A METHOD FOR RECOVERING A CATALYST FROM A REACTION EFFLUENT

FIELD OF THE INVENTION

The present invention relates to a method for recovering a catalyst from a reaction effluent comprising coarse particles.

BACKGROUND OF THE INVENTION

Processes employing solid catalysts in fixed bed(s) and/or as a moving catalyst, e.g., moving bed, ebullated bed, or slurry type, are well known in the art. In the case of the process involving a moving catalyst, some or all of the catalyst may be forwarded to reaction effluent and it may be desired to recover the (spent) catalyst for recycling to reclaim valuable material, for direct or indirect recirculation, or for regeneration. For example, US 7375143 B2 discloses recovery of a Fischer-Tropsch catalyst from a slurry comprising waxy hydrocarbons, followed by oxidizing and recycling and thereby deactivating the catalyst and reclaiming valuable metals.

A problem which has not attracted much attention thus far is that most bio-based materials that have been collected as waste material for use of liquefaction, in particular plant-based materials, may comprise various amounts of dirt, such as sand, minerals and any other (inorganic) materials. Those bio-based materials that have been subjected to liquefaction would contain coarse carbonaceous materials, including coke and char. Such particles may be present not only in the solid raw materials, such as lignocellulosic material, e.g. wood, or in liquid raw materials such as crude or bio-crude processed materials, such as a liquefied product(s).

BRIEF DESCRIPTION OF THE INVENTION

It was found that coarse particles originating from bio-based (raw) materials may accumulate in a reaction or a process.

In the present invention, the method as claimed allows the coarse particles to be recovered from the upgraded liquid bio-based material. Furthermore, the catalysts particles that are separated from the coarse particles are recovered for reuse.

In brief, the present invention relates to one or more of the following items:

1. A method for recovering a catalyst from a reaction effluent, the method comprising

- a liquefaction step to provide a reaction effluent comprising coarse particles, a catalyst and an oil product by means of a liquefaction reaction of a bio-based material,

- a coarse particle separation step comprising separating the coarse particles from the reaction effluent to provide a coarse-particle-depleted reaction effluent, and

- a catalyst separation step comprising separating the catalyst from the coarse-particle-depleted reaction effluent to provide a separated catalyst and a purified oil product.

2. The method according to item 1, wherein the bio-based material is a lignocellulose-based material.

3. The method according to item 1 or 2, wherein the reaction effluent or coarse particles comprise(s) sand and/or dirt originating from a bio-based raw material or from the biobased material.

4. The method according to any one of the preceding items, wherein the coarse particles separation step is a multi-stage step.

5. The method according to any of the preceding items, wherein the coarse particles separation step comprises a first stage of separating coarse particles using a first separation device followed by a second stage of further separating remaining coarse particles from the reaction effluent using a second separation device.

6. The method according to item 5, wherein the first separation device is selected from the group consisting of a filter-type separator, such as a strainer, preferably an automatic strainer, a gravity settling-type separator, such as a settler, or a hydrocyclone.

7. The method according to item 5 or 6, wherein the second separation device in the coarse particles separation step is a cyclone-type separator, such as a hydrocyclone, or a decanter or a strainer or a combination thereof.

8. The method according to any one of the preceding items, wherein the coarse particles have a median particle size (D50) of 0.05 mm or more, such as in the range of 0.10 to 10.0 mm, preferably 0.10 to 5.0 mm.

9. The method according to any one of the preceding items, wherein the coarse particles have a Mohs hardness of in the range of from 3 to 9, such as from 4 to 9, or from 5 to 7, wherein the coarse particles preferably comprise sand.

10. The method according to any one of the preceding items, wherein the catalyst separation step is carried out using a centrifuge-type separator, such as a Disc Stack Separator (DSS) or a centrifuge decanter, or a membrane filtration apparatus such as cross-flow or dead-end membrane filtration apparatus.

11. The method according to any one of the preceding items, further comprising a deoiling step of recovering oil product adhered to the separated coarse particles and/or adhered to the separated catalyst.

12. The method according to item 11, wherein the deoiling step comprises washing the separated coarse particles and/or the separated catalyst, preferably washing with a light fraction of the oil product and/or an organic solvent.

13. The method according to any one of the preceding items, comprising the following steps:

the coarse particles separation step, wherein this coarse particles separation step comprises a first stage of separating large particles, such as particles having a diameter of 1.0 mm or more, using a filter-type separator, preferably an automatic strainer as a first separation device and a second stage of further separating smaller particles from the reaction effluent using a hydrocyclone as a second separation device,

the catalyst separation step of separating catalyst from the coarse-particle-depleted reaction effluent to provide the separated catalyst and upgraded (liquid) lignocellulose-based material, using a centrifuge-type separator, preferably a centrifuge decanter and/or a Disc Stack Separator (DSS), or a membrane filtration apparatus such as cross-flow or dead-end membrane filtration apparatus

wherein the filter-type separator comprises at least two filter units and is operated in alternating mode in which a first filter unit is in operation while a second filter unit is cleaned, preferably by flushing back e.g. with part of the product, nitrogen or steam, and then operation and cleaning of the filters are switched, and

the method further comprises a step of recovering oil product adhered to the separated coarse particles and/or adhered to the separated catalyst, preferably at least from the separated coarse particles, preferably by means of washing with an organic solvent and/or a light fraction of the oil product.

14. The method according to any of the preceding items, wherein the liquefaction step is conversion of solid lignocellulosic material to an upgraded liquid lignocellulose-based material by direct hydrogenation in the presence of a catalyst dispersed in a liquid medium.

15. The method according to any one of the preceding items, comprising a liquefaction step of subjecting a (solid) lignocellulosic material to liquefaction by direct hydrogenation in the presence of a hydrogen source, the catalyst and an optional liquid co-feed.

16. The method according to item 15, wherein the co-feed comprises at least one selected from the group consisting of the purified oil product and/or a fraction thereof, bio-renewable oil(s), bio-renewable fat(s), fossil oil(s), such as fossil heavy oil(s).

17. The method according to any one of the preceding items, further comprising recirculating at least part of the separated catalyst, after optional recovery of oil product and/or optional further purification and/or optional regeneration, to the liquefaction step.

18. The method according to any one of the preceding items, comprising regenerating the separated catalyst, after optional recovery of oil product and/or optional further purification, to provide a regenerated catalyst, the regeneration preferably comprising treating the catalyst with hot water, steam, mild acid(s) and/or aqueous solution(s) of mild acids.

19. The method according to any one of the preceding items, wherein the catalyst has a median particle size (D50, based on particle size distribution determined by laser diffraction) in the range of from 0.01 μm to 100.00 μm, such as 0.10 μm to 50.00 μm, or 1.00 μm to 50.00 μm.

20. The method according to any one of the preceding items, wherein the coarse particles separation step is performed by means of at least one device selected from the group consisting of a filter-type separator, such as a strainer, preferably an automatic strainer, a gravity settling-type separator, such as a settler, a cyclone-type separator, such as a hydrocyclone, or a decanter or any combination thereof.

21. The method according to any one of the preceding items, wherein the reaction effluent comprises relative to 100 wt.-% of the reaction effluent as a whole, 0.1 to 8.0 wt.-% of the non-catalyst particles, 0.1 to 8.0 wt.-% of the catalyst, 80.0 to 99.8 wt.-% of the oil product, and 0 to 10.0 wt.-% of coke.

22. The method according to any one of the preceding items, wherein the catalyst is a sulphided or non-sulphided catalyst made of metals comprising at least one of IUPAC group 6, 8, 9 or 10 of the Periodic Table of Elements.

23. The method according to any one of the preceding items, wherein the catalyst is an unsupported catalyst.

24. The method according to any one of the preceding items, wherein the catalyst comprises at least one of NiMo, CoMo, NiW, NiMoW, Mo and W.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method for recovering a catalyst from a reaction effluent, which may also be referred to as “upgraded liquid bio-based material” or “liquefied bio-based material”, comprising at least an oil product, catalyst and coarse particles. The reaction effluent originates from a liquefaction reaction performed on bio-based (raw) material, also referred to as biomass or biomass feedstock. Preferably, the biomass feedstock is lignocellulosic material. By way of illustration, one example of the lignocellulosic material can be forestry residue, woodchip or sawdust which can contain various amounts of “dirt”.

The reaction effluent may be a crude reaction effluent but preferably has been subjected to separation, in particular gas-liquid separation and/or water separation. The reaction effluent may also be subjected to further treatment. The method of the present

invention comprises a step coarse particles separation step of separating coarse particles from the reaction effluent to provide a coarse-particle-depleted reaction effluent. The method further comprises a catalyst separation step of separating catalyst from the coarse-particle-depleted reaction effluent to provide a separated catalyst and a purified oil product.

In the present invention, the catalyst is particulate and insoluble in the liquid organic part of the reaction effluent, which is also referred to as oil product. The oil product comprises oxygenates and hydrocarbons, and preferably has an oxygen content (determined by elemental analysis using e.g., ASTM D5291 or ASTM D5622) of 25.0 wt.-% or less, preferably 15.0 wt.-% or less, more preferably 10.0 wt.-% or less or 5.0 wt.-% or less.

Generally, even though separation usually aims at high separation efficiency. However, the skilled person will understand that the term "separating A from B" does not mean that nothing of A remains in B (or vice versa). 100% separation of a material is usually hard to achieve. Rather, it means that the one of the separated parts (recovered materials) is enriched in A and another one is depleted in A. Preferably, separating the particles/catalyst means separating at least part thereof, preferably a majority thereof (>50 wt.-%), more preferably most thereof (≥90 wt.-%).

In the present invention, the term "bio-based", or "bio-renewable" or "renewable", indicates a presence of a material derived from renewable sources. Carbon atoms of renewable or biological origin comprise a higher number of unstable radiocarbon (14C) atoms compared to carbon atoms of fossil origin. Therefore, it is possible to distinguish between carbon compounds derived from renewable or biological sources or raw material and carbon compounds derived from fossil sources or raw material by analysing the ratio of 12C and 14C isotopes. Thus, a particular ratio of said isotopes can be used as a "tag" to identify renewable carbon compounds and differentiate them from non-renewable carbon compounds. The isotope ratio does not change in the course of chemical reactions. Examples of a suitable method for analysing the content of carbon from biological or renewable sources are DIN 51637, ASTM D6866 or EN 16640. As used herein, the content of carbon from biological or renewable sources is expressed as the biogenic carbon content meaning the amount of biogenic carbon in the material as a weight percent of the total carbon (TC) in the material, as determined in accordance with ASTM D6866. A biogenic carbon content of the total carbon content in a product, which is completely of biological origin, may be about 100 percent. The biogenic carbon content of the renewable material (e.g. renewable co-feed) according to the invention is lower in cases where other carbonaceous components besides biological components are used in the processing of the product but is preferably at least 5 percent.

In an embodiment of the invention, the bio-based raw material is a lignocellulose-based material.

In an embodiment of the invention, the reaction effluent comprises sand and/or dirt originating from a bio-based raw material.

In the first separation step, which is a coarse particles separation step, coarse particles are separated from the oil product. In other words, the reaction effluent is subjected to separation resulting in a material enriched in solid particles comprising coarse particles and a material enriched in oil product.

In the second separation step, which is a catalyst separation step, catalyst particles are separated from the oil product. In other words, the material enriched in oil product and catalyst is subjected to separation resulting in a material enriched in oil product also referred to as purified oil product and a material enriched in catalyst.

Both the solid particles, in particular the coarse particles, and the catalyst may contain residual oil product, e.g., adhered liquid.

In the present invention, the oil product, e.g., the purified oil product or the the oil product contained in the (crude) reaction effluent, preferably has an oxygen content (determined by elemental analysis using e.g. ASTM D5291 or ASTM D5622) of 25.0 wt.-% or less, preferably 15.0 wt.-% or less, more preferably 10.0 wt.-% or less or 5.0 wt.-% or less.

The “reaction effluent” in the present invention refers to the non-water and non-gas part of the effluent of a liquefaction-of-biomass reaction, i.e. with water and gas, if present, being removed or not considered when determining amounts relative to the “reaction effluent”.

By employing the method of the present invention, the catalyst can be recovered in higher purity from a process employing bio-based (raw) material and thus the catalyst can be recovered more efficiently. Moreover, the inventors found that the service life of the equipment is prolonged as compared to direct removal of all solids, in particular the separation equipment, reactors, pipes etc, can be eroded if the hard coarse particles are not removed, in particular in case feeds are recirculated.

The reaction effluent is a reaction effluent from liquefaction of bio-based material or biomass, thus constituting an upgraded liquid bio-based material. As said above, the method of the invention is particularly relevant for processing of lignocellulose or materials/intermediates derived from lignocellulose, collectively referred to as lignocellulose-based material, because such feed may contain significant amounts of “dirt”, mostly sand, which is not contained in conventional, fossil-based, catalytic processes or in other processes starting out from liquid feed (liquid/fluid raw material). For example, the reaction effluent is a reaction effluent from liquefaction of lignocellulosic material by direct hydrogenation in the presence of a catalyst for promoting liquefaction of lignocellulosic material by direct hydrogenation. In general, lignocellulosic material is solid at NTP (normal temperature and pressure, 25°C, 101.325 kPa absolute) whereas

materials/intermediates derived from lignocellulose material may be liquid at elevated temperatures above NTP. Lignocellulosic biomass, i.e., solid lignocellulose raw material is essentially made up of three natural polymers: cellulose, hemicellulose, and lignin.

The reaction effluent may be a reaction effluent from upgrading bio-crude material, i.e., bio-based raw material, preferably a lignocellulose-based bio-crude material, i.e., lignocellulose-based raw material. The bio-crude is preferably liquid at NTP and is the direct or indirect, preferably direct result of a liquefaction reaction performed on solid biomass. The reaction effluent comprises sand and/or dirt originating from a biomass raw material. In this case, the sand or dirt is present as coarse particles.

The coarse particles separation step may be performed as a multi-stage process comprises at least two-stage steps.

The coarse particles separation step that is a multi-stage process, preferably comprises a first stage and a second stage of separation, wherein the first stage of separating coarse particles, preferably particles having a diameter of 1.0 mm or more, using a first separation device. In the case that the first separation device is a strainer as an illustration, some coarse particles can pass through the strainer.

A second stage is then introduced following from the first stage, further separating the remaining coarse particles, i.e., coarse particles having a particle diameter that is smaller than the particle diameter of the previously separated coarse particles, and they are of sizes typically larger than smaller particles, from the reaction effluent using a second separation device such that smaller particles remain in the reaction effluent. The first separation device and the second separation device are preferably of different type, and preferably employ a different type of separation technique. As these remaining coarse particles can settle faster than smaller particles, they can be separated with the use of hydrocyclone for example, allowing the smaller particles to be retained in the reaction effluent. The reaction effluent containing the smaller particles can be recirculated and/or be processed in the catalyst separation step. Coarse particles typically comprise at least sand particles and may further comprise inorganic materials and also coarse carbonaceous materials, such as coke and char.

The first separation device is preferably selected from the group consisting of a filter-type separator, such as a strainer, preferably an automatic strainer, a gravity settling-type separator, such as a settler, hydrocyclone. The second separation device is preferably a cyclone-type separator, such as a hydrocyclone, or a decanter or a strainer or a combination of two or more thereof.

The coarse particles preferably have a median particle size (D50) of 0.05 mm or more, such as in the range of 0.10 to 10.0 mm, preferably 0.10 to 5.0 mm. Preferably, the coarse particles have a Mohs hardness of in the range of from 3 to 9, such as from 4 to 9, or from 5 to 7. The coarse particles preferably comprise sand.

A suitable method for measuring the sizes of the coarse particles would be, for example, with the use of a sieves. Considering that the coarse particles may have different origin and are thus non-uniform, the reference to Mohs hardness shall mean that more than 50% by mass of these particles have a hardness in the stated range.

The step of separating the catalyst is preferably carried out using a centrifuge-type separator, such as a Disc Stack Separator (DSS) or a centrifuge decanter, or a membrane filtration apparatus such as cross-flow or dead-end membrane filtration apparatus.

The method preferably further comprises a deoiling step of recovering oil product, which may also be referred to as "further oil product" from the separated coarse particles and/or from the separated catalyst. That is, oil product may be adhered to solids, may be entrained with solids or may be intentionally added to the solids, e.g., when cleaning out filters by back-flushing. Such recovery may, for example, be accomplished by washing the separated coarse particles and/or the separated catalyst to which oil product is adhered with a washing liquid. Washing liquid may be circulated and/or used in several stages, e.g., counter-current.

In particular, recovering the further oil product may comprise washing the separated coarse particles and/or the separated catalyst, preferably washing with a light fraction of the oil product from the reaction and/or an organic solvent.

In an embodiment of the invention, the organic solvent is at least one selected from the group comprising a light hydrocarbon solvent (C10 or less), decane, hexane, heptane, acetone, tetrahydrofuran (THF), diethyl ether, toluene, ethanol, methanol, and/or a light fraction of the oil product, or a combination of two or more thereof.

In an embodiment of the invention the deoiling step preferably comprises washing the separated coarse particles and/or the separated catalyst, preferably washing with a light fraction of the oil product and/or an organic solvent.

In an embodiment of the invention, the method comprises the following steps:

the step of separating coarse particles from the reaction effluent to provide the coarse-particle-depleted reaction effluent, wherein this coarse particles separation step comprises a first stage of separating large particles, such as particles having a diameter of 1.0 mm or more, using a filter-type separator, preferably an automatic strainer as a first separation device and a second stage of further separating remaining coarse particles from the reaction effluent using a hydrocyclone as a second separation device,

the catalyst separation step of separating catalyst from the coarse-particle-depleted reaction effluent to provide the separated catalyst and a purified oil product using a centrifuge-type separator, preferably a centrifuge decanter and/or a Disc Stack Separator (DSS), or a membrane filtration apparatus such as cross-flow or dead-end membrane filtration apparatus,

further a step of recovering further oil product from the separated coarse

particles and/or from the separated catalyst particles as “smaller particles”, preferably said step is performed on the coarse particles independently from the separated catalyst particles, preferably by means of washing with an organic solvent and/or a light fraction of the oil product,

wherein the filter-type separator comprises at least two filter units and is operated in alternating mode in which a first filter unit is in operation while a second filter unit is cleaned, preferably by flushing back e.g. with part of the product, nitrogen or steam, and then operation and cleaning of the filters are switched.

The method preferably comprises recirculating at least part of the separated catalyst, after optional recovery of oil product and/or optional further purification and/or optional regeneration, to the liquefaction step.

In an embodiment of the invention, the method comprises regenerating the separated catalyst, after optional recovery of oil product and/or optional further purification, to provide a regenerated catalyst. The regeneration preferably comprises treating the catalyst with hot water, steam, acid(s) and/or aqueous solution(s) of acids. In this respect, hot water refers to water having a temperature in the range of 60 to 300°C, preferably 60°C to 150°C. In cases of temperatures of 90°C or more the regeneration is performed under pressure to maintain liquid form.

Acids and/or aqueous solution(s) of acids preferably refer to acids having a pKa in the range of from -10.0 to 6.0, more preferably in the range of from -1.0 to 6.0, 0.0 to 5.5, 1.0 to 5.0, or 2.0 to 4.0.

In an embodiment of the invention, the spent catalyst is preferably treated with the acid and/or the acidic aqueous solution and the acid is at least one, preferably exactly one, selected from the group consisting of formic acid, acetic acid and propionic acid, and the acid forming the acidic aqueous solution is at least one, preferably exactly one, selected from the group consisting of citric acid, phosphoric acid, sulphuric acid and hydrochloric acid.

The “smaller particles” are referred to as catalyst particles which may have inorganics or coke adhered to the particles, or as coke and/or inorganics respectively without the catalyst. The catalyst preferably has a median particle size (D50, based on particle size distribution determined by laser diffraction) in the range of from 0.01 μm to 100.00 μm, such as 0.10 μm to 50.00 μm, or 1.00 μm to 50.00 μm. These catalyst particles cannot be separated with the means of hydrocyclone or straining.

In an embodiment of the invention, the coarse particles separation step employs at least one device selected from the group consisting of a filter-type separator, such as a strainer, preferably an automatic strainer, a gravity settling-type separator, such as a settler, a cyclone-type separator, such as a hydrocyclone, or a decanter or any combination thereof.

Preferably, the reaction effluent comprises, relative to 100 wt.-% of the reaction effluent as a whole, 0.05 to 8.0 wt.-% of the non-catalyst particles, 0.01 to 6.0 wt.-% of the catalyst, 80.0 to 99.8 wt.-% of the oil product, and 0 to 6.0 wt.-% of coke. Coke may also be adhering to non-catalyst particles and/or to catalyst particles.

The catalyst is preferably composed of metals from IUPAC group 6, 8 and/or 10 of the Periodic Table of Elements.

In an embodiment of the invention, the catalyst is made of metals comprising at least one metal of IUPAC group 6, 8, 9 or 10 of the Periodic Table of Elements.

In an embodiment of the invention, the catalyst is in a particulate form and is insoluble in a reaction effluent such that the catalyst can be suspended in a liquid organic-based medium, e.g., a co-feed in the liquefaction step. Furthermore, the catalyst can be sulphided.

In an embodiment of the invention, the catalyst is preferably an unsupported catalyst.

By way of illustration, examples of the catalyst preferably employed in the present invention can be a sulphided or non-sulphided catalyst comprising at least one of NiMo, CoMo, NiW, NiMoW, Mo and W, and having a median particle size (D50, based on particle size distribution determined by laser diffraction) in the range of from 0.01 μm to 100.00 μm, such as 0.10 μm to 50.00 μm, or 1.00 μm to 50.00 μm. The catalyst is considered to be an active species that is preferably suitable for reuse after recovery from the reaction effluent.

The method comprises a liquefaction step of subjecting a (solid) bio-based (raw) material, also referred to as “biomass” or “biomass feedstock”, such as lignocellulosic material, also referred to as “lignocellulosic feedstock”, with or without co-feed, to liquefaction.

In an embodiment, the method comprises a liquefaction step of subjecting a (solid) lignocellulosic material to liquefaction by direct hydrogenation in the presence of a hydrogen source, preferably hydrogen, the catalyst and an optional liquid co-feed.

The reaction effluent is not necessarily the direct effluent of the liquefaction reaction. That is, while the reaction effluent may be a liquefaction reaction effluent, preferably after separation of gas and/or water, the reaction effluent may similarly be the effluent of a reaction downstream a liquefaction reaction, i.e., employing a liquefaction reaction effluent or a separated and/or treated and/or upgraded liquefaction reaction effluent as a feed.

The reaction effluent in accordance with the present invention comprises oil product originating from liquefaction of biomass, coarse particles originating from impurities in the biomass, i.e., from “dirt”, such as sand, and catalyst, e.g., liquefaction catalyst and/or catalyst from a downstream reaction. Preferably, the reaction effluent from

upgrading a bio-based feed material comprises sand and/or dirt originating from biomass, i.e., a bio-based (raw) material.

In an embodiment of the invention, the liquefaction step is conversion of solid lignocellulosic material to an upgraded liquid lignocellulose-based material by direct hydrogenation in the presence of a catalyst dispersed in a liquid medium.

In an embodiment of the invention, the method comprises a liquefaction step of subjecting a (solid) lignocellulosic material to liquefaction by direct hydrogenation in the presence of a hydrogen source, the catalyst and an optional liquid co-feed.

In an embodiment of the invention, the co-feed comprises at least one selected from the group consisting of the purified oil product and/or a fraction thereof, bio-renewable oil(s), bio-renewable fat(s), fossil oil(s), such as fossil heavy oil(s).

The raw solid biomass is subjected to so called catalytic hydroliquefaction to obtain a liquefaction effluent comprising oil products and solids. Under the catalytic hydroliquefaction, the biomass feedstock, more preferably lignocellulosic feedstock, undergoes multiple reactions, in including, but not limited to any one or more of deoxygenation, such as decarbonylation, decarboxylation, and hydrodeoxygenation (HDO), hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM), hydrodearomatization (HDA), hydrogenation, and hydrocracking. The oil product comprises oxygenates and hydrocarbons. In particular it is preferred that the oil product has an oxygen content of 25 wt.-% or less, preferably 15 wt.-% or less, more preferably 10 wt.-%.

The term “catalytic hydroliquefaction” refers to conversion of biomass feedstock into oil product, preferably being suitable for use as drop-in fuels, fuel components and/or other valuable hydrocarbon products either directly and/or after further valorization and/or upgrading.

The catalytic hydroliquefaction may be carried out at a temperature in the range of from 250 to 450 °C, such as in the range of from 270 to 420 °C, preferably in the range of from 300 to 400 °C, more preferably in the range of from 320 to 390 °C.

The catalytic hydroliquefaction is preferably carried out at a pressure at least 6 MPa, such as in the range of from 6 to 30 MPa, preferably at least 7 MPa, such as in the range of from 7 to 16 MPa, more preferably at least 8 MPa, such as from in the range of 8 to 14 MPa, given as gauge pressure. A skilled person will be competent to select a pressure within these ranges keeping in mind that too low pressure leads to higher heavy oil yield due to incomplete deoxygenation during the hydroliquefaction step.

The catalytic hydroliquefaction step is advantageously performed under high hydrogen partial pressure. Preferably, the hydrogen partial pressure at the inlet of the hydroliquefaction reactor is at least 5 MPa, such as in the range of from 5 to 26 MPa, preferably in the range of at least 6 MPa, such as in the range of from 6 to 14 MPa, more preferably at least 7 MPa, such as in the range of from 7 to 12 MPa, given as gauge pressure.

In the catalytic hydroliquefaction step, the residence time may be from a few minutes up to a few hours depending on the temperature and pressure. A person skilled in the art will be competent to adjust the time to fit the intended purpose, appreciating that at higher temperatures and pressures a shorter residence time is sufficient. Preferably, the residence time is in the range of from 10 minutes to 6 hours, preferably in the range of from 30 minutes to 4 hours, more preferably in the range of from 1 hour to 3 hours.

The catalytic hydroliquefaction step is performed in the presence of at least one catalyst. Suitably, catalyst can be present in an amount in the range of from 0.005 to 5.0 wt.-%, preferably in the range of from 0.010 to 3.0 wt.-%, more preferably in the range of from 0.100 to 1.0 wt.-%.

The catalytic hydroliquefaction may be performed in any suitable reactor in which the indicated conditions may be achieved. Examples of suitable reactors include mixed reactors and/or pipe reactors. Further, the catalytic hydroliquefaction is advantageously performed in continuous mode. Examples of suitable reactors include, but are not limited to, fluidized bed reactors, such as ebullated bed reactors, bubble column reactors, fixed bed reactors, such as percolation reactors with liquid circulation, tubular reactors, such as multitubular reactors, continuous stirred tank reactor (CSTR).

The catalytic hydroliquefaction step can be accomplished in one stage or in two or more consecutive stages. For optimal performance, the hydroliquefaction step is preferably accomplished in two or more, more preferably two consecutive stages.

The catalytic hydroliquefaction being carried out in two consecutive stages preferably comprises subjecting the biomass feedstock to catalytic hydroliquefaction to obtain an intermediate product mixture comprising partially treated biomass, deoxygenated liquid hydrocarbons, and further subjecting the partially treated biomass comprised in the intermediate product mixture to catalytic hydroliquefaction in the presence of deoxygenated hydrocarbons to obtain a liquefaction effluent.

In an embodiment of the invention, the consecutive catalytic hydroliquefaction stages are performed at essentially the same pressure, i.e. each stage preferably being carried out at a pressure at least 6 MPa, such as in the range of from 6 to 30 MPa, preferably at least 7 MPa, such as in the range of from 7 to 16 MPa, more preferably at least 8 MPa, such as in the range of from 8 to 14 MPa, given as gauge pressure. In this respect, the pressure of the first catalytic hydroliquefaction stage preferably determines the pressure of the following consecutive catalytic hydroliquefaction stages. A skilled person will be competent to select a pressure for each consecutive stage within these ranges keeping in mind that complete deoxygenation after the catalytic hydroliquefaction stages is desired.

In an embodiment of the invention, the consecutive catalytic

hydroliquefaction stages are carried out at a temperature in the range of from 270 to 420 °C, more preferably in the range of from 300 to 400 °C, even more preferably in the range of from 320 to 390 °C. A skilled person will be competent to select a temperature for each consecutive stage within these ranges. Advantageously, the temperature of the following stage will be higher than the temperature of the preceding stage. A person skilled in the art will be competent to adjust the residence time of the consecutive catalytic hydroliquefaction stages as described above in general for the catalytic hydroliquefaction step to fit the intended purpose, appreciating that at higher temperatures and pressures a shorter residence time is sufficient.

In an embodiment of the invention, the hydrogen partial pressure at the inlet of each catalytic hydroliquefaction reactor of the respective consecutive hydroliquefaction stage may be as described above in general for the catalytic hydroliquefaction step and may be the same or different.

In an embodiment of the invention, each consecutive catalytic hydroliquefaction step is performed in the presence of at least one catalyst as described above in general for the catalytic hydroliquefaction step. The catalysts for the consecutive hydroliquefaction stages may be the same or different.

In the catalytic hydroliquefaction step, the hydrogen source can be hydrogen (hydrogen gas) and/or a hydrogen donor. The hydrogen donor may, for example, be a hydrogen-containing solvent such as tetralin and/or a hydrogen-containing co-feed. The co-feed can for example be chosen from the list comprising fossil based hydrocarbons, a bio-based oil/fat, and/or re-circulated oil product and/or mixture thereof.

In an embodiment of the invention, the method comprises recirculating at least part of the separated catalyst, after optional recovery of oil product and/or optional further purification and/or optional regeneration, to the liquefaction step.

In an embodiment of the invention, the method comprises regenerating the separated catalyst, after optional recovery of oil product and/or optional further purification, to provide a regenerated catalyst, the regeneration preferably comprising treating the catalyst with hot water, steam, mild acid(s) and/or aqueous solution(s) of mild acids.

In an embodiment of the invention, the catalyst has a median particle size (D50, based on particle size distribution determined by laser diffraction) in the range of from 0.01 μm to 100.00 μm, such as 0.10 μm to 50.00 μm, or 1.00 μm to 50.00 μm.

In an embodiment of the invention the coarse particles separation step is performed by means of at least one device selected from the group consisting of a filter-type separator, such as a strainer, preferably an automatic strainer, a gravity settling-type separator, such as a settler, a cyclone-type separator, such as a hydrocyclone, or a decanter or any combination thereof.

In an embodiment of the invention, the reaction effluent comprises, relative to

100 wt.-% of the reaction effluent as a whole, 0.1 to 8.0 wt.-% of the non-catalyst particles, 0.1 to 8.0 wt.-% of the catalyst, 80.0 to 99.8 wt.-% of the oil product, and 0 to 10.0 wt.-% of coke.

In an embodiment of the invention, the catalyst is a sulphided or non-sulphided catalyst made of metals comprising at least one of IUPAC group 6, 8 or 10 of the Periodic Table of Elements.

In an embodiment of the invention, the catalyst is a sulphided or non-sulphided catalyst made of metals comprising at least one metal of IUPAC group 6, 8, 9 or 10 of the Periodic Table of Elements.

In an embodiment of the invention, the catalyst is an unsupported catalyst.

In an embodiment of the invention, the catalyst comprises at least one of NiMo, CoMo, NiW, NiMoW, Mo and W.

It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above but may vary within the scope of the claims.

Examples

The following examples are provided to better illustrate the claimed invention and are not to be interpreted as limiting the scope of the invention according to the claims.

Experiment 1: Settling

A suspension of oil product and solid particles without coarse particles such as sand but including an unsupported catalyst having a D50 particle size (as measured for unused catalyst) of 3.4 μm to 4 μm was derived from catalytic hydroliquefaction of sawdust. Solids including the catalyst can be separated from oil by gravity or by centrifugation. In this experiment, different types of settling techniques were tested.

Gravity settling was tested for catalyst-containing solids after solvent wash. Settling was tested in 1-pentanol. The solids were settled completely in 90 min. Centrifugation of the solids from the oil product (density 869 kg/m3 at 60 °C, viscosity 6.11 mm2/s at 60 °C) was tested. The solids were separated from the oil by centrifugation with 4300 rpm, 30 min, 60 °C.

In addition, unused NiMoS catalyst settling in dodecane was tested. The catalyst particles were settled in less than 2 min.

Experiment 2: Solvent wash

A reaction effluent from hydroliquefaction of sawdust comprising oil product

was subjected to separation, and solids including catalyst were separated from the oil by decanting. To better recover the oil from the solids, the solids were washed with solvent (deoiling). Table 1 shows the oil and solid recovery of the experiments. In the case of heptane and THF, the solvent was used in a consecutive manner; in the test run 3 the heptane was used first and then without drying the solids from heptane they were washed with THF. In test run 4, the solvents were used in reverse order, THF first followed by wash with heptane. The weight ratio of solvent to decanted solids used in the experiments was between 4.8-7.3.

Table 1.

Test run	**Solvent used**	**Decanted solids**	**Solvent**	**Wet insolubles**	**Dry insolubles***	**Solid recovery**	**Oil recovery**
		g	**g**	**g**	**g**		
1	Acetone	10.2	70.1	2.4	1.9	19 wt.-%	81 wt.-%
2	Toluene	10.2	70	7	3.4	33 wt.-%	67 wt.-%
3	Heptane	10.5	50	10.2			
	THF (for heptane washed solids)	10.2	70		1.5	15 wt.-%	85 wt.-%
4	THF	40	280	27.4			
	Heptane (for THF washed solids)	27.4	200		6.19	23 wt.-%	77 wt.-%

*Dry insolubles are the catalyst particles (including coke and other impurities), and wet insolubles are catalyst particles (including coke and other impurities) containing some of the washing solvent.

CLAIMS

1. A method for recovering a catalyst from a reaction effluent, the method comprising

- a liquefaction step to provide a reaction effluent comprising coarse particles, a catalyst and an oil product by means of a liquefaction reaction of a bio-based material,

- a coarse particle separation step comprising separating the coarse particles from the reaction effluent to provide a coarse-particle-depleted reaction effluent, and

- a catalyst separation step comprising separating the catalyst from the coarse-particle-depleted reaction effluent to provide a separated catalyst and a purified oil product, wherein the coarse particles comprise sand and/or dirt originating from the bio-based material.

2. The method according to claim 1, wherein the bio-based material is lignocellulose-based material.

3. The method according to any one of the preceding claims, wherein the coarse particles separation step comprises a first stage of separating coarse particles using a first separation device, wherein the first separation device is selected from the group consisting of a filter-type separator, such as a strainer, preferably an automatic strainer, a gravity settling-type separator, such as a settler, or a hydrocyclone, optionally followed by a second stage of further separating remaining coarse particles from the reaction effluent using a second separation device wherein the second separation device in the coarse particles separation step is a cyclone-type separator, such as a hydrocyclone, or a decanter or a strainer or a combination thereof.

4. The method according to any one of the preceding claims, wherein the coarse particles have a median particle size (D50) of 0.05 mm or more, such as in the range of 0.10 to 10.0 mm, preferably 0.10 to 5.0 mm, optionally wherein the coarse particles have a Mohs hardness of in the range of from 3 to 9, such as from 4 to 9, or from 5 to 7, wherein the coarse particles preferably comprise sand.

5. The method according to any one of the preceding claims, wherein the catalyst separation step is carried out using a centrifuge-type separator, such as a Disc Stack Separator (DSS) or a centrifuge decanter, or a membrane filtration apparatus such as cross-flow or dead-end membrane filtration apparatus.

6. The method according to any one of the preceding claims, further comprising a deoiling step of recovering oil product adhered to the separated coarse particles and/or adhered to the separated catalyst, wherein the deoiling step preferably comprises washing the separated coarse particles and/or the separated catalyst, preferably washing with a light fraction of the oil product and/or an organic solvent.

7. The method according to any one of the preceding claims, comprising the following steps:

the coarse particles separation step, wherein the coarse particles separation step comprises a first stage of separating large particles, such as particles having a diameter of 1.0 mm or more, using a filter-type separator, preferably an automatic strainer as a first separation device and a second stage of further separating remaining coarse particles from the reaction effluent using a hydrocyclone as a second separation device,

the catalyst separation step of separating catalyst from the coarse-particle-depleted reaction effluent to provide the separated catalyst and purified oil product, using a centrifuge-type separator, preferably a centrifuge decanter and/or a Disc Stack Separator (DSS), or a membrane filtration apparatus such as cross-flow or dead-end membrane filtration apparatus

wherein the filter-type separator comprises at least two filter units and is operated in alternating mode in which a first filter unit is in operation while a second filter unit is cleaned, preferably by flushing back e.g. with part of the product, nitrogen or steam, and then operation and cleaning of the filters are switched, and

the method further comprises a step of recovering oil product adhered to the separated coarse particles and/or adhered to the separated catalyst, preferably at least from the separated coarse particles, preferably by means of washing with an organic solvent and/or a light fraction of the oil product.

8. The method according to any one of the preceding claims, wherein the liquefaction step is conversion of solid lignocellulosic material to an upgraded liquid lignocellulose-based material by direct hydrogenation in the presence of a catalyst dispersed in a liquid medium.

9. The method according to any one of the preceding claims, comprising a liquefaction step of subjecting a (solid) lignocellulosic material to liquefaction by direct hydrogenation in the presence of a hydrogen source, the catalyst and an optional liquid co-feed, optionally

wherein the co-feed comprises at least one selected from the group consisting of the purified oil product and/or a fraction thereof, bio-renewable oil(s), bio-renewable fat(s), fossil oil(s), such as fossil heavy oil(s).

10. The method according to any one of the preceding claims, further comprising recirculating at least part of the separated catalyst, after optional deoiling step and/or optional further purification and/or optional regeneration, to the liquefaction step, and/or the method comprising regenerating the separated catalyst, after optional deoiling step and/or optional further purification, to provide a regenerated catalyst, the regeneration preferably comprising treating the catalyst with hot water, steam, mild acid(s) and/or aqueous solution(s) of mild acids.

11. The method according to any one of the preceding claims, wherein the

catalyst has a median particle size (D50) based on particle size distribution determined by laser diffraction in the range of from 0.01 μm to 100.00 μm, such as 0.10 μm to 50.00 μm, or 1.00 μm to 50.00 μm.

12. The method according to any one of the preceding claims, wherein the reaction effluent comprises, relative to 100 wt.-% of the reaction effluent as a whole, 0.1 to 8.0 wt.-% of the non-catalyst particles, 0.1 to 8.0 wt.-% of the catalyst, 80.0 to 99.8 wt.-% of the oil product, and 0 to 10.0 wt.-% of coke.

13. The method according to any one of the preceding claims, wherein the catalyst is a sulphided or non-sulphided catalyst made of metals comprising at least one of IUPAC group 6, 8, 9 or 10 of the Periodic Table of Elements.

14. The method according to any one of the preceding claims, wherein the catalyst is an unsupported catalyst.

15. The method according to any one of the preceding claims, wherein the catalyst comprises at least one of NiMo, CoMo, NiW, NiMoW, Mo and W.