can be grown in difficult climates.

Due to the increased interest to abate fossil hydrocarbon feedstock to the petrochemical sector (plastic production) and to fuels production, a higher demand is expected for the hydroprocessing of advanced renewable feedstocks, such as pyrolysis oils derived from solid renewable feedstocks. In addition, hydroprocessing is especially beneficial for around a third of plastic waste, which is not sorted according to polymer type.

Pyrolysis oils and the like from waste plastic are highly unsaturated containing olefins,

diolefins, conjugated diolefins, aromatics, vinyl-aromatics as well as saturated hydrocarbons. These oils further contain heteroatoms like nitrogen, oxygen, sulfur and halogens. The exact nature of plastic derived oils depends greatly on the polymer composition of the feedstock to the liquefaction process. In order to fulfil the requirements as petrochemical feedstock (for steam crackers) the olefinic hydrocarbons must be saturated and the number of heteroatoms must be decreased significantly. In addition, pyrolysis oils and the like from biomass may have a very high oxygen content, which needs to be decreased before it efficiently can be used as liquid fuel, i.e. as hydrocarbon fuel boiling in the transportation fuel range. The heteroatoms (like nitrogen, oxygen, sulfur and halogens) are generally removed by hydroprocessing in a catalytic hydrotreatment (HDT) reactor using high pressure (30-200 bar) and high temperature (320-400°C). However, a liquid oil such as pyrolysis oil or a hydrothermal liquefaction oil (hereinafter also referred to as HTL oil) is very unstable and when heated tends to polymerize. This leads to rapid catalyst deactivation and plugging of the catalyst bed of the HDT reactor, due to coking or gum formation. In particular, pyrolysis oil streams often contain polymerisable reactive compounds such as conjugated diolefins, styrene homologues, and oxygenates which cause fouling, such as gum formation or coking in catalyst beds during various hydroprocessing steps. This results in an increase in pressure drop across the reactor bed, which makes cleaning or a replacement of the bed layer/s necessary. Even if mild stabilization is practiced, coking of the catalyst bed can occur leading to rapid deactivation of the hydrotreatment catalyst. Furthermore, where the process temperature is increased in a second step, a similar risk of fouling is present in this step, as less reactive compounds may be activated.

In view of the coking of the catalyst bed and particularly the high pressure drop built up as a result, additional reactors in parallel or in series to a first reactor are normally required. Figure 1 shows a processing unit where two reactors are provided in parallel and Figure 2 shows a processing unit where two reactors are arranged in series. In the arrangements of Figures 1 and 2, due to the high pressure drop built up across the reactor beds during hydrotreatment, the first reactors will need to be shut down or bypassed after a specific period of time. In this case, the second reactors added in parallel or in series continue the normal hydrotreatment operation. However, the addition of second reactors within the processing units in this way increases the overall capital expenditures (CAPEX) and operating expenses (OPEX) of the process unit.

Moreover, when the parallel reactor arrangement of Figure 1 is employed, the catalyst volume requirement is typically doubled, which further increases the overall CAPEX and

OPEX of the process unit. Additionally, when the in series reactor arrangement of Figure 2 is employed, this is typically in the form of a lead-lag configuration. In this case, when pressure drop across the lead reactor bed increases, the lead reactor is shut down for catalyst replacement or cleaning. For this arrangement, auxiliary systems are required containing heaters, compressors, separators and pumps, which leads to further increases in the CAPEX and OPEX of the process unit.

It would thus be desirable to provide a process for stabilising a liquid oil stream that is susceptible to polymerisation that does lead to significant increases in CAPEX and OPEX.

SUMMARY OF THE INVENTION

In one aspect there is provided a process for hydrotreating a liquid oil stream in a continuous operation in a fixed bed reactor;
wherein the liquid oil stream is a thermochemical decomposition oil stream, and contains polymerisable reactive compounds;
wherein the fixed bed reactor comprises at least a first reactor bed containing a first hydrotreatment catalyst and a second reactor bed containing a second hydrotreatment catalyst;
the process comprising the steps of:
(i) in a first operation period, passing as a first reactor bed liquid oil substream at least 50 vol.% of the liquid oil stream through the first reactor bed and subsequently through the second reactor bed;
(ii) in a second operation period, on determination of deposition of material formed from the polymerisable reactive compounds on the first reactor bed, passing a reduced proportion of the liquid oil stream as the first reactor bed liquid oil substream, and passing an increased proportion of the liquid oil stream through the second reactor bed having not passed through the first reactor bed as a second reactor bed liquid oil substream,
wherein during the second operation period the first reactor bed liquid substream volume is at least 10 vol.% and less than 90 vol.% of the first reactor bed liquid oil substream volume of the first operation period.

DETAILED DESCRIPTION OF THE INVENTION

As discussed herein, in one aspect there is provided a process for hydrotreating a liquid

oil stream in a continuous operation in a fixed bed reactor;
wherein the liquid oil stream is a thermochemical decomposition oil stream, and contains polymerisable reactive compounds;
wherein the fixed bed reactor comprises at least a first reactor bed containing a first hydrotreatment catalyst and a second reactor bed containing a second hydrotreatment catalyst;
the process comprising the steps of:
(i) in a first operation period, passing as a first reactor bed liquid oil substream at least 50 vol.% of the liquid oil stream through the first reactor bed and subsequently through the second reactor bed;
(ii) in a second operation period, on determination of deposition of material formed from the polymerisable reactive compounds on the first reactor bed, passing a reduced proportion of the liquid oil stream as the first reactor bed liquid oil substream, and passing an increased proportion of the liquid oil stream through the second reactor bed having not passed through the first reactor bed as a second reactor bed liquid oil substream
wherein during the second operation period the first reactor bed liquid substream volume is at least 10 vol.% and less than 90 vol.% of the first reactor bed liquid oil substream volume of the first operation period.

By the present invention, the thermochemical decomposition oil, e.g. pyrolysis oil or hydrothermal liquefaction oil, is stabilized by the conversion of at least the most reactive compounds in the liquid oil stream, such as furfural, furans, aldehydes, ketones and acids, into alcohols, for instance by efficiently converting carbonyls into alcohols as well as by saturation of conjugated diolefins and styrene homologues. The present invention provides a process for this stabilisation whilst circumventing issues associated with coking of the catalyst bed as a result of the reaction of polymerisable reactive compounds, such as diolefins, within the liquid oil at the temperatures employed. In particular, the process of the present invention provides an arrangement in which an intermediate reactor shut-down can be avoided by having a reactor configurable for by-pass of a first reactor bed. This in turn provides a process for hydrotreating a liquid oil stream that does not lead to significant increases in CAPEX and/or OPEX. Additionally, configuring a second downstream reactor operating at a higher temperature for by-passing a reactor bed in a similar way, may be beneficial under some circumstances.

The process of the present invention provides one or more of the following advantages. The hydrotreatment catalyst volume can be reduced, which in turn leads to a

corresponding % reduction in OPEX. Only one reactor is needed for the hydrotreatment process for the entire catalyst cycle life. This leads to an overall CAPEX saving. This CAPEX saving may be of the order of around 40%. This is in comparison to typical process units that comprise at least two reactors. Since only one reactor is required rather than two or more reactors with significant auxiliary equipment, smaller plot space for the processing unit is needed. The process of the invention has a lower carbon footprint due to lower catalyst volume and less steel required for reactor and auxiliary equipment.

Liquid Oil Stream

As used herein, the terms “liquid stream” and “liquid oil” relate to a feedstock comprising compounds which at above elevated temperatures ($>80\text{ }^{\circ}\text{C}$) but below the temperatures resulting in substantially complete hydrotreatment, may react to form larger molecules, potentially resulting in full or partial blockage of reactors, tubes, heaters, heat exchangers and catalysts. Examples of such mixtures may be feedstock rich in conjugated diolefins or styrene and its homologs from thermochemical decomposition of plastic waste, municipal solid waste, refuse derived fuel and solid recovered fuel, feedstock rich in carbonyls and sugars from thermochemical decomposition of lignocellulosic biomass and feedstock rich in nitrogen from thermochemical decomposition of nitrogen rich biomass, such as manure and sewage sludge, and similar composition from other sources. The reactive compounds may either react within the same functional group (for example, diolefin with diolefin) or across functional groups (for example, aldehyde with phenol).

As discussed herein, the process of the invention relates to hydrotreatment of a liquid oil stream such as a thermochemical decomposition oil stream including a renewable crude oil stream or a biocrude oil stream. In one aspect, the liquid oil stream contains at least 20 wt% oxygen (O), such as at least 30 wt% O, or at least 45 wt% O. In one aspect, the liquid oil stream contains from 1 to 50 wt% O, such as from 5 to 50 wt% O, such as from 10 to 50 wt% O, such as from 15 to 50 wt% O, such as from 20 to 50 wt% O, such as from 25 to 50 wt% O, such as from 30 to 50 wt% O, such as from 35 to 50 wt% O, such as from 40 to 50 wt% O, such as from 45 to 50 wt% O. The oxygen is suitably determined by standard elemental analysis. This oxygen content is representative of particularly reactive liquid oil feeds, such as pyrolysis oils or hydrothermal liquefaction (HTL) oils, as the content of oxygen may serve as a proxy for how reactive the liquid oil

is. Thus, a highly reactive liquid oil stream may contain as much as 45 wt% oxygen or even higher.

In one aspect, the liquid oil stream contains at least 500 ppm wt O, such as 0.1 wt.% O, such as at least 0.5 wt.% O, such as at least 1 wt.%, such as at least 1.5 wt.% O, such as at least 2 wt.% O, such as at least 2.5 wt.% O, such as at least 3 wt.% O, such as at least 3.5 wt.% O, such as at least 4.5 wt.% O, such as at least 5 wt.% O, such as at least 10 wt.% O, such as at least 15 wt.% O, which is representative of feedstock originating from the pyrolysis of material rich in plastic waste. In one aspect, the liquid oil stream contains from 0.1 to 15 wt.% O, such as from 0.5 to 15 wt.% O, such as from 1 to 15 wt.% O, such as from 2 to 15 wt.% O, such as from 3 to 15 wt.% O, such as from 4 to 15 wt.% O, such as from 5 to 15 wt.% O, such as from 6 to 15 wt.% O, such as from 7 to 15 wt.% O, such as from 8 to 15 wt.% O, such as from 9 to 15 wt.% O, such as from 10 to 15 wt.% O, such as from 11 to 15 wt.% O, such as from 12 to 15 wt.% O, such as from 13 to 15 wt.% O, such as from 14 to 15 wt.% O.

In one aspect, the thermochemical decomposition oil stream is a pyrolysis oil stream or a hydrothermal liquefaction oil (HTL oil) stream. In one aspect, the thermochemical decomposition oil stream is a pyrolysis oil stream. In one aspect, the thermochemical decomposition oil stream is a hydrothermal liquefaction oil (HTL oil) stream.

In one aspect the thermochemical decomposition oil stream is a pyrolysis oil stream which comprises at least 0.5 mol/kg of one or more of: aldehyde compounds, ketones, alcohols, furfural, as determined by ASTM E3146-20.

In one aspect, the process of the invention further comprises a prior step of thermal decomposition of a solid renewable feedstock, for producing said thermochemical decomposition oil stream.

As used herein, the term “thermal decomposition” shall be used broadly for any decomposition process, in which a material is partially decomposed at elevated temperature (typically 250°C to 800°C or even 1000°C), in the presence of a substoichiometric amount of oxygen (including no oxygen). The product will typically be a combined liquid and gaseous stream, as well as an amount of solid char. The term shall be construed to include processes known as pyrolysis and hydrothermal liquefaction, both in the presence and absence of a catalyst.

Accordingly, in a particular embodiment, the thermal decomposition is pyrolysis, such as fast pyrolysis, as defined below, thereby producing said pyrolysis oil stream.

It would be understood that the thermal decomposition is conducted in a thermal decomposition section, the pyrolysis is conducted in a pyrolysis section, and the hydrothermal liquefaction is conducted in a hydrothermal liquefaction section.

As used herein, the term “section” means a physical section comprising a unit or combination of units for conducting one or more steps and/or sub-steps. For the purpose of the present invention, the pyrolysis section generates two main streams, namely a pyrolysis off-gas stream and a pyrolysis oil stream. The pyrolysis section may be in the form of a fluidized bed, transported bed, or circulating fluid bed, as is well known in the art. For instance, the pyrolysis section may comprise a pyrolyser unit (pyrolysis reactor), cyclone(s) to remove particulate solids such as char, and a cooling unit for thereby producing said pyrolysis off-gas stream and said pyrolysis oil stream, i.e. condensed pyrolysis oil. The pyrolysis off-gas stream comprises light hydrocarbons e.g. C1-C4 hydrocarbons, CO and CO₂. The pyrolysis oil stream is also referred to as a liquid substance rich in blends of molecules including saturated and unsaturated hydrocarbons, cyclic and aliphatic, as well as hydrocarbons that contain heteroatoms like nitrogen, oxygen, halogens and sulfur. Hydrocarbons that contain heteroatoms includes nitriles, amines, amides, thioles, sulfides, thiophenes, aldehydes, ketones and/or other compounds such as furfural having a carbonyl group, resulting from the depolymerization of the feedstock treated in pyrolysis.

For the purpose of the present invention, the pyrolysis is preferably fast pyrolysis or slow 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 500°C and reaction times of 10 seconds or less, such as 5 seconds or less, such as about 2 seconds or less. Fast pyrolysis may for instance be conducted by autothermal operation e.g. in a fluidized bed reactor. The latter is also referred to 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 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 made to e.g. “Heterodoxy in Fast Pyrolysis of Biomass” by Robert Brown:
<https://dx.doi.org/10.1021/acs.energyfuels.0c03512>

“Intermediate” or “slow” pyrolysis are also suitable for feedstocks originating from waste plastics, and may be even more suitable than fast pyrolysis. One reason is that high N containing feedstocks tend to comprise more alkaline metals, which increases the risk of agglomeration and defluidization. In addition, slow pyrolysis is currently the most widespread form of pyrolysis used for plastic waste and gives good oil yields.

In another embodiment, therefore, 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 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 as char coal; the pyrolysis still produces some gas and renewable crude 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.

It would therefore be understood, that for the purpose of the present invention, the use of autothermal pyrolysis. i.e. autothermal operation, is a particular embodiment for conducting fast pyrolysis.

There are several types of fast pyrolysis where a catalyst is used. Sometimes an acid catalyst, such as zeolite or silica-alumina catalysts, is used in the pyrolysis reactor to upgrade the pyrolysis vapors, this technology is called catalytic fast pyrolysis and can both be operated in an in-situ mode (the catalyst is located in the pyrolysis reactor) and an ex-situ mode (the catalyst is placed in a separate reactor). The use of a catalyst conveys the advantage of lowering the activation energy for reactions thereby significantly reducing the required temperature for conducting the pyrolysis. In addition, increased selectivity towards desired pyrolysis oil compounds may be achieved. In some cases, hydrogen is added to the catalytic pyrolysis which is called reactive catalytic fast

pyrolysis. If the catalytic pyrolysis is conducted at a high hydrogen pressure ($\sim >5$ barg) it is often called catalytic hydropyrolysis and the pyrolysis product will typically contain a lower amount of oxygen, such as 1 wt% to 5 wt%. In one aspect, the pyrolysis stage is fast pyrolysis which is conducted without the presence of a catalyst and hydrogen, i.e. the fast pyrolysis stage is not catalytic fast pyrolysis, hydropyrolysis or catalytic hydropyrolysis. This enables a much simpler and inexpensive process.

In one aspect, said pyrolysis off-gas stream comprises CO, CO₂ and light hydrocarbons such as C1-C4, and optionally also H₂S, HCl, HCN and NH₃.

In one aspect, 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 bio-polymeric structure to mainly liquid components. Typical hydrothermal processing conditions are temperatures in the range of 250-375°C and operating pressures in the range of 40-220 bar. This technology offers the advantage of operation at 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 made 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.

In one aspect, the thermal decomposition further comprises passing said solid renewable feedstock through a solid renewable feedstock preparation section comprising for instance drying for removing water and/or comminution for reduction of particle size. Any water/moisture in the solid renewable feedstock which vaporizes in for instance the pyrolysis section condenses in the pyrolysis oil stream and is thereby carried out in the process, which may be undesirable. Furthermore, the heat used for the vaporization of water withdraws heat which otherwise is necessary for the pyrolysis. By removing water and providing a smaller particle size in the solid renewable feedstock, the thermal efficiency of the pyrolysis section is increased.

In one aspect, the solid renewable feedstock is a lignocellulosic biomass including: wood products, forestry waste, and agricultural residue. In another aspect the solid renewable feedstock is municipal waste, in particular the organic portion thereof. For the purposes of the present application, the term "municipal waste" is interchangeable with the term "municipal solid waste" and means a feedstock containing materials of items discarded

by the public, such as mixed municipal waste given the waste code 200301 in the European Waste Catalogue.

In one aspect, the lignocellulosic biomass is forestry waste and/or agricultural residue and comprises biomass originating from plants including grass such as nature grass (grass originating from natural landscape), wheat e.g. wheat straw, oats, rye, reed grass, bamboo, sugar cane or sugar cane derivatives such as bagasse, maize and other cereals.

In one aspect, the solid renewable feedstock is waste plastic.

Any combinations of the above is also envisaged.

As used herein, the term "lignocellulosic biomass" means a biomass containing, cellulose, hemicellulose and optionally also lignin. The lignin or a significant portion thereof may have been removed, for instance by a prior bleaching step.

As discussed herein, the liquid stream contains polymerisable reactive compounds. In one aspect, the polymerisable reactive compounds are at least conjugated diolefins. In one aspect, the polymerisable reactive compounds are at least carbonyls. In one aspect, the polymerisable reactive compounds are at least sugars. In one aspect, the polymerisable reactive compounds are at least styrene homologues. In one aspect, the polymerisable reactive compounds are at least vinyl-aromatics.

In one aspect, the liquid stream has a diene number of from 1 gl/100g to 25 gl/100g, such as from 2 gl/100g to 25 gl/100g, such as from 3 gl/100g to 25 gl/100g, such as from 4 gl/100g to 25 gl/100g, such as from 5 gl/100g to 25 gl/100g, such as from 6 gl/100g to 25 gl/100g, such as from 7 gl/100g to 25 gl/100g, such as from 8 gl/100g to 25 gl/100g, such as from 9 gl/100g to 25 gl/100g, such as from 10 gl/100g to 25 gl/100g, such as from 15 gl/100g to 25 gl/100g, such as from 20 gl/100g to 25 gl/100g. In one aspect, the liquid stream has a diene number of from 1 gl/100g to 20 gl/100g, such as from 1 gl/100g to 15 gl/100g, such as from 1 gl/100g to 10 gl/100g, such as from 1 gl/100g to 9 gl/100g, such as from 1 gl/100g to 8 gl/100g, such as from 1 gl/100g to 7 gl/100g, such as from 1 gl/100g to 6 gl/100g, such as from 1 gl/100g to 5 gl/100g, such as from 1 gl/100g to 4 gl/100g, such as from 1 gl/100g to 3 gl/100g, such as from 1 gl/100g to 2 gl/100g. In one aspect, the liquid stream has a diene number of at least 1 gl/100g, such as at least 2 gl/100g, such as at least 3 gl/100g, such as at least 4 gl/100g, such as at least 5 gl/100g,

such as at least 6 gl/100g, such as at least 7 gl/100g, such as at least 8 gl/100g, such as at least 9 gl/100g, such as at least 10 gl/100g, such as at least 15 gl/100g, such as at least 20 gl/100g, such as at least 25 gl/100g. The diene number of the liquid stream can be derived using the standard, ASTM UOP-326.

Hydrotreatment

As discussed herein, the process of the invention relates to hydrotreating a liquid oil stream in a continuous operation in a fixed bed reactor, wherein the fixed bed reactor comprises at least a first reactor bed containing a first hydrotreatment catalyst and a second reactor bed containing a second hydrotreatment catalyst.

The process for hydrotreating a liquid oil stream of the present invention is a continuous operation. 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 is in contrast to a batch 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.

In one aspect the liquid oil is hydrotreated in the fixed bed reactor at a temperature of less than 400°C, such as less than 390°C, such as less than 380°C, such as less than 370°C, such as less than 360°C, such as less than 350°C, such as less than 340°C, such as less than 330°C, such as less than 320°C, such as less than 310°C, such as less than 300°C, such as less than 290°C, such as less than 280°C, such as less than 270°C, such as less than 260°C, such as less than 250°C, such as less than 240°C, such as less than 230°C, such as less than 220°C, such as less than 210°C, such as less than 200°C, such as less than 190°C, such as less than 180°C, such as less than 170°C, such as less than 160°C, such as less than 150°C, such as less than 140°C, such as less than 130°C, such as less than 120°C, such as less than 110°C, such as less than 100°C, such as less than 90°C, such as less than 80°C, such as less than 70°C.

In one aspect the liquid oil is hydrotreated in the fixed bed reactor at a temperature of from 70 to 400°C, such as from 70 to 390°C, such as from 70 to 380°C, such as from 70 to 370°C, such as from 70 to 360°C, such as from 70 to 350°C, such as from 70 to 340°C, such as from 70 to 330°C, such as from 70 to 320°C, such as from 70 to 310°C,

such as from 70 to 300°C, such as from 70 to 290°C, such as from 70 to 280°C, such as from 70 to 270°C, such as from 70 to 260°C, such as from 70 to 250°C, such as from 70 to 240°C, such as from 70 to 230°C, such as from 70 to 220°C, such as from 70 to 210°C, such as from 70 to 200°C, such as from 70 to 190°C, such as from 70 to 180°C, such as from 70 to 170°C, such as from 70 to 160°C, such as from 70 to 150°C, such as from 70 to 140°C, such as from 70 to 130°C, such as from 70 to 120°C, such as from 70 to 110°C, such as from 70 to 100°C, such as from 70 to 90°C, such as from 70 to 80°C.

In one aspect, the liquid oil is hydrotreated in the fixed bed reactor at a temperature in the range 70-250°C, such as in the range 80-200°C. In one aspect, the liquid oil is hydrotreated in the fixed bed reactor at a temperature in the range 250-400°C.

In one aspect, the temperature is in the range 250-400°C; the pressure is 20-175 barg; and the LHSV is 0.5-8 h⁻¹, and the H₂-to-oil ratio is from 5 to 2000 NI/L.

In one aspect, the first and second hydrotreatment catalysts convert at least one of the conjugated diolefins into the corresponding mono-olefin or paraffins. In one aspect, the first and second hydrotreatment catalysts convert styrene into ethyl benzene. In one aspect, the first and second hydrotreatment catalysts convert halogenated hydrocarbons into non-halogenated hydrocarbons. In one aspect, the first and second hydrotreatment catalysts convert at least one of furfural, furans, aldehydes, ketones and acids, into alcohols, and/or converts carbonyls into alcohols. The alcohols can further be converted to saturated organic compounds during the stabilization, and/or in a subsequent hydroprocessing stage such as HDO.

In one aspect, the first and second hydrotreatment catalysts are each independently selected from the group consisting of Mo, Ni, W, Pt, Pd, Cu, Fe, Zn and Ru based catalysts and combinations thereof. In one aspect, the catalyst is in sulfided, partially sulfided (i.e., surface-passivated with sulfur) or reduced form.

In one aspect, the catalyst is a supported catalyst wherein the support is selected from alumina, silica, titania, magnesia and combinations thereof; optionally in combination with a molecular sieve having topology MFI, BEA or FAU. The combinations may be as physical mixtures or as oxide systems, such as silica-alumina, alumina-magnesia spinel and other spinel-group oxide systems.

In one aspect, the catalyst is Ni-based, Mo-based, CoMo-based, NiMo-based, W-based,

NiW-based or Ru-based, optionally in sulfided or reduced form.

In one aspect, the Ni-based catalyst comprises Ni in an amount of at least 90 wt% based on the Group 1 – 12 materials in the catalyst, such as at least 95 wt.% such as at least 99 wt.% such as 100 wt.%. In one aspect, the Mo-based catalyst comprises Mo in an amount of at least 90 wt% based on the Group 1 – 12 materials in the catalyst, such as at least 95 wt.% such as at least 99 wt.% such as 100 wt.%. In one aspect, the W-based catalyst comprises W in an amount of at least 90 wt% based on the Group 1 – 12 materials in the catalyst, such as at least 95 wt.% such as at least 99 wt.% such as 100 wt.%. In one aspect, the Ru-based catalyst comprises Ru in an amount of at least 90 wt% based on the Group 1 – 12 materials in the catalyst, such as at least 95 wt.% such as at least 99 wt.% such as 100 wt.%.

In one aspect, the Ni-based catalyst comprises from 2-30 wt% Ni sulfided or reduced. In one aspect, the Mo-based catalyst comprises from 2-30 wt% Mo preferably sulfided. In one aspect, the CoMo-based catalyst comprises from 1-10 wt% Co and from 2-30 wt% Mo preferably sulfided. In one aspect, the NiMo-based catalyst comprises from 1-10 wt% Ni and from 2-30 wt% Mo preferably sulfided. In one aspect, the W-based catalyst comprises from 2-30 wt% W preferably sulfided. In one aspect, the NiW-based catalyst comprises from 1-10 wt% Ni and from 2-30 wt% W preferably sulfided. In one aspect, the Ru-based catalyst comprises from 0.1-10 wt% Ru preferably reduced.

In one aspect, the first and/or second hydrotreatment catalyst comprises Mo. In one aspect, the first and/or second hydrotreatment catalyst comprises Ni. In one aspect, the first and/or second hydrotreatment catalyst comprises W. In one aspect, the first and/or second hydrotreatment catalyst comprises Pt. In one aspect, first and/or second hydrotreatment catalyst comprises Pd. In one aspect, the first and/or second hydrotreatment catalyst comprises Cu. In one aspect, the first and/or second hydrotreatment catalyst comprises Fe. In one aspect, the first and/or second hydrotreatment catalyst comprises Zn. In one aspect, the first and/or second hydrotreatment catalyst comprises Ru.

In one aspect, the catalyst is sulphided. In one aspect, the hydrotreatment catalyst is a Ni-Mo based catalyst in sulfided form, i.e. NiMoS. The catalyst may be pre-sulfided by exposure to a sulfur containing stream or it may be sulfided in-situ i.e. during operation, for instance by sulfur present in the pyrolysis oil.

In one aspect, the Ni-Mo based catalyst is a supported catalyst having a Ni content of 3-5 wt%, Mo content of 15-25 wt%, and optionally also a P content of 1-3 wt%, based on the total weight of the catalyst. In one aspect, the Ni-Mo based catalyst is a supported catalyst wherein the support is selected from alumina, silica, titania and combinations thereof; optionally in combination with a molecular sieve having topology MFI, BEA or FAU.

By the present invention it has been found that an alcohol in the pyrolysis oil or hydrothermal liquefaction oil is first dehydrated to the respective unsaturated organic compound e.g. alkene and then hydrogenated to the respective saturated organic compound, e.g. alkane. For instance, 1-octanol present in the pyrolysis oil or hydrothermal liquefaction oil is first dehydrated to octene and then hydrogenated to octane. On the other hand, a ketone such as cyclopentanone (a cyclic ketone) is first hydrogenated to the respective alcohol, namely cyclopentanol and then dehydrated to cyclopentene, prior to being hydrogenated to cyclopentane. The dehydration is inhibited by pyridine (C_5H_5N , i.e. a compound having an organic nitrogen) present in the pyrolysis oil, thus indicating that pyridine is adsorbed on the acid sites. However, the hydrogenation is not inhibited by pyridine, thus showing that the catalyst according to the conditions of the present invention is able to convert aldehydes and ketones or other compounds having carbonyl groups in the pyrolysis oil, which normally contains organic sulfur and nitrogen, to alcohols. In other words, the desired reaction in which compounds having carbonyl groups such as aldehydes and ketones, are converted by hydrogenation to their corresponding alcohols is enabled. The alcohols may be dehydrated to the corresponding alkanes, either as part of the reactions taking place in the stabilization, or in a subsequent hydrodeoxygenation. In addition, saturation of conjugated diolefins and styrene homologues in the liquid oil as well as a reduction in the amount of heteroatoms is enabled.

As discussed herein, the fixed bed reactor comprises at least a first reactor bed and a second reactor bed. In one aspect, the fixed bed reactor comprises a mixer between the first reactor bed and the second reactor bed. In one aspect, the mixer is a quench mixer. The quench system installed between the beds ensures proper mixing of the second reactor bed feed and effluent from the first reactor bed, thus avoiding flow maldistribution in the second reactor bed.

In one aspect, the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 80:20. In one aspect, the volume ratio of the first reactor bed to the second

reactor bed is from 20:80 to 75:25. In one aspect, the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 70:30. In one aspect, the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 65:35. In one aspect, the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 60:40. In one aspect, the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 55:45. In one aspect, the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 50:50.

First Operation Period

As discussed herein, the process of the invention comprises a first operation period wherein at least 50 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed as the first reactor bed liquid oil substream.

In the first operation period at least 50 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 55 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 60 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 65 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 70 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 75 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 80 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 85 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 90 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 95 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, at least 99 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed. In one aspect, 100 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed.

In one aspect, in the first operation period, from 50 to 100 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed, such as from 55 to 100 vol.%, such as from 60 to 100 vol.%, such as from 65 to 100 vol.%, such as from 70 to 100 vol.%, such as from 75 to 100 vol.%, such as from 80 to 100 vol.%, such as from 85 to 100 vol.%, such as from 90 to 100 vol.%, such as from 95 to 100 vol.%, such as from 99 to 100 vol.%.

Second Operation Period

As discussed herein, the process of the present invention comprises a second operation period wherein on determination of deposition of material formed from the polymerisable reactive compounds on the first reactor bed, a reduced proportion of the liquid oil stream is passed through the first reactor bed, and an increased proportion of the liquid oil stream is passed through the second reactor bed having not passed through the first reactor bed. This stream is also denoted as a second reactor bed liquid oil substream. For the present invention during this period a first reactor bed liquid oil substream is maintained to avoid reverse flow in the first reactor bed.

As discussed herein, during hydrotreatment of a liquid oil stream containing polymerisable reactive compounds, reaction of the reactive compounds, such as diolefins, causes coking (gum formation) in the catalyst beds. This leads to a pressure drop in the reactor bed, which has a detrimental effect on the hydrotreatment process and leads to increased process unit CAPEX and OPEX. To address this problem, in the process of the present invention, the liquid oil stream can be at least partially diverted so as to run through a second reactor bed when it is deduced that material has been deposited in the first reactor bed.

In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced by at least 10% compared to the first operation period. In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced by at least 20% compared to the first operation period. In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced by at least 30% compared to the first operation period. In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced by at least 40% compared to the first operation period. In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first

reactor bed is reduced by at least 50% compared to the first operation period. In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced by at least 60% compared to the first operation period. In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced by at least 70% compared to the first operation period. In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced by at least 80% compared to the first operation period. In one aspect, in the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced by at least 90% compared to the first operation period.

In one aspect, in the second operation period, the proportion of the liquid oil stream passing through the first reactor bed is reduced by from 10 to 90% compared to the first operation period, such as from 20 to 90%, such as from 30 to 90%, such as from 40 to 90%, such as from 50 to 90%, such as from 60 to 90%, such as from 70 to 90%, such as from 80 to 90%.

In one aspect, during the second operation period the proportion of the liquid oil stream passing through the first reactor bed is reduced over time and the proportion of the liquid oil stream passing through the second reactor bed having not passed through the first reactor bed is increased over time.

In one aspect, the deposition of material formed from the polymerisable reactive compounds on the first reactor bed is determined by at least one of pressure drop, outlet gas temperature, concentration of reactant, concentration of product, catalyst bed temperature, time on of the first operation period and combinations thereof. In one aspect, the deposition of material formed from the polymerisable reactive compounds on the first reactor bed is determined by pressure drop. In one aspect, the deposition of material formed from the polymerisable reactive compounds on the first reactor bed is determined using a pressure differential indicator controller (PDIC).

In one aspect, the determination of deposition of material formed from the polymerisable reactive compounds will initiate in process control signals initiating the second operation period.

In one aspect shown in Figure 3, the flow to the first and second reactor beds can be adjusted using a 3-way valve located on a main feed line. In one aspect shown in Figure

4, the flow to the first and second reactor beds can be adjusted using a control valve on a feed line to the second reactor bed. In the embodiments of Figures 3 and 4, the control valve opening will be controlled by a signal from the PDIC measuring pressure drop across the first reactor bed.

Further Reactor Beds and Operation Periods

In one aspect, the fixed bed reactor further comprises a third reactor bed containing a third hydrotreatment catalyst. In this case, the process comprises a third operation period, wherein on determination of deposition of material formed from the polymerisable reactive compounds on the second reactor bed, a reduced proportion of the liquid oil stream is passed through the first reactor bed and the second reactor bed, and an increased proportion of the liquid oil stream is passed through the third reactor bed having not passed through the first reactor bed or the second reactor bed.

In one aspect, the fixed bed reactor comprises a mixer, such as a quench mixer, between the second reactor bed and the third reactor bed. The quench system installed between the beds ensures proper mixing of the third reactor bed feed and effluent from the second reactor bed, thus avoiding flow maldistribution in the third reactor bed.

In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 10% compared to the first and second operation periods. In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 20% compared to the first and second operation periods. In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 30% compared to the first and second operation periods. In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 40% compared to the first and second operation periods. In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 50% compared to the first and second operation periods. In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 60% compared to the first and second operation periods. In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 70% compared to the

first and second operation periods. In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 80% compared to the first and second operation periods. In one aspect, in the third operation period the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by at least 90% compared to the first and second operation periods.

In one aspect, in the third operation period, the proportion of the liquid oil stream passing through the first and second reactor beds is reduced by from 10 to 90% compared to the first and second operation periods, such as from 20 to 90%, such as from 30 to 90%, such as from 40 to 90%, such as from 50 to 90%, such as from 60 to 90%, such as from 70 to 90%, such as from 80 to 90%.

In one aspect, during the third operation period the proportion of the liquid oil stream passing through the first and/or second reactor beds is reduced over time and the proportion of the liquid oil stream passing through the third reactor bed having not passed through the first and/or second reactor beds is increased over time.

In one aspect, the deposition of material formed from the polymerisable reactive compounds on the second reactor bed is determined by at least one of pressure drop, outlet gas temperature, concentration of reactant, concentration of product, catalyst bed temperature, and combinations thereof. In one aspect, the deposition of material formed from the polymerisable reactive compounds on the second reactor bed is determined by pressure drop. In one aspect, the deposition of material formed from the polymerisable reactive compounds on the second reactor bed is determined using a pressure differential indicator controller (PDIC).

The process of the present invention may comprise one or more further steps. These one or more further steps may be before, after, or intermediate to the steps recited herein.

In one aspect, the process further comprises passing the stabilized pyrolysis oil stream through a hydrotreatment (HDT) step, which commonly is operated in a separate reactor at higher temperature. Thereby, any organic heteroatoms like nitrogen, sulfur, oxygen, chlorine, bromine and fluorine present in the stabilized pyrolysis oil stream is removed and a hydrotreated stream is produced, which can be further treated for producing hydrocarbon products boiling in the transportation fuel range, such as diesel,

jet fuel and naphtha. The further treatment may include any of: hydrodewaxing or isomerization, as is well known in the art of fossil oil refining. Other types of hydrotreating are also envisaged, for instance hydrodearomatization (HDA). 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, magnesia or titania, or combinations thereof).

In one aspect, the hydrotreatment (HDT) reactor is configured for operation in a first period of operation and a second period of operation, corresponding to those of the fixed bed reactor, but under the same or independent criteria.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present invention are explained by way of examples and with reference to the accompanying drawings. The appended drawings illustrate only examples of embodiments of the present invention, and they are therefore not to be considered limiting of its scope, as the invention may admit to other alternative embodiments.

Fig. 1 shows a process unit comprising two reactors in a parallel arrangement.
Fig. 2 shows a process unit comprising two reactors in an in-series arrangement.
Fig. 3 shows a process unit in accordance with the present invention wherein the flow to each reactor bed is adjusted using one 3-way valve located on the main feed line.
Fig. 4 shows a process unit in accordance with the present invention wherein the flow to each reactor bed is adjusted using one control valve on the feed line to the second reactor bed

The invention will now be described with reference to the following non-limiting examples.

Examples

Scenarios	A (Reactors in parallel / spare)	B (Reactors in series (lead-lag))	C (Proposed scheme)
No of reactors	2	2	1

No of beds in each reactor	1	1	2
Catalyst volume	Base	Base - 50%	Base - ~40-50%
Auxiliary startup / shutdown system	Not required	Required (refer figure 2)	Not required
Operability	Deblinding, operating high pressure manual valves while unit is in operation is required or unit needs to shut down and depressured when spare reactor is taken online	Blinding & deblinding, operating high pressure manual valves while unit is in operation is required or unit needs to shut down and depressured when spare reactor is taken online. Also, the auxiliary system has to be operated when the catalyst changeover is required in the deactivated reactor	No such specific requirements
CAPEX (reactor + auxiliary equipment installed cost)	Base	Base + 75%	Base - ~45-50%
OPEX (catalyst cost & auxiliary system operation cost)	Base	Base - ~40-50%	Base - ~40-50%

In the above example, scenario A (not in accordance with the present invention) is when two reactors are in parallel arrangement and the catalyst volume requirement is typically doubled. The first reactor is in operation while the second reactor is loaded with the hydrotreatment catalyst and bypassed fully but not in operation. When pressure drop is increased in the first reactor bed or the activity of the catalysts in the first reactor is insufficient to operate the process, the process unit would typically need to be shutdown for short time to remove the first reactor from the operation and take the second reactor in the operation. The CAPEX and OPEX are called as "Base" in this scenario for the comparative purposes. The higher amount of hydrotreatment catalysts, number of reactors, duration needed to shutdown the process unit, swap the reactors and startup the process unit with second reactor translate to higher CAPEX and OPEX in scenario A.

In scenario B (not in accordance with the present invention), when the reactors arrangement is in series (also called as lead-lag operation), the first and second reactors operate in series and each reactor is employed with half of the total catalyst volume requirement. In this scenario, when pressure drop across the lead reactor bed increases, the lead reactor is shut down for catalyst replacement or cleaning. For this arrangement, auxiliary systems are required containing heaters, compressors, separators and pumps, which leads to further increases in the CAPEX and OPEX of the process unit. The

process unit may continue the operation with second reactor until the first reactor is ready with the replaced catalysts. The first reactor, loaded with fresh catalyst is taken in operation as a lag reactor where second reactor is kept in the operation as a lead reactor until pressure drop in second reactor increases.

In the proposed scheme in scenario C in accordance with the present invention, the reactor is employed with the two or more beds, each bed capable of receiving fresh feed. In this example, the first bed may be bypassed while second bed receives the bypassed feed, thus removing the need to shut down the unit, or requirements such as auxiliary equipment, additional catalysts or reactors. In this inventive example, the CAPEX and OPEX savings are highest for each of scenarios A, B and C.

Various modifications and variations of the present invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.

CLAIMS

1. A process for hydrotreating a liquid oil stream in a continuous operation in a fixed bed reactor;
wherein the liquid oil stream is a thermochemical decomposition oil stream, and contains polymerisable reactive compounds;
wherein the fixed bed reactor comprises at least a first reactor bed containing a first hydrotreatment catalyst and a second reactor bed containing a second hydrotreatment catalyst;
the process comprising the steps of:
(i) in a first operation period, passing as a first reactor bed liquid oil substream comprising at least 50 vol.% of the liquid oil stream through the first reactor bed and subsequently through the second reactor bed;
(ii) in a second operation period, on determination of deposition of material formed from the polymerisable reactive compounds on the first reactor bed, passing a reduced proportion of the liquid oil stream as the first reactor bed liquid oil substream, and passing an increased proportion of the liquid oil stream through the second reactor bed having not passed through the first reactor bed as a second reactor bed liquid oil substream,
wherein during the second operation period the first reactor bed liquid substream volume is at least 10 vol.% and less than 90 vol.% of the first reactor bed liquid oil substream volume of the first operation period.
2. A process according to claim 1 wherein the polymerisable reactive compounds are selected from the group consisting of conjugated diolefins, sugars, carbonyls, styrene homologues and vinyl-aromatics.
3. A process according to any one of claims 1 or 2 wherein in the first operation period the first reactor bed liquid oil substream comprises at least 70 vol.%, such as at least 90 vol.%, such as at least 99 vol.% of the liquid oil stream.
4. A process according to any one of claims 1 to 3 wherein in the second operation period the proportion of the liquid oil stream comprised in the first reactor bed liquid oil substream is reduced by at least 10%, such as at least 20%, such as at least 40%, such as at least 80% compared to the first operation period.
5. A process according to any one of claims 1 to 4 wherein

(i) in the first operation period from 50 to 100 vol.% of the liquid oil stream is comprised in the first reactor bed liquid oil substream, and from 0 to 50 vol.% of the liquid oil stream is passed through the second reactor bed having not passed through the first reactor bed; and

(ii) in the second operation period from 25 to 75 vol.% of the liquid oil stream is passed through the first reactor bed and subsequently through the second reactor bed, and from 25 to 75 vol.% of the liquid oil stream is passed as a second reactor bed liquid oil substream.

6. A process according to any one of claims 1 to 5 wherein during the second operation period the first reactor bed liquid oil substream is reduced over time and the second reactor bed liquid oil substream is increased over time.

7. A process according to any one of claims 1 to 6 wherein the deposition of material formed from the polymerisable reactive compounds on the first reactor bed is determined by at least one of pressure drop, outlet temperature, concentration of reactant, concentration of product, catalyst bed temperature, and combinations thereof.

8. A process according to any one of claims 1 to 7 wherein the fixed bed reactor comprises a mixer between the first reactor bed and the second reactor bed, such as wherein the mixer is a quench mixer.

9. A process according to any one of claims 1 to 8 wherein the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 80:20, such as wherein the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 50:50, such as wherein the volume ratio of the first reactor bed to the second reactor bed is from 20:80 to 40:60.

10. A process according to any one of claims 1 to 9 wherein the fixed bed reactor further comprises a third reactor bed containing a third hydrotreatment catalyst; the process comprising further the step of:

(iii) in a third operation period, on determination of deposition of material formed from the polymerisable reactive compounds on the second reactor bed, passing a reduced proportion of the liquid oil stream as the first reactor bed liquid oil substream and the second reactor bed liquid oil substream, and passing an increased proportion of the liquid oil stream as a third reactor bed liquid oil substream through the third reactor bed having not passed through the first reactor bed or the second reactor bed.

11. A process according to claim 10 wherein the fixed bed reactor comprises a mixer, such as a quench mixer, between the second reactor bed and the third reactor bed.

12. A process according to any one of claims 1 to 11 wherein the first hydrotreatment catalyst and the second hydrotreatment catalyst are independently selected from the group comprising Mo, Ni, W, Pt, Pd, Cu, Fe, Zn and Ru based catalysts and combinations thereof.

13. A process according to claim 12 wherein the first hydrotreatment catalyst and/or the second hydrotreatment catalyst is a supported Ni-Mo based catalyst having a Ni content of 3-5 wt%, Mo content of 15-25 wt%, and optionally also a P content of 1-3 wt%, based on the total weight of the catalyst, such as wherein the support is selected from alumina, silica, titania, magnesia and combinations thereof; optionally in combination with a molecular sieve having topology MFI, BEA or FAU, optionally wherein the Ni-Mo based catalyst is in sulfided form, i.e. NiMoS.

14. A process according to any one of claims 1 to 13 wherein the thermochemical decomposition oil stream is provided by thermal decomposition of a solid renewable feedstock.

15. A process according to claim 14 wherein the thermal decomposition is:

- pyrolysis, such as slow pyrolysis, fast pyrolysis and catalytic fast pyrolysis, to produce a pyrolysis oil stream; or
- hydrothermal liquefaction, to produce a hydrothermal liquefaction oil stream.

16. A process according to claim 14 or 15 wherein the solid renewable feedstock is:

- a lignocellulosic biomass including: wood products, forestry waste, sewage sludge and agricultural residue; and/or
- a fraction rich in waste plastic ; and/or
- municipal waste, in particular (a) the organic portion thereof, where the municipal waste is defined as a feedstock containing materials of items discarded by the public, such as mixed municipal waste given the waste code 200301 in the European Waste Catalog; and/or (b) a fraction comprising at least 50 wt% plastic waste.

17. A process plant configured for carrying out the process according to any one of claims 1 to 16.