

## BIOASPHALTENE CONVERSION

### FIELD OF THE INVENTION

The present invention relates to a method for bioasphaltenes conversion.

### BACKGROUND OF THE INVENTION

- 5           Liquefaction of (solid) biomaterial has attracted increased attention in recent years. Such liquefaction processes are generally known in the art. For example, WO2022058128 A1 discloses direct hydrogenation of lignocellulosic material using unsupported NiMo catalyst. US 2011/0167713 A1 also discloses direct hydrogenation of lignocellulosic material.
- 10           While conventional method for processing (fossil) asphaltenes are known, e.g. from WO 2014/120490 A1, bioasphaltenes are recognised to be by-products, and they are known to be challenging to convert to upgraded products in the industry. That is, it was previously thought that bioasphaltenes would be hard to convert thus it is at least deterring a skilled person from considering if not preventing him/her from employing a recirculation step to complement the liquefaction step. Therefore, fossil based asphaltenes were conventionally separated (e.g. using SDA=solvent deasphalting process) and discarded or otherwise used (burnt) instead of being converted into upgraded products. The same has been conventionally expected of bioasphaltenes resulting from liquefaction of biomass thus a yield
- 15           loss in the liquefaction of biomass to liquid products is a commonly accepted outcome. Since bioasphaltenes/asphaltenes have been known for deactivating catalysts, processing any material in the presence of bioasphaltenes/asphaltenes at high temperature will lead to coke formation affecting any catalyst performance downstream.

### 25 BRIEF DESCRIPTION OF THE INVENTION

- In the biomass liquefaction process, it has been observed that the liquefaction effluent directly obtained from the liquefaction contains heavy substances herein referred to as bioasphaltenes. These bioasphaltenes have a tendency to cause fouling in the liquefaction process and are known to be a problematic substance in downstream processing. Therefore, they have often been discarded as a
- 30           byproduct leading to a yield loss in the liquefaction process. The present invention

provides the solutions overcoming the drawbacks of the prior art and thereby allows for utilisation of the bioasphaltenes formed in the overall biomass liquefaction process. The step of liquefying biomass is referred to as liquefaction step or hydroliquefaction step.

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

1. A method of processing liquefied biomass, the method comprising the steps of  
providing a liquefaction effluent by liquefying biomass in the presence  
10 of a hydrogen source and a slurry-type catalyst and at elevated temperatures (hydroliquefaction step), wherein the liquefaction effluent comprises oil product, bioasphaltenes and solids, and

converting at least part of the bioasphaltenes into components of lower boiling points (conversion step), wherein the hydroliquefaction step and the conversion step are operating in continuous mode,  
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wherein the conversion step comprises recirculating at least a portion of the liquefaction effluent comprising bioasphaltenes (bioasphaltene portion) to the hydroliquefaction step (recirculation step) and/or subjecting at least a portion of the liquefaction effluent comprising bioasphaltenes (bioasphaltene portion) to hydroprocessing (hydroprocessing step).  
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2. The method according to item 1, wherein the hydrogen source is hydrogen gas and/or a hydrogen donor.

3. The method according to item 2, wherein the hydrogen donor is a hydrogen-containing solvent and/or co-feed.

25 4. The method according to any one of the preceding items, wherein the conversion step comprises both the recirculation step and the hydroprocessing step.

5. The method according to any one of the preceding items, wherein the at least a portion of the liquefaction effluent comprising bioasphaltenes (bioasphaltene portion) is obtained by means of a separation step, wherein the separation step comprises separating the liquefaction effluent into at least one bioasphaltene portion, optionally further an oil product portion such that the bioasphaltene portion comprises at least bioasphaltenes and the oil product portion comprises oil product that is predominantly liquid hydrocarbons (separation step).  
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35 6. The method according to any one of the preceding items, wherein at least part of the liquefaction effluent is further subjected to a treatment step,

wherein the treatment step is solvent deasphalting and/or distilling.

7. The method according to item 6, wherein the treatment step is a combination of solvent deasphalting and distilling, wherein distilling is performed either before or after solvent deasphalting.

5           8. The method according to item 6 or 7, wherein the distilling comprises recovering at least one distillate fraction and a bottom fraction, and the bottom fraction is the bioasphaltene portion.

9. The method according to item 8, wherein the bottom fraction is the bioasphaltene portion and has 5% recovered at 360°C or more, or 5% recovered at  
10   480°C or more.

10. The method according to item 8 or 9, wherein at least a part of at least one distillate fraction derived from the distillation of the liquefaction effluent (distillation step) is employed as a co-feed in the hydroliquefaction step.

11. The method according to any one of the preceding items, wherein  
15   the bioasphaltene portion further comprises spent or fresh slurry-type catalyst for recirculation.

12. The method according to any one of the preceding items, wherein at least part of the hydroprocessed liquefaction effluent or at least part of the hydro-processed bioasphaltene portion is recirculated as a co-feed back to the hydroliquefaction step.  
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13. The method according to any one of the preceding items, wherein the hydroprocessing step is a hydrotreatment step and/or a hydrocracking step.

14. The method according to any one of the preceding items, wherein the hydroprocessing step is performed in at least one hydroprocessing reactor  
25   which comprises a fixed bed reactor and/or an ebullated reactor.

15. The method according to any of the preceding items, wherein the hydroprocessing reactor comprises a supported hydroprocessing catalyst.

16. The method according to any one of the preceding items, wherein the co-feed in the hydroliquefaction step is a renewable liquid medium and/or a fossil based medium.  
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17. The method according to any one of the preceding items, wherein the co-feed in the hydroliquefaction step is a blend of renewable liquid medium and/or a fossil based medium, and the bioasphaltene portion.

18. The method according to item 16 or 17, wherein the content of the  
35   co-feed of the total feed in the hydroliquefaction step is in the range of 0 to 95 wt.-%, preferably 40 wt.-% to 90 wt.-%, 50 wt.-% to 85 wt.-% or 60 wt.-% to 80 wt.-%.

19. The method according to any one of the preceding items, wherein the content of bioasphaltenes in the bioasphaltene portion that is untreated is 4-20wt%, preferably 6-10wt%.

20. The method according to any one of the preceding items, wherein  
5 the content of bioasphaltenes in the bioasphaltene portion that has been treated by deasphalting is 50-100wt%, preferably 80-98wt%.

21. The method according to any one of the preceding items, wherein the content of bioasphaltenes in the bioasphaltene portion that has been treated by distillation, and of the 5% recovered at 360°C distillate bottom is 6-30wt%, preferably  
10 ably 10-20wt%; and of the 5% recovered at 480°C distillate bottom is 30-100wt%, preferably 60-80wt%.

22. The method according to any of the preceding items, wherein the wt.-% of the bioasphaltene portion as the recirculation feed of the total feed in the hydroliquefaction step is 40.0 to 95.0 wt.-%, preferably 70.0 to 90.0 wt.-%.

15 23. The method according to any one of the preceding items, wherein the content of the bioasphaltene portion in the total oil feed of the hydroprocessing step is at least 5.0 wt.-%, preferably in the range of from 5.0 wt.-% to 100.0 wt.-%.

24. The method according to any one of the preceding items, wherein the slurry-type 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.

25. The method according to any one of the preceding items, wherein the hydroliquefaction step is carried out with slurry-type sulphided catalyst, at temperature of 350°C to 390 °C, and at pressure in the range of 7 to 16 MPa.  
26. The method according to any one of the preceding items, wherein the hydroliquefaction step is carried out with slurry-type sulphided catalyst at temperature of 350°C to 390 °C, and at pressure in the range of 8 to 14 MPa.

27. The method according to any one of the preceding items, wherein the hydroliquefaction step is carried out with a slurry-type sulphided catalyst comprising or composed of one or more metals from IUPAC group 6, 8, 9 and/or 10 of the Periodic Table of Elements.

28. The method according to any one of the preceding items, wherein the hydroliquefaction step is carried out with a slurry-type sulphided catalyst of NiMo and/or CoMo and/or Mo and/or NiW and/or W, preferably the hydroliquefaction step is carried out with a slurry-type sulphided catalyst of NiMo and/or  
35 CoMo and/or Mo.

29. The method according to any one of the preceding items, wherein the residence time in the hydroliquefaction step is in the range of 10 minutes to 6 hours, preferably from 30 minutes to 4 hours, more preferably from 1 hour to 3 hours.

5 30. The method according to any one of the preceding items, wherein the hydroliquefaction step is carried out in a continuous flow-type reactor.

31. The method according to any one of the preceding items, wherein the conversion step comprises at least the recirculation step.

10 32. The method according to any one of the preceding items, wherein the conversion step comprises the hydroprocessing step, wherein hydroprocessing step is hydrotreating and/or hydrocracking, performed in the presence of a catalyst and at pressures in the range of 40-300 bar and a temperature in the range of 300-450 °C.

15 33. The method according to any one of the preceding items, further comprising recirculating at least part of the slurry-type catalyst to the hydroliquefaction step.

34. The method according to any one of the preceding items, wherein the oxygen content (wt%) in the bioasphaltenes is in the range of about 0.8 to about 10 wt%, about 0.8 to about 7 wt% or about 1 to about 3 wt%.

20 35. A bioasphaltene product obtained by a method comprising the steps of providing a liquefaction effluent by liquefying biomass in the presence of a hydrogen source and with slurry-type sulphided catalyst, at temperature of 350 to 390 °C, and at pressure of 7 to 16 MPa, preferably 8 to 14 MPa, wherein the liquefaction effluent comprises oil product, bioasphaltenes and solids, wherein bioasphaltenes are characterised by being insoluble in n-heptane at room temperature and soluble to THF (at room temperature), and have a molecular mass in the range of 150 to 1500 g/mol, more preferably 150-1000 g/mol, or 150-600 g/mol, most preferably 150-300 g/mol, and are aromatic in nature with a double bond equivalent number in the range of 4 to 30 as measured by HRMS APCI NEG (high resolution mass spectroscopy using negative mode atmospheric pressure chemical ionisation).

30 36. The bioasphaltene product of item 35, wherein the hydroliquefaction step is carried out with a slurry-type sulphided catalyst comprising or composed of one or more metals from IUPAC group 6, 8, 9 and/or 10 of the Periodic Table of Elements.

37. The bioasphaltene product of item 35 or 36, wherein the slurry-type

sulphided catalyst is a sulphided catalyst of NiMo and/or CoMo and/or Mo and/or NiW and/or W, preferably the slurry-type sulphided catalyst is a sulphided catalyst of NiMo and/or CoMo and/or Mo.

38. The bioasphaltene product of any of items 35 - 37, wherein the oxygen content (wt%) in the bioasphaltenes is in the range of about 0.8 to about 10 wt%, about 0.8 to about 7 wt% or about 1 to about 3 wt%.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the following the invention will be described in greater detail by means of preferred embodiments with reference to the accompanying drawings, in which

FIG. 1 shows H/C vs O/C van Krevelen plot of bioasphaltenes by HRMS by APCI ionization.

FIG. 2 shows SIMdist results of the feed and product of Example 1.

FIG. 3 shows SIMdist results of the feed and product of Example 2 Detailed description of the invention.

FIG. 4 to 8 show flow charts of embodiments of the method of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method for processing bioasphaltenes formed in catalytic hydroliquefaction of biomass. The method comprises a step of providing a liquefaction effluent comprising oil product, bioasphaltenes and solids (the solids comprising slurry-type catalyst), by means of liquefying biomass material in the presence of a hydrogen source and a slurry-type catalyst in a continuous mode. The step of liquefying biomass is referred to as liquefaction step or hydroliquefaction step.

In an embodiment the hydroliquefaction step comprises liquefying biomass in the presence of a hydrogen source and a slurry-type catalyst at elevated temperatures to provide a liquefaction effluent comprising oil product, bioasphaltenes and solids.

The method furthermore comprises steps of processing the liquefaction effluent to convert the bioasphaltenes contained therein to components of lower boiling points, referred to as the conversion step. The conversion step comprises the steps of recirculating a portion of the liquefaction effluent (comprising at least

bioasphaltenes) back to the liquefaction step, referred to as the recirculation step, and/or subjecting a portion of the liquefaction effluent (comprising at least the bioasphaltenes) to hydroprocessing, such as hydrotreatment or hydrocracking as an example, also referred to as the hydroprocessing step, thus upgrading the at least  
5 part of the bioasphaltenes in the liquefaction effluent to other hydrocarbon products. Tests of the present disclosure show that bioasphaltenes can be converted under hydroliquefaction conditions with the same slurry catalyst used in liquefaction step, which makes the recirculation step an effective way of converting bioasphaltenes.

10 In an embodiment, at least 30 %, at least 40 %, at least 50 %, at least 60 %, at least 70 %, at least 80 % or at least 85 % of the bioasphaltenes are converted, more preferably 90 % of the bioasphaltenes are converted, even more preferably at least 95 % of the bioasphaltenes are converted. Conversion rate of the bioasphaltenes can be obtained by measuring n-heptane insoluble compounds of both liquefaction effluent and the liquefaction effluent subjected to conversion step(s) (i.e. subjected to recirculation step(s) and/or hydroprocessing step (s)) and comparing  
15 the amounts of n-heptane insoluble compounds in each.

Tests of the present disclosure surprisingly show that after hydroprocessing the hydroliquefaction effluent (conversion step) the heaviest mass fraction  
20 of compounds with boiling point of >480 °C (including bioasphaltenes) decreased significantly, while the mass fraction of components with boiling point within the range 180-360 °C increased. Thus, it is clear that hydroprocessing of hydroliquefaction effluent (conversion step) results in conversion of bioasphaltenes into lighter hydrocarbon products, i.e. the bioasphaltenes are upgraded to valuable hydrocarbon products. In addition to obtaining valuable hydrocarbon products, the  
25 tests also show that the disclosed process has the benefits of decreased accumulation in long term, improved miscibility and reduced fouling in comparison to common processing methods.

In one embodiment the conversion step comprising converting at least  
30 part of the bioasphaltenes into components of lower boiling points, and the hydroliquefaction step are operated in continuous mode.

In one embodiment, the conversion step comprises recirculating at least a portion of the liquefaction effluent comprising bioasphaltenes to the hydroliquefaction step and/or subjecting at least a portion of the liquefaction effluent comprising bioasphaltenes to hydroprocessing. The portion of the liquefaction effluent  
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comprising bioasphaltenes is referred to as a bioasphaltene portion, the step of recirculating this portion to the hydroliquefaction step is referred to as a recirculation step, and the step of subjecting at least a portion of the liquefaction effluent comprising bioasphaltenes to hydroprocessing is referred to as a hydroprocessing step.

In one embodiment of the invention the conversion step comprises both the recirculation step and the hydroprocessing step. The term "**biomass**" used herein includes, but is not limited to, algae, lignocellulosic biomass including lignocellulosic biomass components such as cellulose, hemicellulose and/or lignin. The process contemplated herein is particularly suitable and optimized for lignocellulosic biomass and its components. Lignocellulosic biomass is essentially made up of three natural polymers: cellulose, hemicellulose and lignin.

The lignocellulosic starting material in the present invention can be of any types of lignocellulosic material. An non-exhaustive list of examples of the lignocellulosic material includes 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; 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. Prior to being fed to the hydroliquefaction step, the biomass feedstock may be grinded and/or dried as found suitable by a skilled person by any conventional means found suitable for the purpose to render it processable in the hydroliquefaction step.

In the present invention, the term "**renewable**" indicates the presence of a material derived from renewable sources. Carbon atoms of renewable or biological origin comprise a higher number of unstable radiocarbon ( $^{14}\text{C}$ ) 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  $^{12}\text{C}$  and  $^{14}\text{C}$  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.

The term "catalyst or slurry-type catalyst" used herein is defined as an unsupported solid catalyst comprising or composed of one or more metals from IUPAC group 6, 8, 9 and/or 10 of the Periodic Table of Elements. Preferably the catalyst is unsupported. Unsupported catalyst can be sulphided catalyst particles suspended in a liquid 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. The catalyst can be in a particulate form and is insoluble in a liquefaction effluent such that the catalyst can be suspended in a liquid organic based medium. Furthermore, the catalyst can be sulphided.

Examples of the slurry-type catalyst can be a sulphided catalyst comprising at least one of NiMo, CoMo, NiW, NiMoW, Mo and W, and has a median particle size (D50, based on particle size distribution determined by laser diffraction) in the range of from 0.01  $\mu\text{m}$  to 100.00  $\mu\text{m}$ , such as 0.10  $\mu\text{m}$  to 50.00  $\mu\text{m}$ , or 1.00  $\mu\text{m}$  to 50.00  $\mu\text{m}$ .

In one embodiment the catalyst present in the hydroliquefaction step is a slurry-type sulphided catalyst of NiMo and/or CoMo and/or Mo.

The term "**liquefaction effluent**" in the present invention refers to the non-water and non-gas part of the effluent of the hydroliquefaction step, i.e. with water and gas removed or not considered when determining amounts relative to the "liquefaction effluent". The liquefaction effluent comprises oil product, bioasphaltenes and solids. The "**oil product**" comprises oxygenates and hydrocarbons and comprises predominantly (more than 50 wt.-%) liquid hydrocarbons. In particular it is preferred that the oil product has an oxygen content of 25 wt.-% or less, preferably 20 wt.-% or less, more preferably 15 wt.-% or less, even more preferably 10 wt.-%. The term "**oxygenates**" used herein refers to oxygen-containing organics.

The term “**separation step**” is intended to mean that e.g. the liquefaction effluent has been subjected to a separation process. In one embodiment of the separation step, the liquefaction effluent is separated into at least a bioasphaltene portion. In another embodiment of the separation step, the liquefaction effluent is separated into an oil product portion and into at least a bioasphaltene portion, such that the bioasphaltene portion comprising at least bioasphaltenes and the oil product portion comprising oil product that is predominantly (more than 50 wt.-%) liquid hydrocarbons. The separation may be performed in separation vessel(s).

The “**bioasphaltene portion**” is a portion of the liquefaction effluent and it can be untreated or treated. In the case that the bioasphaltene portion is untreated, it would mean that it is obtained directly as a portion from the liquefaction effluent or directly from further gas/liquid separators, such as flash separator. The untreated processing pathway can be referred to as a separation step where no heat input is involved.

In another embodiment, the bioasphaltene portion is treated, which means that it has been subjected to a treatment step such as solvent deasphalting and/or distillation. In the case distillation is performed then at least one distillate fraction and a bottom fraction is recovered, and the bottoms fraction is taken as the bioasphaltene portion. The respective bottom fractions obtained by distillation, preferably has 5% recovered at 360°C or more, or 5% recovered at 480°C or more respectively. Oil product portion is a portion of liquefaction effluent that comprises predominantly the oil product. At least a portion of at least one distillation fraction other than the bioasphaltene portion may be employed as a recirculated co-feed in the hydroliquefaction step.

In case the solvent deasphalting and/or the distillation have been performed the aim of such is to increase the content of bioasphaltenes in one of the resulting portions, the portion having increased bioasphaltene content would serve as the bioasphaltene portion for recirculation and/or hydroprocessing directly or after further work-up.

In one embodiment the treatment step is a combination of solvent deasphalting and distilling, and the distilling is performed either before or after solvent deasphalting.

In one embodiment the treatment step, the treatment step is performed by distilling, also referred to as a distillation step, wherein distilling comprises recovering at least one distillate fraction and a bottom fraction, and the bottom fraction is the bioasphaltene portion and has 5% recovered at 360°C or more, or 5%

recovered at 480°C or more.

In an embodiment the bioasphaltene portion employed in the recirculation step further comprises spent or fresh slurry-type catalyst.

The term "**bioasphaltene**" refers to asphaltenes-type compounds in the present invention, and characterisations of the bioasphaltenes indicate that there are important differences compared to the asphaltenes that are of fossil origin. A characterisation used in the present invention to define the bioasphaltenes is by means of a solubility test with the use of solvent thereby characterising their physical properties as a heterogeneous group of compounds. In the present invention, the bioasphaltenes were found to be insoluble in n-heptane but soluble in tetrahydrofuran (THF).

In the present invention, the content of bioasphaltenes can be measured as the n-heptane insoluble (at room temperature, i.e. 25°C by method ASTM D3279-12) but THF soluble (at room temperature) material in a sample. Specifically, the content of bioasphaltenes in a sample can be measured in the following way:

The insoluble residue of filtration of the sample is washed with THF at room temperature, dried and weighed. The difference between original sample weight and dried insoluble residue is taken as the THF soluble material (THF solubles).

Using a further sample, the content of n-heptane insolubles can be determined at room temperature (25°C) in accordance with ASTM D3279-12.

The content (% by mass) of bioasphaltenes is calculated as  
[mass-% of n-heptane insolubles relative to original sample] - [mass-% of THF insolubles relative to original sample].

In the present invention, the bioasphaltenes obtained are unlike fossil-based asphaltenes as bioasphaltenes have an oxygen content. The oxygen in bioasphaltenes is mainly in the form of functional groups such as phenols, polyphenols and other aromatic oxygen containing compounds. In one embodiment, the oxygen content (wt%) in the bioasphaltenes is in the range of about 0.1 to about 10 wt%, about 0.8 to about 10 wt%, about 0.8 to about 7 wt%, about 0.8 to about 5 wt% or about 1 to about 3 wt%. In one embodiment, the oxygen content (wt%) in the bioasphaltenes is in the range of about 1.0 to about 2.0 wt%.

In an embodiment more than 30 %, more than 40 % or more than 50 wt% of oxygen in bioasphaltenes is removed during conversion step. Preferably more than 60 wt% of oxygen is removed. More preferably more than 70 wt% of

oxygen is removed. Even more preferably more than 80 wt% of oxygen is removed. Most preferably more than 85 wt% of oxygen is removed.

Furthermore, bioasphaltenes obtained with the method of the present invention can be characterized to have a molecular mass in the range of 150 to 1500 g/mol, more preferably 150-1000 g/mol, or 150-600 g/mol, most preferably 150-300 g/mol. The bioasphaltenes are aromatic in nature and may have a double bond equivalent number in the range of 4 to 30 as measured by HRMS APCI NEG (high resolution mass spectroscopy using negative mode atmospheric pressure chemical ionisation).

The term “**hydroprocessing**” herein is referred to as any downstream hydroprocessing of the liquefied biomass (liquefaction effluent or a portion thereof) with the use of a hydrogen rich environment and catalyst. In other words, the hydroprocessing is carried out downstream after the hydroliquefaction step. Hydroprocessing can be carried out in a fixed bed reactor and/or ebullated reactor. The process takes place typically at pressures of 40-300 bar and temperature of 300-450 °C.

All standards referred to herein are the latest revisions available on January 1, 2023, unless otherwise mentioned. All embodiments (such as all preferred values and/or ranges within the embodiments) of the present invention may be combined with each other to give new (preferred) embodiments, unless explicitly specified otherwise or unless such a combination would result in a contradiction. Moreover, unless stated to the contrary, pressure values presented herein refer to absolute pressure and contents or ratios (such as percentages) are provided on a mass basis.

The present invention is providing a liquefaction effluent containing bioasphaltenes that can be easily processed, by liquefying biomass in the presence of a hydrogen source and a slurry-type catalyst at elevated temperatures. The biomass is subjected to so called catalytic hydroliquefaction to obtain a liquefaction effluent comprising oil product, bioasphaltenes and solids. Without being bound to any particular theory, it is considered that under the catalytic hydroliquefaction, biomass feedstock, more preferably lignocellulosic feedstock, undergoes multiple reactions, 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 com-

prises oxygenates and hydrocarbons. In particular it is preferred that the oil product has an oxygen content of 25 wt.-% or less, preferably 20 wt.-% or less, more preferably 15 wt.-% or less, even more preferably 10 wt.-%.

The term "*catalytic hydroliquefaction*" refers to as a continuous process of conversion of solid biomass feedstock into oil product suitable for use as e.g. drop-in fuels, fuel components and/or other valuable hydrocarbon products that can be either vaporized directly and/or further upgraded.

The step of liquefying biomass preferably comprises a continuous process for the conversion of solid biomass such as lignocellulosic raw material into a liquefaction effluent comprising oil product, bioasphaltenes and solids, wherein the lignocellulosic raw material, the catalyst, and optionally a co-feed, are mixed and subjected to elevated pressure and temperature, for example in the range of 350 - 390°C in the presence of the hydrogen source. Evidently, solid biomass, catalyst, and optionally co-feed would constitute as part of the composition of "**fresh feed**" when they are being fed into the liquefaction process for the first time. "**Fresh feed**" is thus defined as a feed that is subjected to the liquefaction process for the first time. In this process, the catalyst is preferably introduced into the mixture of lignocellulosic starting materials in the form of a slurry of catalyst particles dispersed in a hydrocarbon co-feed. A co-feed may be present and the co-feed is preferably chosen from vegetable oils and fats, liquid hydrocarbons, or a re-circulated product obtained in said process.

In one aspect, the catalytic hydroliquefaction is carried out at a temperature from 270 to 450 °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 conversion and higher amount of solids and THF-solubles.

In another aspect, the catalytic hydroliquefaction is carried out at a pressure of at least 6 MPa, such as from 6 to 30 MPa. 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.

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 for continuous catalytic hydroliquefaction is 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. Suitably, the catalyst can be present in an amount from 0.005 to 5.00 wt.-%, preferably from 0.01 to 3.00 wt.-%, more preferably from 0.10 to 1.00 wt.-%. The catalyst is preferably fed to the hydroliquefaction step dispersed in a liquid medium.

As the catalytic hydroliquefaction is performed in a continuous mode, the hydroliquefaction can be performed in any suitable reactor wherein the indicated conditions may be achieved such that the catalyst can be introduced in ebullated bed and/or in bubbling bed as long as it allows for a continuous operating mode. Examples of suitable reactors include mixed reactors and/or pipe reactors. Further 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 accomplished in two or more, preferably two consecutive stages.

In one embodiment the catalytic hydroliquefaction step is performed in at least two consecutive stages. First, the biomass feedstock is subjected to catalytic hydroliquefaction to obtain an intermediate product mixture comprising partially treated biomass and deoxygenated liquid hydrocarbons. The partially treated biomass comprised in the intermediate product mixture is further subjected to catalytic hydroliquefaction in the presence of deoxygenated hydrocarbons to obtain the liquefaction effluent.

The catalytic hydroliquefaction step, the consecutive catalytic hydroliquefaction stages are performed at essentially the same pressure, i.e. each stage typically is carried out at a pressure at least 6 MPa, such as from 6 to 30 MPa, and 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 maximal deoxygenation after the catalytic hydroliquefaction

stages is desired.

In the catalytic hydroliquefaction step, the consecutive catalytic hydroliquefaction stages are carried out at a temperature from 270 to 450 °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 one preferred embodiment of invention, the hydroliquefaction step is carried out with slurry-type sulphided catalyst of NiMo and/or CoMo and/or Mo, at temperature of 350°C to 390 °C, and at pressure in the range of 8 to 14 MPa. It has been observed that the bioasphaltenes obtained from the hydroliquefaction under these operating conditions have the best conversion results. The conversion result is directed to the high conversion rate of bioasphaltenes, i.e. the oxygen in the bioasphaltenes are being removed and the bioasphaltenes are thus converted to less oxygen containing substances in the respective recirculation step and the hydroprocessing step.

In the catalytic hydroliquefaction step, the hydrogen source can be 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 hydrogen-containing co-feed can be chosen from the list selected from the group consisting of fossil-based hydrocarbons, a bio-based oil/fat, and/or recirculated product obtained in the catalytic hydroliquefaction step.

In the present invention, after the liquefaction of biomass, the heavy substances contained in the liquefaction effluent obtained from liquefaction of biomass have been identified to be bioasphaltenes and it was surprisingly found that these bioasphaltenes can be converted into valuable materials by recirculating the liquefaction effluent or at least a portion of the liquefaction effluent (bioasphaltene

portion) back to the hydroliquefaction step and/or by subjecting the liquefaction effluent or at least a portion of the liquefaction effluent (bioasphaltene portion) to downstream hydroprocessing, or in any combinations thereof. Specifically, it is possible that at least a portion of the liquefaction effluent (i.e. a part of the liquefaction effluent) is recirculated back to the hydroliquefaction step. It is also possible that at least a portion of the liquefaction effluent (such as a part of the liquefaction effluent or all of the liquefaction effluent) is forwarded to the hydroprocessing step. Moreover, it is possible that at least a portion of the liquefaction effluent (preferably a portion enriched in bioasphaltenes, i.e. having a higher bioasphaltenes content than the liquefaction effluent as a whole) be recirculated to the hydroliquefaction step and a further portion (such as at least the remaining bioasphaltenes and oil product) be forwarded to the hydroprocessing step. In other words, the method of the present invention may comprise either the recirculation step or the hydroprocessing step, or it may comprise both the recirculation step and the hydroprocessing step.

In the context of recirculating the liquefaction effluent back to the hydroliquefaction step, it was surprisingly found that the present invention does not suffer from accumulation of bioasphaltenes.

It was surprisingly found that recirculation of the liquefaction effluent or at least a portion of the liquefaction effluent (bioasphaltene portion) containing (some) of the valuable products (hydrocarbons) mainly results in conversion of the bioasphaltenes while the (valuable) hydrocarbons are not being substantially converted and thus valuable material is maintained. In the context of subjecting the liquefaction effluent to downstream hydroprocessing, the bioasphaltenes can be hydroprocessed or upgraded to valuable products together with the oil product contained in the liquefaction effluent. The combination of these surprising effects allows for a design of the biomass to liquid conversion process with an optimised yield of valuable products. In the upgrading or conversion of bioasphaltenes, a majority of the oxygen contained in the bioasphaltene substances have been removed and the respective bioasphaltenes have been converted such that there is substantially no n-heptane insoluble content and no THF soluble content remained in the converted product. By means of illustration, the bioasphaltene conversion has been found to be as high as 95% and the oxygen removal to be as high as 88%. The hydroprocessed bioasphaltene product can be used as transportation fuel blend component or as petchem feed.

In a preferred embodiment, the hydroliquefaction is carried out in a continuous mode in the presence of a slurry-type sulphided catalyst of NiMo and/or CoMo and/or Mo, at temperature in the range of 350 to 390 °C, and at pressure in the range of 7 to 16 MPa, more preferably 8 to 14 MPa. The inventors of the present invention surprisingly found that these specific conditions are particularly suitable for the present invention. Without wanting to be bound by any theory, it is assumed that these specific conditions result in the formation of bioasphaltenes which differ from those formed under other conditions, and that these bioasphaltenes can be further converted under the same conditions (i.e. by recirculation or same hydroprocessing conditions) and/or by subsequent (downstream) hydroprocessing and thus can contribute to valuable (oil) product with high efficiency. Even though the reasons and the specific structures obtained under these conditions are not fully understood, the inventors characterized the bioasphaltenes obtained under these conditions to confirm their unique nature (cf. FIG. 1) with regards to the oxygen containing substances in various amounts.

In view thereof, the present invention furthermore relates to a bioasphaltene product obtainable by a method comprising the steps of providing a liquefaction effluent by liquefying biomass in a continuous mode in the presence of a hydrogen source and with slurry-type sulphided catalyst of NiMo and/or CoMo and/or Mo, at temperature of 350 to 390 °C, and at pressure of 7 to 16 MPa more preferably 8 to 14 MPa, wherein the liquefaction effluent comprises oil product, bioasphaltenes and solids. Bioasphaltenes are characterised by being insoluble in n-heptane at room temperature and soluble in THF (at room temperature).

In one embodiment the bioasphaltenes in the bioasphaltene product are further characterised in that they have a molecular mass in the range of 150 to 1500 g/mol, more preferably 150-1000 g/mol, or 150-600 g/mol, most preferably 150-300 g/mol, and are aromatic in nature with a double bond equivalent number in the range of 4 to 30 as measured by HRMS APCI NEG (high resolution mass spectroscopy using negative mode atmospheric pressure chemical ionisation).

Oxygen in the form of functional groups would be present in the bioasphaltenes. In particular, oxygen-containing compounds, such as phenols, polyphenols and other aromatic oxygen containing compounds would typically be present in the substance. The bioasphaltenes in the present invention (and in particular in the bioasphaltene product) may for example be characterized to have a molecular mass in the range of 150 to 1500 g/mol, more preferably 150-1000 g/mol, or 150-600 g/mol, most preferably 150-300 g/mol. The bioasphaltenes are aromatic in nature and may have double bond equivalent number in the range of 4 to 30.

In an embodiment, the liquefaction effluent directly obtained from the liquefaction step is subjected to a separation step before the conversion step. In the case that the liquefaction effluent has been subjected to a separation step, a bioasphaltene portion is thereby obtained. The bioasphaltene portion can be employed as untreated or treated. In the case that it is untreated, the bioasphaltene portion is preferably obtained by separating the liquefaction effluent in separation vessel(s) such as flash separator without being further subjected to any processing step.

In the case that the liquefaction effluent is treated, the bioasphaltene portion is preferably obtained by solvent deasphalting and/or by distilling. Distillation can be performed by any means involving a heat input such that at least two fractions are obtained. In the case that distillation is performed then at least one distillate fraction and a bottom fraction are recovered, and the bottom fraction is the bioasphaltene portion. Similarly, distilling may comprise recovering at least a lighter (lower-boiling) fraction and a heavier (higher-boiling) fraction, and the heavier fraction is used as the bioasphaltenes fraction. The content of bioasphaltenes in the bioasphaltene portion that has been treated by distillation, and of the 5% recovered at 360°C distillate bottom is 6-30wt%, preferably 10-20wt%; and of the 5% recovered at 480°C distillate bottom is 30-100wt%, preferably 60-80wt%.

In the case that the solvent deasphalting has been performed on at least part of liquefaction effluent then the liquefaction effluent would result in a treated

bioasphaltene portion and an oil product portion, the bioasphaltene portion comprising at least bioasphaltenes and the oil product portion comprising oxygenates and hydrocarbons and being predominantly hydrocarbons. In particular it is preferred that the oil product has an oxygen content of 25 wt.-% or less, preferably 20 wt.-% or less, more preferably 15 wt.-% or less, even more preferably 10 wt.-%. The content of bioasphaltenes in the bioasphaltene portion that has been treated by deasphalting is 50-100wt%, preferably 80-98wt%. The resultant bioasphaltene portion would then be used respectively in the conversion step.

One aspect of the liquefaction effluent being treated is that the bioasphaltene portion obtained from the liquefaction effluent has been subjected to a combination of solvent deasphalting and distilling, wherein the distillation can be performed either before or after solvent deasphalting.

Another aspect of the conversion step comprises both the recirculation step and the hydroprocessing step. In this combination of processing steps, bioasphaltenes are converted in a recirculation step and then subsequently being further hydroprocessed, i.e further converted to an upgraded product. In particular, in a continuous flow process, a part of the liquefaction effluent may be recirculated, and another part thereof may be subjected to the hydroprocessing step.

The bioasphaltene portion may further comprise (fresh and/or spent) slurry-type catalyst. That is, since the bioasphaltene portion is usually the heaviest portion of the liquefaction effluent, it will often also contain residual solids. In particular, since slurry-type catalyst has a rather small particle size, it may be entrained with the oil product within the liquefaction effluent. In the present invention, when employing recirculation (of the bioasphaltene portion), it is neither necessary nor desirable to fully remove the slurry-type catalyst since this catalyst may be recirculated as well without adverse effects. In addition or alternatively, the slurry-type catalyst may be recirculated as such (together with or independently of the bioasphaltenes portion), even when no recirculation step (of bioasphaltene portion) is employed.

One aspect of the bioasphaltene portion is that it may serve as a recirculation feed, the wt.-% of the bioasphaltene portion as the recirculation feed of

the total feed in the hydroliquefaction step is 40.0 to 95.0 wt.-%, preferably 70.0 to 90.0 wt.-%.

Another aspect of the bioasphaltene portion is that it is serving as a hydroprocessing feed, the content of the bioasphaltene portion in the total oil feed of the hydroprocessing step is at least 5.0 wt.-%, preferably in the range of from 5.0 wt.-% to 100.0 wt.-%.

One aspect of the conversion step comprises the hydroprocessing step performed in at least one hydroprocessing reactor and preferably comprises a fixed bed reactor and/or an ebullated bed reactor. In an embodiment, the hydroprocessing reactor comprises a supported hydroprocessing catalyst. In this respect, a supported catalyst has an active site and preferably comprises or is preferably composed of one or more metals from IUPAC group 6, 8, 9 and/or 10 of the Periodic Table of Elements. Specifically, the catalyst is preferably a supported catalyst and comprises at least Mo and at least one further transition metal on a support, such as a supported NiMo catalyst or a supported CoMo catalyst, wherein the support preferably comprises alumina and/or silica. Hydroprocessing preferably comprises hydrotreating and/or hydrocracking. The process takes place typically at pressures in the range of 40-300 bar and a temperature in the range of 300-450 °C.

In an embodiment liquid co-feed is fed to the hydroliquefaction step. In this respect, the liquid co-feed is different from bioasphaltenes recirculation feed, but it may be derived from the hydroliquefaction step (e.g. a hydrocarbon fraction, such as a deasphalted oil or a light product fraction such as distillate fraction 180-360 °C). Such a recirculated co-feed is not to be considered as "*fresh feed*". When employing the hydroprocessing step, at least a portion of the hydroprocessed material (such as hydroprocessed bioasphaltene portion and/or hydroprocessed liquefaction effluent) may be employed as a (recirculated) co-feed as well.

Alternatively or in addition, a liquid co-feed may be a fossil co-feed, such as fossil hydrocarbons, a bio-based oil/fat, or bio-oils other than recirculated product fraction (all of which are regarded as part of the "*fresh feed*").

The liquid co-feed may not necessarily contain a hydrogen donor or may contain a hydrogen donor.

The liquid co-feed preferably has a lower asphaltenes content than the liquefaction effluent. More preferably, the liquid co-feed is essentially free of bioasphaltenes. In this respect, essentially free of bioasphaltenes means a bioasphaltenes content of 1.0 wt.-% or less, preferably 0.5 wt.-% or less, 0.2 wt.-% or less, or 0.1 wt.-% or less.

The content of the (liquid) co-feed in the total feed (excluding catalyst) of the hydroliquefaction step is preferably in the range of 0 to 95 wt.-%, more preferably in the range of 40 wt.-% to 90 wt.-%, in the range of 50 wt.-% to 85 wt.-% or in the range of 60 wt.-% to 80 wt.-%.

In general, the (total) co-feed of the hydroliquefaction step may be at least one selected from a renewable liquid medium (fresh feed), fossil based medium (fresh feed), the bioasphaltene portion (recirculation feed), and a recirculated material other than the bioasphaltene portion. For example, the co-feed may be a fresh feed, a recirculation feed or a combination of both. In particular, the co-feed may comprise at least a blend of bioasphaltene portion with at least one of renewable liquid medium and a fossil based medium.

When the conversion step comprises the recirculation step, the content of bioasphaltenes in the recirculated bioasphaltene portion is preferably at least 1.05 times the content of bioasphaltenes in the liquefaction effluent, more preferably at least 1.10 times, at least 1.20 times, such as in the range of from 1.05 times to 50.0 times, 1.10 times to 40.0 time, or 1.20 times to 30.0 times. In this respect, the content is determined in the following way: "1.05 times" means  $[\text{wt.-% content of bioasphaltenes in the recirculated bioasphaltene portion}] / [\text{wt.-% content of bioasphaltenes in the liquefaction effluent}] = 1.05$ .

When the conversion step comprises the hydroprocessing step, the content (wt.-% relative to all liquid components) of bioasphaltenes in the bioasphaltene portion subjected to hydroprocessing is preferably at least 1.05 times the content (wt.-% relative to all liquid components) of bioasphaltenes in the liquefaction effluent, more preferably at least 1.10 times, at least 1.20 times, such as in the range

of from 1.05 times to 50.0 times, 1.10 times to 40.0 time, or 1.20 times to 30.0 times. In this respect, the content is determined in the following way: "1.05 times" means [wt.-% content of bioasphaltenes in the bioasphaltene portion subjected to hydro-processing] / [wt.-% content of bioasphaltenes in the liquefaction effluent] = 1.05.

5 In this respect, all (liquid) material that is not (directly) recirculated to the hydroliquefaction step may be subjected to the hydroprocessing step. It is also possible that only a portion (part) of the (liquid) material that is not (directly) recirculated to the hydroliquefaction step may be subjected to the hydroprocessing step. In this respect, "directly" recirculating refers to material which is not sub-  
10 jected to hydroprocessing before (optionally) being recirculated.

In one aspect of the conversion step comprising the hydroprocessing step the bioasphaltene portion is co-processed with another feed such as a renewable based feed and/or fossil-based feed, such that the content of the bioasphaltene portion in the total liquid feed of the hydroprocessing step is preferably at least 5.0  
15 wt.-%, more preferably in the range of from 5.0 wt.-% to 100.0 wt.-%.

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.

20

## 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.

25

### Example 1

Conversion of bioasphaltenes was studied in a semi-batch conversion test runs with non-supported slurry-type sulphided NiMo catalyst (about 4 wt.-% relative to total feed) under catalytic hydroliquefaction conditions. Test run conditions were temperature 380 °C and pressure 14 MPa, and a reaction time of 2 hours. The feed-  
30 stock in the test run was derived from a sawdust liquefaction experiment wherein 20 wt.-% of sawdust was liquefied in a fossil co-feed, using slurry type sulphided NiMo catalyst, 380 °C and 14 MPa H<sub>2</sub> pressure.

Content of bioasphaltenes was analysed from filtered hydroliquefaction effluent by measuring the n-heptane insoluble compounds in accordance with the

method recited above. The same n-heptane insoluble amount was measured from the filtered hydroprocessed product. Showing significantly lower amount as can be seen from Table 1. The result thus shows that bioasphaltenes can be converted under sawdust hydroliquefaction conditions with the same slurry catalyst as used in liquefaction. In addition, the catalyst and possible other solid material was filtered from the liquid product and washed with n-heptane and THF. The mass of the dried material corresponded to the amount of catalyst used in the experiment indicating that bioasphaltenes were converted to lower boiling compounds and not to e.g. coke.

The bioasphaltene conversion was 95% and oxygen removal 52%.

Table 1.

| Property                  | Feedstock | Filtered hydroprocessed product |
|---------------------------|-----------|---------------------------------|
| n-heptane insoluble wt.-% | 6.2%      | 0.3%                            |
| Oxygen content, wt.-%     | 1.6%      | 0.77%                           |

The hydroliquefaction effluent and the hydroprocessed product were furthermore analysed by SIMdist analysis (GC-based). The results (cf. FIG. 2) indicate similar mass fractions according to the boiling point for the test hydroliquefaction effluent and liquid products. This indicates that during the process of hydrotreating of the bioasphaltenes under hydroliquefaction conditions (i.e. under recirculation conditions), there is virtually no cracking of the product although asphaltenes are converted. In other words, valuable products of the feedstock are also recovered in recirculated product.

Example 2

Hydroprocessing was repeated under the conditions of Example 1, except for employing supported sulphided NiMo catalyst at 420 °C and 15.5 MPa (i.e. not corresponding to preferable hydroliquefaction conditions). The evaluation was carried out in the same manner as for Example 1 (cf. Table 2 and 3, and FIG. 3). As can be seen from the below result (cf. Table 2), n-heptane insoluble content was zero in the product. Solid hydroprocessing catalyst was filtered out from the product before the analysis. The resulting solids from the filtration (retentate without

catalyst) were mostly n-heptane soluble and minor part was THF soluble such that the bioasphaltene conversion was 95%. The oxygen removal was 88%.

Table 2.

| Property                           | Hydroliquefaction<br>effluent | Filtered hydroprocessed product |
|------------------------------------|-------------------------------|---------------------------------|
| Density at 60 °C kg/m <sup>3</sup> | 869.22                        | 857.9                           |
| n-heptane insoluble wt.-<br>%      | 6.2%                          | 0%                              |
| oxygen, wt.-%                      | 1.6%                          | 0.2%                            |

5                      Table 3 shows the contents (relative to filtered liquid product) of frac-  
tions with boiling point in the range of 0-180 °C, 180-360 °C, 360-480 °C and with  
boiling point higher than 480 °C. After the hydroprocessing, the mass fraction (con-  
tent) of compounds between 180-360 °C increased by 30 wt.-% and mass fraction  
of the heaviest fraction (>480 °C boiling point) decreased by 68%. The oxygen con-  
10 tent of the feedstock was reduced by 87% in the hydroprocessing.

Table 3.

|                    | Hydroliquefaction<br>effluent, wt.-% | Filtered hydroprocessed product wt.-% |
|--------------------|--------------------------------------|---------------------------------------|
| IBP-180°C fraction | 4%                                   | 11%                                   |
| 180-360°C fraction | 47%                                  | 60%                                   |
| 360-480°C fraction | 27%                                  | 22%                                   |
| >480°C fraction    | 22%                                  | 7%                                    |

## CLAIMS

1. A method of processing liquefied biomass, the method comprising the steps of
- providing a liquefaction effluent by liquefying biomass in the presence  
5 of a hydrogen source and a slurry-type catalyst and at elevated temperatures (hydroliquefaction step), wherein the liquefaction effluent comprises oil product, bioasphaltenes and solids, and
- converting at least part of the bioasphaltenes into components of lower boiling points (conversion step), wherein the hydroliquefaction step and the conversion step are operating in continuous mode,  
10 wherein the hydroliquefaction step is carried out with slurry-type sulphided catalyst, at temperature of 350 to 390 °C, and at pressure in the range of 7 to 16 MPa, preferably 8 to 14 MPa,
- wherein the conversion step comprises recirculating at least a portion  
15 of the liquefaction effluent comprising bioasphaltenes (bioasphaltene portion) to the hydroliquefaction step (recirculation step) and/or subjecting at least a portion of the liquefaction effluent comprising bioasphaltenes (bioasphaltene portion) to hydroprocessing (hydroprocessing step).
2. The method according to claim 1, wherein the hydroliquefaction step  
20 is carried out with slurry-type sulphided catalyst of NiMo and/or CoMo and/or Mo.
3. The method according to claim 1 or 2, wherein the conversion step comprises both the recirculation step and the hydroprocessing step.
4. The method according to any one of the preceding claims, wherein  
25 the at least a portion of the liquefaction effluent comprising bioasphaltenes (bioasphaltene portion) is obtained by means of a separation step, wherein the separation step comprises separating the liquefaction effluent into at least one bioasphaltene portion, and optionally further into an oil product portion, such that the bioasphaltene portion comprises at least bioasphaltenes and the oil product portion comprises predominantly liquid hydrocarbons (separation step).
5. The method according to any one of the preceding claims, wherein  
30 the method further comprises a treatment step, wherein the treatment step is solvent deasphalting and/or distilling and the treatment step is performed on at least part of the liquefaction effluent.
6. The method according to any one of preceding claims, wherein the  
35 treatment step is a combination of solvent deasphalting and distilling, wherein distilling is performed either before or after solvent deasphalting.

7. The method according to claim 5 or 6, wherein the treatment step is performed by distilling (distillation step), wherein distilling comprises recovering at least one distillate fraction and a bottom fraction, wherein the bottoms fraction is the bioasphaltene portion and has 5% recovered at 360°C or more, or 5% recovered at 480°C or more.

8. The method according to any one of the preceding claims, wherein the hydrogen source is hydrogen gas and/or a hydrogen donor, wherein the hydrogen donor is preferably a hydrogen-containing solvent and/or co-feed.

9. The method according to any one of the preceding claims, wherein the bioasphaltene portion employed in the recirculation step further comprises spent or fresh slurry-type catalyst.

10. The method according to any one of the preceding claims, wherein at least part of the hydroprocessed liquefaction effluent or at least part of the hydroprocessed bioasphaltene portion is recirculated as a co-feed back to the hydroliquefaction step.

11. The method according to any one of the preceding claims, wherein the wt.-% of the bioasphaltene portion as the recirculation feed of the total feed in the hydroliquefaction step is 40.0 to 95.0 wt.-%, preferably 70.0 to 90.0 wt.-%.

12. The method according to any one of the preceding claims, wherein wherein the content of the bioasphaltene portion in the total oil feed of the hydroprocessing step is at least 5.0 wt.-%, preferably in the range of from 5.0 wt.-% to 100.0 wt.-%.

13. The method according to any one of the preceding claims, wherein the hydroprocessing step is a hydrotreatment step and/or a hydrocracking step.

14. The method according to any one of the preceding claims, wherein the hydroprocessing step is performed in at least one hydroprocessing reactor which comprises a fixed bed reactor and/or an ebullated bed reactor.

15. The method according to claim 14, wherein the hydroprocessing reactor comprises a supported hydroprocessing catalyst.

16. The method according to any one of the preceding claims, wherein a co-feed in the hydroliquefaction step is a renewable liquid medium and/or a fossil based medium and/or hydroprocessed bioasphaltene portion.

17. The method according to any one of the preceding claims, wherein the content of a co-feed in the total feed of the hydroliquefaction step is in the range of 0 to 95 wt.-%, preferably 40 wt.-% to 90 wt.-%, 50 wt.-% to 85 wt.-% or 60 wt.-% to 80 wt.-%.

18. The method according to any one of the preceding claims, wherein the content of bioasphaltenes in the bioasphaltene portion that is untreated is 4-20 wt%, preferably 6-10wt%.

19. The method according to any one of the preceding claims, wherein  
5 the content of bioasphaltenes in the bioasphaltene portion that has been treated by deasphalting is 50-100wt%, preferably 80-98wt%.

20. The method according to any one of the preceding claims, wherein the content of bioasphaltenes in the bioasphaltene portion that has been treated by distillation, and of the 5% recovered at 360°C distillate bottom is 6-30wt%, preferably 10-20wt%; and of the 5% recovered at 480°C distillate bottom is 30-100wt%,  
10 preferably 60-80wt%.

21. A bioasphaltene product obtained by a method comprising the steps of

15 providing a liquefaction effluent by liquefying biomass in the presence of a hydrogen source and with slurry-type sulphided catalyst, at temperature of 350 to 390 °C, and at pressure of 7 to 16 MPa, more preferably 8 to 14 MPa, wherein the liquefaction effluent comprises oil product, bioasphaltenes and solids,

obtaining the at least a portion of the liquefaction effluent comprising bioasphaltenes (bioasphaltene portion) by means of a separation step, wherein the  
20 separation step comprises separating the liquefaction effluent into at least one bioasphaltene portion, and optionally further into an oil product portion, such that the bioasphaltene portion comprises at least bioasphaltenes and the oil product portion comprises predominantly liquid hydrocarbons (separation step),

wherein bioasphaltenes are characterised by being insoluble in n-heptane at room temperature and soluble in THF (at room temperature), and have a  
25 molecular mass in the range of 150 to 1500 g/mol, more preferably 150-1000 g/mol, or 150-600 g/mol, most preferably 150-300 g/mol, and are aromatic in nature with a double bond equivalent number in the range of 4 to 30 as measured by HRMS APCI NEG (high resolution mass spectroscopy using negative mode atmospheric pressure chemical ionisation).  
30

22. The bioasphaltene product of claim 21, wherein the slurry-type sulphided catalyst is a sulphided catalyst of NiMo and/or CoMo and/or Mo.  
23. The bioasphaltene product of claim 21 or 22, wherein the oxygen content (wt%) in the bioasphaltenes is in the range of about 0.8 to about 10 wt%, about 0.8 to about 7  
35 wt% or about 1 to about 3 wt%.