METHOD FOR CATALYST REGENERATION, REGENERATED CATALYST OBTAINED THEREBY; ITS USE IN UPGRADING REACTION OF LIGNOCELLULOSE-BASED MATERIAL

FIELD OF THE INVENTION

The present invention relates to a method for catalyst regeneration and to a re-generated catalyst.

BACKGROUND OF THE INVENTION

Processes employing solid catalysts are well known in the art. After a catalyst has reached its dedicated service life (which may be a single use in some cases) it is usual to recover the (spent) catalyst for recycling, that is reclaiming valuable material, or regeneration. For example, US 7375143 B2 discloses recovery of a Fischer-Tropsch catalyst from a slurry comprising waxy hydrocarbons followed by oxidizing and recycling, i.e., deactivating the catalyst and reclaiming valuable metals. Processes for reactivating spent catalyst are also known in the art.

A problem related to upgrading of lignocellulose-based materials is that the processing of lignocellulose-based materials results in deposits of various impurities on the catalyst surface, which leads to catalyst deactivation. An object of the present invention is to provide a solution to this problem by providing a regeneration method which is specifically adapted for catalysts which have been used in a reaction for upgrading lignocellulose-based material.

BRIEF DESCRIPTION OF THE INVENTION

It was surprisingly found in the present invention that catalyst used for upgrading lignocellulose-based materials can be regenerated and lignocellulose derived inorganic compounds can be removed by treating the used catalyst with water, steam, acid or acidic aqueous solution instead of leaching the catalyst metals and re-making the catalyst as is typically reported for conventional fossil feeds. It was found that processing of lignocellulose-based materials results in deposits of various impurities (Ca-based impurities being one major part thereof) on the catalyst surface, thus leading to deactivation. In view of this finding, it is developed a regeneration method which is specifically adapted for catalysts having been used in a reaction for upgrading a lignocellulose-based material.

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

1. A method for regenerating a spent catalyst from an upgraded liquid lignocellulose-based material, the method comprising a regeneration treatment step of treating the spent catalyst with at least one treatment fluid selected from water, steam, liquid

acid aqueous acidic solution and any combination thereof to provide a regenerated catalyst, separating and recovering the regenerated catalyst

2. The method according to item 1 wherein the method comprises a separation step wherein the spent catalyst is recovered from the upgraded liquid lignocellulose-based material by separating the spent catalyst from the oil product before the regeneration treatment step.

3. The method according to item 1 or 2 wherein the method comprises a de-oiling step wherein the spent catalyst is subjected to washing with an organic solvent to re-move residual oil product from the spent catalyst before the regeneration treatment step.

4. The method according to item 3, wherein the organic solvent is selected from the group comprising at least one of a hydrocarbon solvent such as a light hydrocarbon solvent (C10 or less), decane, hexane, heptane, acetone, tetrahydrofurane (THF), diethyl ether, toluene, ethanol, methanol, and/or a light fraction of the oil product.

5. The method according to any one of the preceding items, further comprising at least one step for removing coarse non-catalyst particles having a particle size (maximum diameter) of 0.3 mm or more from the spent catalyst before the regeneration treatment step.

6. The method according to any one of the preceding items, wherein the regeneration treatment step is carried out at a temperature in the range of from 15°C to 400°C, preferably 15°C to 200°C, more preferably 20°C to 150°C.

7. The method according to any one of the preceding items, wherein the regeneration treatment step is carried out with water at a temperature in the range of from 15°C to 300°C, preferably 20°C to 150°C (inorganic removal stage).

8. The method according to any one of items 1 to 6, wherein the re-generation treatment step is carried out with steam at a temperature in the range of from 100°C to 400°C, preferably 100°C to 250°C (inorganic removal stage).

9. The method according to any one of items 1 to 6, wherein the re-generation treatment step is carried out with liquid acid and/or acidic aqueous solution at a temperature in the range of from 15°C to 200°C, preferably 20°C to 100°C, more preferably 25 to 80°C (inorganic removal stage).

10. The method according to items 1 to 6 and 9, wherein the liquid acid and/or the acid forming the acidic aqueous solution is at least one acid, wherein acid has a pKa in the range of from -10.0 to 6.0.

11. The method according to item 9, wherein the liquid acid and/or the acid forming the acidic aqueous solution is at least one mild acid, wherein a mild acid has a pKa in the range of from -1.0 to 6.0, preferably in the range of from 0.0 to 5.5, 1.0 to 5.0, or 2.0 to 4.0.

12. The method according to any one of items 9 to 11, wherein the acidic aqueous solution comprises at least water and an acid and the acid is in a concentration of 3.0 to 80.0 wt.-%, preferably 5.0 to 60.0 wt.-%, based on the total acidic aqueous solution.

13. The method according to any one of items 9 to 12, wherein the liquid acid is at least one, preferably exactly one, selected from the group consisting of formic acid, acetic acid and propionic acid, wherein 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.

14. The method according to any one of items 9 to 13, wherein the acid washed spent catalyst is subjected to further washing with water and/or steam to remove residual acid.

15. The method according to any one of the preceding items, wherein at least part of the spent catalyst having been subjected to the regeneration treatment step is recirculated to or reused in an upgrading reaction, optionally after subjected to further purification and/or treatment.

16. The method according to any one of the preceding items, wherein the ratio (spent catalyst/treatment fluid) by mass between spent catalyst (dry weight) and treatment fluid (water, steam, liquid acid and/or acidic aqueous solution) is in the range of from 0.05 to 10.0, preferably 0.10 to 8.

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

18. The method according to item 17, wherein the spent catalyst comprises at least one of NiMo, CoMo, NiW, NiMoW, Mo and W, and/or a mixture thereof.

19. The method according to any one of the preceding items, wherein the method further comprises an upgrading step of subjecting a lignocellulose-based material to upgrading in the presence of catalyst, an optional liquid co-feed and optional further reactant(s), such as hydrogen or a hydrogen donor.

20. The method according to any one of the preceding items, wherein the spent catalyst

(a) is a sulfided catalyst or non-sulfided catalyst made of metals comprising at least one of metals from IUPAC group 6, 8, 9 or 10 of the Periodic Table of Elements, and preferably at least one of NiMo, CoMo, NiW, NiMoW, Mo, W and/or a mixture thereof; and/or

(b) is supported or unsupported, preferably unsupported.

21. A regenerated catalyst obtainable from the method according to any one of items 1 to 19, after optional further treatment.

22. A use of a regenerated catalyst according to item 21 as a catalyst in a

reaction for upgrading a lignocellulose-based material.

DETAILED DESCRIPTION OF THE INVENTION

In an aspect, the present invention provides a method for regenerating a spent catalyst from an upgraded liquid lignocellulose-based material, the method comprising a regeneration treatment step of treating the spent catalyst with at least one of water, steam, liquid acid and aqueous acidic solution to provide a regenerated catalyst, separating and recovering the regenerated catalyst.

In the present invention, the term “upgraded liquid lignocellulose-based material” is a reaction effluent from an upgrading process of a biobased material. The reaction effluent comprises spent catalyst–containing solids and/or a spent catalyst suspended in the reaction effluent. The spent catalyst and spent catalyst-containing solids are particulates and insoluble in the liquid organic part of a reaction effluent. The liquid organic part of the reaction effluent is also referred to as “oil product”. The oil product is thus a bio-based product, more specifically the oil product is the organic portion of the reaction effluent. The oil product may contain oxygenates and hydrocarbons. In an embodiment, the oil product contains at least hydrocarbons. In an embodiment, the oil product contains more than 50 wt.% of hydrocarbons. In an embodiment, the oxygen content of the oil product is 25.0 wt.% or less. In another embodiment, the oxygen content is 15.0 wt.% or less. In a further embodiment, the oxygen content is 10.0 wt.%. In a still further embodiment, the oxygen content is 5.0 wt.% or less. The oxygen content has been determined by ASTM D5291.

The term “reaction effluent” in the present invention refers to a non-aqueous and a non-gaseous part of the effluent of a reaction for upgrading a bio-based material (up-grading reaction), such as a liquefaction-of-biomass reaction, i.e., with aqueous phases and gas, if present, being removed when determining amounts relative to the “reaction effluent”.

Generally, separation usually aims at high separation efficiency. However, the skilled person understands 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 a material from another means of separating at least part thereof (of the material), preferably a majority thereof (>50 wt.%), more preferably most thereof (≥90 wt.%)

In an embodiment of the invention, the spent catalyst is recovered from the upgraded liquid lignocellulose-based material by separating the spent catalyst from the oil product (separation step) before the regeneration treatment step.

In the present invention, the term “bio-based” 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 iso-topes. 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 wt.%.

In the present invention, the term "acidic aqueous solution" means a mixture of water and acid(s) and optionally further component(s) as long as the solution has a pH in the acidic range. i.e., below 7.

The term "liquid acid" means essentially pure acid in liquid form with essentially no water in it.

In the present invention, the term "spent catalyst" means a catalyst after having been used for an upgrading reaction, such as lignocellulose liquefaction, e.g., by catalytic hydroliquefaction, or hydrotreatment or hydroprocessing of a previously liquefied lignocellulose-based material. such as a lignocellulose-based hydrothermal liquefaction (HTL) product or pyrolysis product, or tall oil pitch or crude tall oil.

In an embodiment, the spent catalyst is recovered from the reaction effluent of the upgrading reaction from the lignocellulose-based material. After regeneration of the spent catalyst, the regenerated catalyst is in its active form and thus ready for being re-used in an upgrading reaction, either directly or after optional further treatment.

In one embodiment, at least part of the spent catalyst having been subjected to the regeneration treatment step is recirculated to or reused in an upgrading reaction of the liquid lignocellulose-based material, optionally after being subjected to further purification and/or treatment. In an embodiment, the spent catalyst is a sulphided heterogeneous metal catalyst including, but not limited to, a catalyst comprising metals from IUPAC group 6, 8, 9 or 10 of the Periodic Table of Elements. Preferably at least one of

NiMo, CoMo, NiW, NiMoW, Mo and W, more preferably sulphided NiMo, sulphided CoMo, and sulphided Mo based catalysts. The catalyst can be unsupported or supported. Examples of suitable supports include silica and/or alumina. Preferably the catalyst is unsupported. Unsupported catalyst can be a sulphided catalyst or it can be fed to the process as a precursor such as oil soluble molybdenum compounds or as partially sulphided catalyst. In case of using catalyst precursor, the catalyst precursor forms the active catalyst particles during the process.

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

In an embodiment, the spent catalyst (e.g. the sulphided or non-sulphided catalyst) comprises at least one of NiMo, CoMo, NiW, NiMoW, Mo and W. The method of the invention provides a regenerated catalyst, which can be re-used as such, or after optional further workup and/or purification. In the context of the present invention, the spent catalyst comprises at least partially deactivated catalyst. Although it is not desired to be bound by any theory, it is currently understood that deactivation occurs by contacting with lignocellulose-based impurities, one main impurity being Ca which is thereafter usually present at least on the surface of the spent catalyst. Other impurities include K, P, Si, Mg, Mn, Cl, Al, Fe, Na, Ba, Zn, Mo, Sb, Cr by way of example. Such types of impurities (also referred to as “inorganic compounds” in the context of the present invention), in particular rather large amounts of Ca-based impurities, do not normally occur (in these amounts) in processes for converting fossil feeds.

It was surprisingly found in the present invention that this type of spent catalyst from upgrading of bio-based or lignocellulosic material can be regenerated using this rather simple though efficient process. Thus, inorganic impurities can be removed from recirculation and their accumulation, and eventually drop of reaction performance can be minimized. In addition, the method of the present invention provides high regeneration efficiency of recovered spent catalyst.

The spent catalyst is preferably recovered from the upgraded liquid bio-based or lignocellulose-based material before the regeneration treatment step.

The upgraded bio-based or lignocellulose-based material is the reaction product of the upgrading reaction and comprises an oil and a spent catalyst, and may comprise coarse non-catalyst particles e.g. originating from dirt, such as sand and may further optionally comprise coke and/or char. In other words, the reaction effluent is usually in the form of a dispersion or a slurry. The upgraded bio-based or lignocellulose-based material may thus correspond to the “reaction effluent” mentioned above or may e.g. be a treated

reaction effluent.

Suitable means for separating the spent catalyst from the oil product comprise filtration, or centrifugation or a sequence of at least one of decanter, hydrocyclone separation, filtration (including strainer), and centrifugation separation. A recovered spent catalyst may comprise coke and/or char, e.g. a solid by-product of the upgrading reaction. The recovered spent catalyst usually still comprises and is contaminated with an oil product. For example, the oil product may adhere to the spent catalyst even after separation, and this oil product adhered to the spent catalyst is referred to as residual oil.

The spent catalyst is preferably subjected to deoiling before the regeneration treatment step. The deoiling preferably comprises washing the spent catalyst with an organic solvent. The oil product recovery preferably comprises washing the spent catalyst with at least one selected from the group comprising an organic solvent, such as 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. The deoiling is thus suited to separate residual (e.g. adhering) oil product from the (spent) catalyst.

In an embodiment, the spent catalyst is subjected to washing with an organic solvent to remove residual oil product from the spent catalyst (deoiling step) before the regeneration treatment step.

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

Washing with organic solvent is easily achieved and the solvent may remain in (or be blended into) the residual oil product or may be separated.

This regeneration treatment step may also be referred to as “inorganic removal stage”, i.e., a stage in which inorganic material including inorganic compounds, i.e., inorganic impurities, are removed from the spent catalyst.

The regeneration treatment step is preferably carried out at a temperature in the range of from 15°C to 400°C, preferably 15°C to 200°C, more preferably 20°C to 150°C.

When the regeneration treatment step is carried out with water, it is preferably carried out at a temperature in the range of from 15°C to 300°C, preferably 20°C to 150°C.

When the regeneration treatment step is carried out with steam, it is preferably carried out at a temperature in the range of from 100°C to 400°C, preferably 100°C to 250°C (inorganic removal stage).

When the regeneration treatment step is carried out with liquid acid and/or aqueous acidic solution, it is preferably carried out at a temperature in the range of from

15°C to 200°C, preferably 20°C to 100°C, more preferably 25 to 80°C (inorganic removal stage).

The method of the invention may further comprise removing coarse non-catalyst particles having a particle size (maximum diameter) of 0.3 mm or more from the spent catalyst before the regeneration treatment step. The coarse non-catalyst particles may for example originate from dirt contained in the raw material of an upgrading reaction. The coarse non-catalyst particles may be hard particles, e.g. particles having a Mohs hard-ness of in the range of from 3 to 9, such as from 4 to 9, or from 5 to 7. Such coarse non-catalyst particles may comprise e.g. sand.

In an embodiment, the method further comprises at least one step for removing coarse non-catalyst particles having a particle size (maximum diameter) of 0.3 mm or more from the spent catalyst before the regeneration treatment step.

The method may further comprise an upgrading step of subjecting a lignocellulose-based material to upgrading in the presence of catalyst, an optional liquid co-feed and optional further reactant(s), such as hydrogen or a hydrogen donor. Optionally, an upgrading step, e.g., a liquefaction step, which can be integrated to the method steps as claimed in the present invention which is referred to as an “integrated process”. In general, lignocellulosic material, e.g., a lignocellulose-based material, is solid at NTP (normal temperature and pressure, 25°C, 101.325 kPa absolute). One embodiment of the lignocellulose-based material is material(s) and/or intermediate(s) derived from lignocellulosic material such as hydrothermal liquefaction oil, tall oil pitch, crude tall oil, pyrolysis oil (from pyrolysis of lignocellulosic material), catalytic pyrolysis oil (from catalytic pyrolysis of lignocellulosic material).

In another embodiment of the upgrading step (and in particular a liquefaction step) may be accomplished in the presence of a (liquid) co-feed, such as a renewable oil, a renewable fat, or a fossil oil, such as a heavy fossil oil fraction.

The method may further comprise recirculating at least part of the regenerated catalyst having been subjected to the regeneration treatment step and/or inorganic removal stage, after optional further purification and/or treatment, to an upgrading reaction of a lignocellulose-based material.

The upgrading reaction may be a liquefaction reaction of subjecting a lignocellulosic material to liquefaction by catalytic hydroliquefaction in the presence of a hydrogen source, e.g. hydrogen or a hydrogen donor, such as a hydrogen-containing solvent, the (not yet spent) catalyst and an optional liquid co-feed. 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 be chosen from the list comprising fossil-based hydrocarbons, a bio-based oil/fat, and/or re-circulated product obtained in the catalytic hydroliquefaction step and/or mixture thereof.

The liquid acid and/or the acid forming the acidic aqueous solution is preferably at least one acid, wherein acid has a pKa in the range from -10.0 to 6.0. The liquid acid and/or the acid forming the acidic aqueous solution is preferably at least one mild acid, wherein a mild acid has a pKa in the range from -1.0 to 6.0, preferably in the range from 0.0 to 5.5, 1.0 to 5.0, or 2.0 to 4.0.

In an embodiment, the liquid acid and/or the acid forming the acidic aqueous solution is at least one acid, wherein acid has a pKa in the range of from -10.0 to 6.0.

In an embodiment, the liquid acid and/or the acid forming the acidic aqueous solution is at least one mild acid, wherein a mild acid has a pKa in the range of from -1.0 to 6.0, preferably in the range of from 0.0 to 5.5, 1.0 to 5.0, or 2.0 to 4.0.

In an embodiment, the acidic aqueous solution comprises at least water and an acid and the acid is in a concentration of 3.0 to 80.0 wt.%, preferably 5.0 to 60.0 wt.%, based on the total acidic aqueous solution.

The spent catalyst is preferably treated with the liquid acid and/or the acidic aqueous solution. The liquid acid is at least one, preferably exactly one, selected from the group consisting of formic acid, acetic acid and propionic acid. The acid forming an 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.

In an embodiment, the at least one, preferably exactly one, liquid acid selected from the group consisting of formic acid, acetic acid and propionic acid. The acid forming an 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 acid treated spent catalyst, i.e., the spent catalyst after having been treated, e.g., with liquid acid and/or an acidic aqueous solution, is preferably subjected to further washing with water and/or steam to remove residual acid.

The weight ratio between the spent catalyst (dry weight) and the treatment liquid, i.e., water, steam, liquid acid and/or aqueous acidic solution, is preferably in the range of from 0.05 to 10.0, more preferably 0.10 to 8.0.

The acidic aqueous solution preferably comprises at least water and an acid and the acid is in a concentration of 3.0 to 80.0 wt.%, preferably 5.0 to 60.0 wt.%, based on weight of the total acidic aqueous solution. The sum of water and acid (relative to acidic aqueous solution as a whole) is preferably at least 95 wt.%, at least 97 wt.%, at least 98 wt.%, at least 99 wt.%, or even 100%.

The method of the invention may comprise a step of liquefying biomass, e.g., a hydroliquefaction step, as an upgrading reaction which comprises a process for the conversion of lignocellulosic starting material(s) into at least an aqueous phase and an oil products phase, wherein the lignocellulosic starting material, the (not yet spent) catalyst, and optionally a co-feed, are mixed. When a co-feed is present, the co-feed is preferably

chosen from vegetable oil(s) and fat(s), liquid hydrocarbon(s), or a re-circulated fraction of the oil product.

In an embodiment, the method further comprises an upgrading step of subjecting a lignocellulose-based material to upgrading in the presence of catalyst, an optional liquid co-feed and optional further reactant(s), such as hydrogen or a hydrogen donor.

The lignocellulosic starting material is preferably chosen from wood chips and/or saw dust with a dry content of 50 wt.% or more; forestry residue chosen from bark, and/or roots, and/or branches with a dry content of 50 wt.% or more; wood having been subjected to drying or a torrefaction process; municipal waste products such as packaging wastes containing lignocellulosic materials; lignocellulose from agriculture like for example straw from crops like oats, wheat, barley and rye, corn stover, grasses and herbs, forage crops, oat husks, rice husks, construction waste containing at least 50 wt.% originating from lignocellulosic matter; and mixtures thereof.

In the present invention, the term “catalytic hydroliquefaction”, refers to conversion of carbonaceous feedstock, such as lignocellulosic starting material(s), into liquid hydrocarbons suitable for use as drop-in fuels, fuel components and/or other valuable hydro-carbon products either directly and/or after further valorisation. Catalytic hydroliquefaction is a preferred embodiment of an upgrading reaction referred to in the present invention.

The catalytic hydroliquefaction is carried out at a temperature in the range of from 250 to 450°C, such as from 270 to 420°C, preferably from 300 to 400°C, more preferably from 320 to 390°C. A skilled person will be competent to select a temperature within these ranges keeping in mind that increasing the temperature will increase the liquid hydrocarbon yield, but a higher temperature will also tend to increase gas yield and cracking, in particular at above 400°C. Lower temperatures on the other hand will lead to incomplete con-version and higher amount of solids and increase of residence time.

In an embodiment, the catalytic hydroliquefaction is 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 from 7 to 16 MPa, more preferably at least 8 MPa, such as from 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. Typically, 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 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. Typically, the residence time is in the range of from 10 minutes to 6 hours, preferably from 30 minutes to 4 hours, more preferably from 1 hour to 3 hours.

The catalytic hydroliquefaction step is performed in the presence of at least one catalyst. After the catalyst has passed through the reactor at least once and flows out with the reaction effluent, the catalyst is referred to as “spent catalyst” in the present invention. Suitable catalysts for the catalytic hydroliquefaction include known hydroconversion catalysts, sulphided catalysts, such as sulphided heterogeneous metal catalysts, are preferred.

Examples of suitable sulphided heterogeneous metal catalysts include, but are not limited to, a catalyst composed of metals from IUPAC group 6, 8, 9 or 10 of the Periodic Table of Elements such as sulphided NiMo, sulphided CoMo, and sulphided Mo based catalysts. The catalyst can be unsupported and/or supported. Examples of suitable supports include silica and/or alumina. Preferably the catalyst is unsupported. Unsupported catalyst can be a sulphided catalyst or it can be fed to the process as a precursor such as oil soluble molybdenum compounds or as partially sulphided catalyst. In case of using catalyst precursor, the catalyst precursor forms the active catalyst particles during the process. A person skilled in the art will be competent to adjust the catalyst type and the amount of the catalyst present in the hydroliquefaction step to fit the intended purpose. Suitably, catalyst can be present in an amount from 0.005 to 5.00 wt.-%, preferably from 0.010 to 3.00 wt.-%, more preferably from 0.10 to 1.00 wt.-%. The catalyst can be in a particulate form and can have 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 typically is insoluble in a reaction effluent such that the catalyst can be suspended in a liquid organic based medium. Furthermore, the catalyst can be sulphided.

In an embodiment of the catalytic hydroliquefaction, it may be performed in any suitable reactor wherein the indicated conditions may be achieved such that the catalyst may be embedded for example in ebullated bed and/or in bubbling bed. Examples of suitable reactors include mixed reactors and/or pipe reactors. Further, the catalytic hydroliquefaction in step 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).

In an embodiment of the catalytic hydroliquefaction step, it 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.

In an embodiment of the catalytic hydroliquefaction step, the consecutive catalytic hydroliquefaction stages are typically performed at essentially the same pressure, i.e. each stage typically 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 prefer-ably at least 8 MPa, such as in the range of from 8 to 14 MPa, given as gauge pressure, while the pressure of the first catalytic hydroliquefaction stage 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 catalytic hydroliquefaction step, the consecutive catalytic hydroliquefaction stages are typically carried out at a temperature in the range of from 270 to 420 °C, preferably from 300 to 400 °C, more preferably 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. Typically, 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. 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 an embodiment of the catalytic hydroliquefaction step, the hydrogen source can be selected between 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 be chosen from the list comprising vegetable oils and fats, liquid hydrocarbons, or a re-circulated product obtained in the catalytic hydroliquefaction step.

In another aspect, the present invention provides a regenerated catalyst

obtainable by a method of the invention.

In a further aspect, the present invention provides use of a regenerated catalyst of the invention as a catalyst in a reaction for upgrading a lignocellulose-based material.

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.

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.

Example 1 (deactivation effect)

Liquefaction test runs were carried out in laboratory scale stirred tank reactors operating with semi-batch mode with continuous hydrogen flow rate. In the test run, dodecane was used as co-feed. In the test run, sawdust, used as lignocellulose-based raw material, was mixed to the co-feed with catalyst. In all test runs, sawdust and catalyst concentration was kept as constant.

Deactivating effect of the inorganic compounds was tested with the model compound from the (lignocellulosic) biomass. Calcium oxalate ($CaC_2O_2 \cdot H_2O$) was analysed to be present as one of the main inorganic compounds in the lignocellulosic material. Test run 2 was carried with addition of calcium oxalate and liquid yield and product density was compared to test run 1 without addition. Test runs were carried out at 380 °C, pressure 140 bar (absolute). Test run time in target conditions was 2 hours.

Liquid yield from sawdust in these test runs is calculated by dividing liquid product amount after subtracting the amount of co-feed by the sawdust amount in the start of the test run. Product density is analysed from the liquid organic product containing the co-feed. Lower liquid yield and higher hydrocarbon product density was obtained in the test run with calcium oxalate (see Table 1). This shows that calcium oxalate causes a de-crease in the catalyst activity.

Table 1

	Liquid yield %	Product density kg/m^3
Test run 1 - without calcium oxalate	38	741.3
Test run 2 - with additional calcium oxalate	34	757.4

Examples 2 and 3 (treating the spent catalyst with acid aqueous solution)

Acid treatment of solids including catalyst, coke and inorganic compounds was tested from pilot reactor samples with citric acid (Example 1) and phosphoric acid (Example 2). The samples were obtained from a continuous lignocellulosic material liquefaction pilot run. The liquid product sample that contained the solids, was first filtered and then washed with heptane and THF to de-oil the solids. After solvent wash, the solids were treated either with an aqueous solution of 50 wt.% citric acid (pH 0.44) or an aqueous solution of 20 wt.% phosphoric acid (pH 0.32) to reduce the amount of inorganic compounds (impurities) on the catalyst. The weight ratio between treatment fluid (acidic aqueous solution) and solids was 13 g/g (aqueous solution/solids). Acid used in the treatment was analysed with ICP to measure the content of inorganic compounds.

SEM-EDS analysis which was carried out for the solids prior to acid treatment is presented in Table 2. Solids from the test run showed high content of Ca and other inorganic impurities originating from lignocellulosic material. SEM-EDS is a semi-quantitative method for analysis and results are considered as indicative.

Table 2

	Solid sample 1, elemental content in wt.%
Ca	3.6
Na	0.1
Mg	0.4
P	0.3
K	0.9

Impurities concentration in the treated solution after treatment with citric acid and phosphoric acid is presented in Table 3. Both citric acid and phosphoric acid showed elevated content of inorganic impurity compounds after treatment. The results indicate efficient impurity removal from the solids by acid treatment.

	Ex. 2: Aqueous citric acid mg/kg	**Ex. 3:** Aqueous phosphoric acid mg/kg
Ca	1713	1943
Na	467	53
Mg	155	53
P	81	n. a.
K	631	629

n.a. = not analyzed

Based on the mass balance calculated from the SEM-EDS results of solid

sample and amount of Ca in the washing solvent, 60-70% of Ca was removed in the acid treatment. Also, other inorganic impurities could be measured in the washing solvents, thus impurity removal can be considered good.

CLAIMS

1. A method for regenerating a spent catalyst from an upgraded liquid lignocellulose-based material, the method comprising a regeneration treatment step of treating the spent catalyst with at least one treatment fluid selected from water, steam, liquid acid aqueous acidic solution and any combination thereof to provide a regenerated catalyst,

wherein the spent catalyst

(a) is a sulfided catalyst or non-sulfided catalyst made of metals comprising at least one of metals from IUPAC group 6, 8, 9 or 10 of the Periodic Table of Elements, and preferably at least one of NiMo, CoMo, NiW, NiMoW, Mo, W and/or a mixture thereof; and/or

(b) is preferably unsupported.

2. The method according to claim 1, wherein the method comprises separating and recovering the regenerated catalyst.

3. The method according to any one of the preceding claims, wherein the method comprises a separation step wherein the spent catalyst is recovered from the upgraded liquid lignocellulose-based material by separating the spent catalyst from the oil product before the regeneration treatment step.

4. The method according to any one of the preceding claims, wherein the method comprises a deoiling step wherein the spent catalyst is subjected to washing with an organic solvent to remove residual oil product from the spent catalyst before the regeneration treatment step.

5. The method according to claim 4, wherein the organic solvent is selected from the group comprising at least one of a hydrocarbon solvent such as a light hydrocarbon solvent (C10 or less), decane, hexane, heptane, acetone, tetrahydrofurane (THF), diethyl ether, toluene, ethanol, methanol, and/or a light fraction of the oil product.

6. The method according to any one of the preceding claims, wherein the regeneration treatment step is carried out at a temperature in the range of from 15°C to 400°C, preferably 15°C to 200°C, more preferably 20°C to 150°C.

7. The method according to any one of the preceding claims, wherein the regeneration treatment step

(a) is carried out with water at a temperature in the range of from 15°C to 300°C, preferably 20°C to 150°C; and/or

(b) is carried out with steam at a temperature in the range of from 100°C to 400°C, preferably 100°C to 250°C.

8. The method according to any one of claims 1 to 6, wherein the regeneration treatment step is carried out with liquid acid and/or acidic aqueous solution at a

temperature in the range of from 15°C to 200°C, preferably 20°C to 100°C, more preferably 25 to 80°C.

9. The method according to any one of claims 1 to 6 or 8, wherein the liquid acid and/or the acid forming the acidic aqueous solution is at least one acid, wherein acid has a pKa in the range of from -10.0 to 6.0, or at least one mild acid, wherein a mild acid has a pKa in the range of from -1.0 to 6.0, preferably in the range of from 0.0 to 5.5, 1.0 to 5.0, or 2.0 to 4.0.

10. The method according to any one of claims 8 to 9, wherein the acid treated spent catalyst is subjected to further washing with water and/or steam to remove residual acid.

11. The method according to any one of the preceding claims, wherein at least part of the spent catalyst having been subjected to the regeneration treatment step is recirculated to or reused in an upgrading reaction, optionally after subjected to further purification and/or treatment.

12. The method according to any one of the preceding claims, wherein the ratio (spent catalyst/treatment fluid) by mass between spent catalyst (dry weight) and treatment fluid selected from water, steam, liquid acid, acidic aqueous solution or any combination thereof is in the range of from 0.05 to 10.0, preferably 0.10 to 8.

13. The method according to any one of the previous claims, wherein the method may further comprise an upgrading step of subjecting a lignocellulose-based material to upgrading in the presence of catalyst, an optional liquid co-feed and optional further reactant(s), such as hydrogen or a hydrogen donor.

14. A regenerated catalyst obtainable by a method according to any one of claims 1 to 9.

15. A use of a regenerated catalyst according to claim 14 as a catalyst in a reaction for upgrading a lignocellulose-based material.