

HYDROLIQUEFACTION OF CARBONACEOUS FEEDSTOCK

FIELD OF THE INVENTION

The present invention relates to hydroliquefaction of carbonaceous feedstock, in particular biomass feedstock. The present invention relates to a method for the production of hydrocarbon composition, in particular renewable hydrocarbon composition, from a carbonaceous feedstock. Specifically, the present invention relates to catalytic hydroliquefaction of carbonaceous feedstocks, in particular carbonaceous feedstock having high oxygen content, e.g. due to comprising or consisting of, preferably consisting of, biomass feedstock, such as lignocellulosic biomass feedstock.

BACKGROUND OF THE INVENTION

Catalytic hydroliquefaction of carbonaceous feedstock having high oxygen content is both hydrogen intensive and produces substantial amounts of waste water. A significant amount of carbon of the feed remains in partially converted products, such as phenols, ketones and alcohols. Due to high water solubility of such oxygenates, sour water is challenging to purify. Light oxygenates, that have lower boiling point than water, require specific sour water stripper off-gas treatment and contaminate the recovered adsorbent solution thus limiting its use. Heavy oxygenates, on the other hand, remain in the water effluent and increase chemical oxygen demand (COD).

BRIEF DESCRIPTION OF THE INVENTION

An object of the present invention is thus to provide a method so as to overcome the above problems. The objects of the invention are achieved by a method which is characterized by what is stated in the independent claims. The preferred embodiments of the invention are disclosed in the dependent claims.

The invention is based on the surprising realization that issues caused by both waste water and hydrogen consumption can be solved simultaneously by introducing a conversion unit comprising a combination of a gas-phase

deoxygenation of light oxygenates and shifting carbon monoxide to carbon dioxide and hydrogen between high pressure hot separator and high pressure condenser. The hydrogen recovery efficiency may be further maximized by its optimized recovery and recirculation.

5 BRIEF DESCRIPTION OF THE DRAWINGS

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

Figure 1 illustrates the 1st exemplary process flow of the present method;

Figure 2 illustrates the 2nd exemplary process flow of the present method;

10 Figure 3 illustrates the 3rd exemplary process flow of the present method;

Figure 4 illustrates the 4th exemplary process flow of the present method.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method for the production of liquid hydrocarbon composition, comprising

- 15 i) providing carbonaceous feedstock (a);
- ii) subjecting the carbonaceous feedstock (a) to catalytic hydroliquefaction in the presence of hydrogen to obtain a product mixture comprising liquid hydrocarbons and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;
- 20 iii) separating the liquid hydrocarbons and the off-gas to obtain a first liquid fraction (b-1) comprising liquid hydrocarbons and a first gaseous fraction (c-1) comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;
- iv) converting in gas phase at least part of the light oxygenates comprised in the first
- 25 gaseous fraction (c-1) to deoxygenated hydrocarbons, carbon monoxide (CO), carbon dioxide (CO₂), and water vapor (H₂O), and

- v) converting in the presence of water steam at least part of the carbon monoxide (CO) comprised in the first gaseous fraction (c-1) and/or produced in step iv) to carbon dioxide (CO₂) and hydrogen (H₂) by water gas shift reaction,
- to obtain a CO₂ and H₂ enriched first gaseous fraction (c-1e), wherein steps iv) and
- 5 v) are preferably accomplished in the same reactor step-up, more preferably in a fixed bed reactor; and
- vi) separating non-condensables from the CO₂ and H₂ enriched first gaseous fraction (C-1e) to obtain a second gaseous fraction (c-2) comprising CO, CO₂, H₂, and non-condensable hydrocarbons and a second liquid fraction (b-2) comprising
- 10 condensable hydrocarbons;
- vii) recovering at least part, such as 50 to 80 %, preferably essentially all, of H₂ from the second gaseous fraction (c-2) and recirculating at least part, preferably all, of the recovered H₂ to step ii);
- viii) recovering the first liquid fraction (b-1) and/or the second liquid fraction (b-2) to
- 15 provide a liquid hydrocarbon composition.

In the present description, weight percentages (wt%) are calculated based on the total weight of the material in question (typically a blend or a mixture). Any amounts defined as ppm (parts per million), are based on weight (i.e. mg/kg). In the present description, volume percentages (v/v%) are calculated based on the total volume of

20 the material in question (typically a gaseous mixture). "Essentially all" refers to substantially or most of the referred amount and may include, for example, 100%, at least 95%, at least 90%, at least 80%, at least 70%, and at least 60%.

Feedstock, Step i)

The term "carbonaceous feedstock" refers to carbonaceous material which is

25 intended to be converted by hydroprocessing into liquid hydrocarbons, such as renewable hydrocarbons, or other valuable hydrocarbon products, such as valuable renewable hydrocarbon products, including fuels and fuel components, such as renewable fuels and renewable fuel components, but which need to be liquefied to allow further valorization of the material.

The term “renewable” in the context of renewable feedstock or renewable hydrocarbons or renewable fuel or fuel component refers to one or more organic compounds derived from any renewable source (contrary to source of fossil origin). Thus renewable compounds or compositions are obtainable, obtained, derivable,
5 derived, or originating from plants, animals and/or microbes, including compounds or compositions obtainable, obtained, derivable, derived, or originating from fungi and/or algae, in full or in part, whether these compounds or compositions are in their virgin, recycled or reclaimed form.

The ^{14}C -isotope content can be used as evidence of the renewable or biological
10 origin of a feedstock or product. Carbon atoms of renewable material comprise a higher number of unstable radiocarbon (^{14}C) atoms compared to carbon atoms of fossil origin. Therefore, it is possible to distinguish between carbon compounds derived from biological sources, and carbon compounds derived from fossil sources by analyzing the ratio of ^{12}C and ^{14}C isotopes. Thus, a particular ratio of said
15 isotopes can be used to identify and quantify renewable carbon compounds and differentiate those from non-renewable i.e. fossil carbon compounds. The isotope ratio does not change in the course of chemical reactions. Example of a suitable method for analyzing the content of carbon from biological sources is ASTM D6866 (2020). An example of how to apply ASTM D6866 to determine the renewable
20 content in fuels is provided in the article of Dijs et al., Radiocarbon, 48(3), 2006, pp 315-323. For the purpose of the present invention, a renewable material, such as a feedstock or product, is considered to be of renewable origin if it contains 90 % or more modern carbon (pMC), such as about 100 % modern carbon, as measured using ASTM D6866.

25 Terms “fuel” and “fuel components” refer to fuels usable as such and as fuel components, respectively, which fulfill the requirements of standards for the respective use. For example, within the EU, the standard for gasoline is EN228:2017, for paraffinic diesel EN15940:2023, and for aviation turbine fuel containing synthesized hydrocarbons D7566-22.

30 The carbonaceous feedstock contemplated herein typically comprises high amounts of carbon and oxygen but relatively low amounts of hydrogen in form of a solid

material comprising said elements bound to various compounds. Carbon, oxygen and hydrogen may be present in the carbonaceous feedstock in various chemical forms in varying oxygen, carbon and/or hydrogen containing compounds, such as hydrocarbons, oxygen containing hydrocarbons, and/or polymers. For being able to
5 produce renewable hydrocarbons from the carbonaceous feedstock, it is therefore necessary to liquify the material and process it to lower the oxygen content and increase the hydrogen:carbon ratio. The feedstock may further comprise other heteroatoms, such as sulfur and nitrogen, and/or various inorganic compounds.

As used herein, "hydrocarbons" refer to compounds consisting of carbon and
10 hydrogen. Examples of hydrocarbons include paraffins, including n-paraffins and i-paraffins, naphthenes, aromatics, and olefins (alkenes). "Oxygen containing hydrocarbons" and "oxygenates" refer herein to hydrocarbons comprising covalently bound oxygen and are used interchangeably.

The carbonaceous feedstock contemplated herein typically comprises at least 10
15 wt%, preferably at least 20 wt%, more preferably at least 30 wt%, oxygen on a dry basis (i.e. excluding water), measured as elemental oxygen. The carbonaceous feedstock may comprise up to 45 wt%, such as from 35 to 45 wt% oxygen, measured as elemental oxygen.

As used herein the oxygen content "on a dry basis" means that the oxygen content
20 is determined under the assumption that all of the water is removed before determining the content. The oxygen content on a dry basis can be determined by drying the carbonaceous feedstock and determining the oxygen content (e.g. by elemental analysis). Alternatively, the oxygen content on a dry basis can be determined from a wet carbonaceous feedstock as follows:

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$$\text{oxygen content (dry basis)} = 100 \text{ percent} * \frac{\{(\text{total oxygen content of the wet carbonaceous feedstock, e.g. by elemental analysis}) - (\text{oxygen contained in the wet carbonaceous feedstock in the form of water})\}}{\{(\text{mass of wet carbonaceous feedstock}) - (\text{mass of water in the wet carbonaceous feedstock})\}}$$

The content (mass) of water contained in the wet carbonaceous feedstock can be determined by any suitable means (e.g. Karl-Fisher titration according to ASTM D6304, or distillation according to ASTM D95).

Further the carbonaceous feedstock typically comprises from 45 to 55 wt%, carbon, and less than 10 wt%, such as from 5 to 8 wt%, hydrogen, measured as elemental carbon and hydrogen on a dry basis, respectively.

Further, it is preferred that the total content of hydrogen (H) and carbon (C) in the carbonaceous feedstock, on a dry basis, is at least 50 wt%, preferably at least 55 wt%, more preferably at least 60 wt%. The contents of hydrogen and carbon in the carbonaceous feedstock can be determined by elemental analysis using e.g. ASTM D5291.

The process contemplated herein is particularly suitable for carbonaceous feedstock comprising or consisting of, preferably consisting of, biomass feedstock, such as lignocellulosic biomass feedstock.

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.

Prior to being fed to the hydroliquefaction step ii) the carbonaceous feedstock, such as the biomass feedstock, may be e.g. 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.

Step ii): Catalytic Hydroliquefaction of the Feedstock

Hydroliquefaction is a thermal conversion process to convert biomass and other macromolecules into biofuels under moderate temperature and high pressure. Hydroliquefaction is an efficient conversion process for the production of bio-derived fuels and chemicals.

In step ii) the carbonaceous feedstock (a) is subjected to catalytic hydroliquefaction in the presence of hydrogen to obtain a product mixture comprising liquid hydrocarbons and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates.

5 Without bounding to theory, under the catalytic hydroliquefaction in step ii) the carbonaceous feedstock, preferably biomass feedstock, more preferably lignocellulosic feedstock, undergoes multiple reactions, including, but not limited to, any one or more of deoxygenation, such as decarbonylation, decarboxylation, hydrodeoxygenation (HDO), hydrodesulfurization (HDS), hydrodenitrogenation

10 (HDN), hydrodemetallization (HDM), hydrodearomatization (HDA), hydrogenation, and hydrocracking, cleaving e.g. CO, CO₂, H₂, H₂S, NH₃, H₂O, and lighter oxygenates and hydrocarbons from the various compounds and polymers composing the carbonaceous feedstock to render both gaseous and liquid hydrocarbons. The term "oxygenates" as used herein refers to oxygen containing

15 hydrocarbons. The term "light oxygenates" refers to oxygenates retained in gaseous phase under the prevailing conditions.

The term "catalytic hydroliquefaction" refers to conversion of carbonaceous feedstock into liquid hydrocarbons suitable for use as drop-in fuels, fuel components and/or other valuable hydrocarbon products either directly and/or after further

20 valorization.

Oxygen present in the carbonaceous feedstock is typically rejected as CO₂, CO, H₂O, and light oxygenates at the end of the catalytic hydroliquefaction and comprised in the produced off-gas when it is separated from the liquid hydrocarbons produced in the hydroliquifaction step ii). Advantageously, the produced liquid

25 hydrocarbons comprise less than 10 wt% oxygen, such as 1 to 5 wt% of the total weight of the liquid hydrocarbons, when measured as elemental oxygen.

The catalytic hydroliquefaction in step ii) is typically carried out at a temperature 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

30 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 and increase of residence time.

The catalytic hydroliquefaction in step ii) is typically carried out at a pressure of at least 6 MPa, such as 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 residence time in the catalytic hydroliquefaction step 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 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 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 from 5 to 26 MPa, preferably at least 7 MPa, such as from 6 to 14 MPa, more preferably at least 7 MPa, such as from 7 to 12 MPa, given as gauge pressure.

The catalytic hydroliquefaction step is performed in the presence of at least one catalyst. Suitable catalysts for the catalytic hydroliquefaction are known hydroconversion catalysts. Sulfided catalysts, such as sulfided heterogeneous metal catalysts, are preferred. Examples of suitable sulfided heterogeneous metal catalysts include, but are not limited to, sulfided NiMo, sulfided CoMo, and sulfided 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. 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, the catalyst can be present in step ii) in an amount from 0.005 to 5 wt%, preferably from 0.01 to 3 wt%, more preferably from 0.1 to 1 wt%.

The catalytic hydroliquefaction in step ii) may be performed in any suitable reactor wherein the indicated conditions may be achieved. Examples of suitable reactors include mixed reactors and/or pipe reactors. Further, the catalytic hydroliquefaction in step ii) is advantageously performed in continuous mode. Examples of suitable
5 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).

Catalyst may be embedded for example in ebullated bed and/or in bubbling bed.

- 10 The catalytic hydroliquefaction step ii) 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 an embodiment the catalytic hydro liquefaction step ii) comprises

- 15 ii-1) subjecting the carbonaceous feedstock (a) to catalytic hydroliquefaction in the presence of hydrogen to obtain an intermediate product mixture comprising partially treated carbonaceous material, deoxygenated liquid hydrocarbons, and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;

- 20 ii-2) optionally separating and removing at least part of the non-hydrogen gases comprised in the off-gas formed in step ii-1 from the intermediate product mixture to obtain and a hydrogen enriched off-gas fraction (c-h) and an off-gas fraction (c-o) comprising carbon monoxide (CO), carbon dioxide (CO₂), light (C₁-C₃) hydrocarbons, and light oxygenates; and

- 25 ii-3) subjecting the intermediate product mixture to catalytic hydroliquefaction in the presence of hydrogen and optionally hydrogen enriched off-gas resulting from step ii-2) to obtain a product mixture comprising liquid hydrocarbons and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates.

It is appreciated that the conditions described above in general for the catalytic hydroliquefaction step ii) apply to all hydroliquefaction stages, such as steps ii-1) and ii-3), comprised in the catalytic hydroliquefaction sequence of step ii).

Typically the consecutive catalytic hydroliquefaction stages are performed at
5 essentially the same pressure, i.e. each stage typically carried out at a pressure of
at least 6 MPa, such as 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, while the pressure of the first catalytic hydroliquefaction stage
determines the pressure of the following consecutive catalytic hydroliquefaction
10 stages. As an example, the pressure of steps ii-1) and ii-3) is the same. A skilled
person will be competent to select a pressure for each consecutive stage within
these ranges keeping in mind that essentially complete deoxygenation after the
catalytic hydroliquefaction stages is desired.

Further, the consecutive catalytic hydroliquefaction stages are typically carried out
15 at a temperature 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. As
an example, the temperature of step ii-1) may be 10 to 60 °C lower than the
20 temperature of step ii-3).

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 ii) to fit the intended purpose, appreciating that at
higher temperatures and pressures a shorter residence time is typically sufficient.

25 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 ii) and may
be the same or different.

Each consecutive catalytic hydroliquefaction step is performed in the presence of at
30 least one catalyst as described above in general for the catalytic hydroliquefaction

step ii). The catalysts for the consecutive hydroliquefaction stages may be the same or different.

When the catalytic hydroliquefaction step ii) is performed in two or more consecutive stages, at least part, preferably essentially all, of the non-hydrogen gases comprised in the off-gas formed in the preceding catalytic hydroliquefaction stage may be separated and removed from the intermediate product mixture to obtain an off-gas fraction (c-o) comprising carbon monoxide (CO), carbon dioxide (CO₂), light (C₁-C₃) hydrocarbons, and light oxygenates while the hydrogen enriched off-gas fraction is advantageously returned to the latter catalytic hydroliquefaction stage.

10 In an embodiment the catalytic hydroliquefaction step ii) comprises

ii-1) subjecting the carbonaceous feedstock (a) to catalytic hydroliquefaction in the presence of hydrogen to obtain an intermediate product mixture comprising partially treated carbonaceous material, deoxygenated liquid hydrocarbons, and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;

ii-2) separating and removing at least part of the non-hydrogen gases comprised in the off-gas formed in step ii-1) from the intermediate product mixture to obtain a hydrogen enriched off-gas fraction (c-h) and an off-gas fraction (c-o) comprising carbon monoxide (CO), carbon dioxide (CO₂), light (C₁-C₃) hydrocarbons, and light oxygenates; and

ii-3) subjecting the intermediate product mixture to catalytic hydroliquefaction in the presence of hydrogen and optionally the hydrogen enriched off-gas fraction (c-h) resulting from step ii-2) to obtain a product mixture comprising liquid hydrocarbons and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates.

Separation and removal of the non-hydrogen gases comprised in the off-gas may be performed by any suitable method known by the skilled person for the indicated purpose. The separation and removal are advantageously performed at the same temperature and pressure as the preceding catalytic hydroliquefaction stage.

Preferably the separation and removal of the non-hydrogen gases comprised in the off-gas is performed such that only non-hydrogen gases are removed. This increases the hydrogen purity in the latter hydroliquefaction stage as at least part of the non-hydrogen gases is removed. This enables lower total pressure and/or smaller reactor volume for the latter catalytic hydroliquefaction stage.

Advantageously consecutive catalytic hydroliquefaction stages are performed directly after each other, i.e. without removal of non-hydrogen off-gases in between. This avoids the risk of fouling and/or plugging of the separation vessel.

After the hydroliquefaction step is completed the produced product mixture comprising liquid hydrocarbons, and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), light (C₁-C₃) hydrocarbons, and light oxygenates is subjected separation of the liquid hydrocarbons and the off-gas.

Step iii): Separation of the liquid hydrocarbons and the off-gas

In step iii) the liquid hydrocarbons and the off-gas are separated to obtain a first liquid fraction comprising liquid hydrocarbons (b-1) and a first gaseous fraction (c-1) comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates.

The separation is typically achieved at high temperature and high pressure. It is preferred that the conditions of the preceding hydroliquefaction step ii) are essentially maintained in the separation step iii).

Thus, typically the separation step iii) is carried out at a pressure of at least 6 MPa, such as 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 for the separation step keeping in mind that preferably the last preceding catalytic hydroliquefaction stage determines the pressure of the following separation step.

Further, typically the separation step iii) is carried out at a temperature 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 keeping in mind that preferably the

last preceding catalytic hydroliquefaction stage determines the temperature of the following separation step.

The separation in step ii) may be accomplished by any unit operation suitable for separation of a gaseous phase and a liquid phase and wherein the indicated
5 conditions may be achieved, such as by a separator or by distillation, preferably by a separator.

After the separation the first gaseous fraction is subjected to conversion of light oxygenates to deoxygenated hydrocarbons.

The first liquid fraction (b-1) comprising liquid hydrocarbons may then be recovered,
10 optionally together with the later obtained second liquid fraction (b-2) as a liquid hydrocarbon composition which then can be utilized as such and/or after further valorization as fuels, fuel components, and/or other valuable hydrocarbon products, in particular renewable fuels, renewable fuel components, and/or other valuable renewable hydrocarbon products.

15 **Step iv) and Step v): Conversion of light oxygenates to deoxygenated hydrocarbons, and water-gas shift (WGS)**

In step iv) at least part of the light oxygenates comprised in the first gaseous fraction (c-1) in gas phase are deoxygenated to hydrocarbons, carbon monoxide (CO), carbon dioxide (CO₂), and water vapor (H₂O). Conversion of light oxygenates is
20 desired as significant amount of carbon of the carbonaceous feedstock remains in partially converted products of the hydroliquefaction step i) and are comprised in the first gaseous fraction (c-1) as e.g. light oxygenates. Further, light oxygenates that have lower boiling point than water, require specific sour water stripper off-gas treatment and/or contaminate the recovered liquid CO₂ absorbent, such as aqueous
25 ammonia solution or cryogenic methanol, thus limiting its use. Condensable light oxygenates having boiling point higher than water, on the other hand, remain in the water effluent and increase chemical oxygen demand (COD).

The term "light oxygenates" as used herein refers to oxygen containing hydrocarbons, in particular oxygen containing C₁-C₃ hydrocarbons, comprised in the

carbonaceous feedstock and/or resulting from the hydroliquefaction step ii) and not separated to liquid hydrocarbons under the conditions of the separation step iii).

Advantageously 80 to 98 % of the light oxygenates present in the first gaseous fraction is converted to deoxygenated hydrocarbons, carbon monoxide (CO),
5 carbon dioxide (CO₂), and water vapor (H₂O) by the end of the conversion step.

Further in step v) at least part, preferably at least 50 %, such as 80 to 98%, of the carbon monoxide (CO) comprised in the first gaseous fraction (c-1) and/or produced in step iv) is converted to carbon dioxide (CO₂) and hydrogen (H₂). The conversion is typically achieved in the presence of water vapor (H₂O) by water-gas shift (WGS)
10 reaction. Conversion of CO to CO₂ is desired as CO₂ can be more easily removed from the hydrogen recycle loop and further, while converting CO to CO₂ with a water gas shift reaction, hydrogen can be generated from water vapor comprised in the off-gas and/or brought into the WGS step and thus reduce the need for external hydrogen.

15 As a result of conversion steps iv) and v) a CO₂ and H₂ enriched first gaseous fraction (c-1e) comprising deoxygenated hydrocarbons, CO₂, H₂, and water vapor (H₂O) is obtained. The CO₂ and H₂ enriched first gaseous fraction may further comprise hydrocarbons and/or other gaseous impurities resulting from steps ii) and iii) and not necessarily affected by conversion steps iv) and v). The CO₂ and H₂
20 enriched first gaseous fraction (c-1e) typically comprises 70 to 95 mol% H₂. The generated hydrogen reduces the need for external hydrogen. The CO₂ and H₂ enriched first gaseous fraction (c-1e) advantageously comprises less than 15 mol%, such as 1 to 5 mol%, carbon monoxide of the total weight of the CO₂ and H₂ enriched first gaseous fraction (c-1e). The CO₂ and H₂ enriched first gaseous fraction (c-1e)
25 advantageously comprises less than 10 mol%, such as 0.1 to 2 mol%, light oxygenates of the total weight of the CO₂ and H₂ enriched first gaseous fraction (c-1e). The reduced amount of light oxygenates reduces dissolved organic compounds in the waste water, which improves the hydrocarbon yield of the process as less carbon is lost to waste water and facilitates waste water purification. Benefits in
30 waste water purification are significant as the waste water stream is large compared to the hydrocarbon product stream. The present invention thus improves potential

for water re-use and reduced fresh water consumption. The reduced amount of light oxygenates further reduces emulsion formation in cold high pressure separator and sour water systems and simplifies the gas processing as the light oxygenates are not absorbed in sour water contaminating adsorbents that are used in the gas effluent processing. The CO₂ and H₂ enriched first gaseous fraction (c-1e) is advantageously suitable for utilization as steam methane reformer (SMR) feedstock.

The conversion steps iv) and v) may be accomplished concurrently and/or consecutively. The conversion steps iv) and v) are preferably accomplished in the same reactor step-up, such as in consecutive catalyst beds.

The conversion in steps iv) and v) may be performed in any suitable reactor(s) wherein the indicated conditions may be achieved. A fixed bed reactor is preferred for combined performance of steps iv) and v) as the conversion of the oxygenates has sufficient residence time distribution while setting the gas composition to equilibrium.

The conversions in steps vi) and v) are typically carried out at a temperature from 200 to 500 °C, such as from 250 to 400 °C, preferably from 300 to 350 °C, more preferably from 310 to 320 °C. Typically the conversions in step vi) and v) are performed at essentially the same temperature or 3 to 10 °C higher temperature as the hydroliquefaction step ii). A skilled person will be competent to select a temperature within these ranges keeping in mind that equilibrium is such that reaction is more on H₂+CO₂ side at low temperatures. Due to the exothermic nature of the reactions a two-stage or multi-stage operation with cooling can be beneficial. The reactor temperature can be optimized with e.g. heat integration coolers and it is possible to have a cooler between reactor beds to push the WGS equilibrium further if considered to make economic sense or necessary due to downstream steam methane reformer feed specification.

The conversions in steps iv) and v) are typically carried out at a pressure from 0.5 to 30 MPa, such as from 0.5 to 15 MPa or 0.5 to 10 MPa, preferably from 2 to 8 MPa, more preferably from 4 to 8 MPa, given as gauge pressure. A skilled person will be competent to select a pressure within these ranges keeping in mind that

preferably the pressure of the separation step iii) is suitably maintained in the conversion steps iv) and v).

- The residence time in the conversion step may be from a fraction of a second up to a minute 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. The gas hourly space velocity (GHSV) in conversion steps iv) and v) is typically from 1500 to 15000 h⁻¹, preferably from 2000 to 10000, more preferably from 3000 to 5000 h⁻¹.
- 10 The conversions in steps iv) and v) are performed in the presence of at least one catalyst. The first gaseous fraction (c-1) typically contains hydrogen sulfide. Because of this, so-called clean shift catalysts are preferably not used. Suitable catalysts for the conversion steps iv) and v) thus include sulfided catalysts, such as sulfided heterogeneous metal catalysts. Examples of suitable sulfided heterogeneous metal catalysts include, but are not limited to, sulfided NiMo and sulfided CoMo. The catalyst can be unsupported and/or supported. Further suitable catalysts, in particular for cases where minor amounts of hydrogen sulfide is present, include mixed metal oxide catalysts, such as mixed Fe-Cr-oxide catalysts, such as catalysts containing Fe₂O₃ and Cr₂O₃. Examples of suitable supports include silica and/or alumina. Preferably the catalyst is supported. A person skilled in the art will be competent to adjust the amount of the catalyst present in the conversion step to fit the intended purpose. Suitably, the catalyst can be present in step vi) in an amount from 0.005 to 5 wt%, preferably from 0.01 to 3 wt%, more preferably from 0.1 to 1 %.
- 25 Typically, the first gaseous fraction (c-1) has a sufficient amount of hydrogen to hydrogenate light oxygenates and a sufficient amount of water vapor to drive the WGS reaction. The relative amount of water vapor controls the H₂/CO ratio of the produced CO₂ and H₂ enriched first gaseous fraction via WGS reaction. Preferably the ratio of H₂O to CO in the WGS is at least 2, preferably from 4 to 30, more preferably from 15 to 20. If required the ratio can be controlled by adding water steam to step v).
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After conversions in steps iv) and v) at least part, preferably all, of the CO₂ and H₂ enriched first gaseous fraction (c-1e) produced in said steps is subjected to separation of non-condensables.

Step vi): Separation of non-condensables

- 5 In step vi) non-condensables are separated from the CO₂ and H₂ enriched first gaseous fraction (C-1e) to obtain a second gaseous fraction (c-2) comprising CO, CO₂, H₂, and light (C₁-C₂) hydrocarbons and a second liquid fraction (b-2) comprising condensable hydrocarbons (and H₂O).

10 The separation of non-condensables in step vi) is typically achieved in reduced temperature and at high pressure. It is preferred that the pressure conditions of the preceding steps are essentially maintained in step vi).

Thus, typically the separation step is carried out at a pressure at least 6 MPa, such as 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
15 skilled person will be competent to select a pressure for the separation step within these ranges keeping in mind that preferably the last catalytic hydroliquefaction stage determines the pressure of the separation step.

Thus, typically separation in step vi) is accomplished at a temperature below 100 °C such as from 20 to 100 °C, preferably below 80 °C, such as from 30 to 80 °C, more
20 preferably below 60 °C, such as from 40 to 60 °C. A skilled person will be competent to select a temperature within these ranges.

Condensables separated in the separation step vi) are rendered as a liquid fraction (b-2). The second liquid fraction (b-2) typically comprises phenol, phenol derivatives such as benzene, cyclohexane, toluene, methylcyclohexane, and/or C₃+
25 hydrocarbons. The second liquid fraction (b-2) may then be recovered, optionally together with the earlier obtained first liquid fraction (b-1), as a liquid hydrocarbon composition which then can be utilized as such and/or after further valorization as fuels, fuel components, and/or other valuable hydrocarbon products, in particular renewable fuels, renewable fuel components, and/or other valuable renewable
30 hydrocarbon products.

After step vi) the second gaseous fraction (c-2) is subjected to hydrogen recovery₂.

Step vii): Hydrogen Recovery

In step vii) at least part, such as 50 to 80 %, preferably essentially all, of H₂ comprised in the second gaseous (c-2) fraction is recovered and at least part,
5 preferably all, of the recovered H₂ is recirculated to step ii).

The hydrogen recovery in step vii) may be accomplished in any suitable unit operation or combination of unit operations suitable for (selective) hydrogen recovery from gaseous phase, including, but not limited to, separation by hydrogen membrane diffusion, pressure swing adsorption (PSA), cryogenic hydrogen
10 recovery, hydrocarbon absorption, or any combination thereof. Separation by hydrogen membrane diffusion is preferred. Alternatively or additionally hydrogen recovery may be accomplished by purification of the gas stream by removal of non-hydrogen gases by e.g. absorption scrubber, such as an amine scrubber for H₂S and/or CO₂.

15 The hydrogen recovery in step vii) is typically achieved at near ambient temperature and at high pressure. It is preferred that the pressure conditions of the preceding steps are essentially maintained in step vii) to allow efficient utilization of the hydrogen in the hydrogen recycle loop.

Thus, typically the hydrogen recovery step vii) is carried out at a temperature from
20 20 to 150°C, preferably from 40 to 120 °C, more preferably from 60 to 100 °C, or in case of cryogenic hydrogen recovery at a temperature from -120 to -40 °C. A skilled person will be competent to select a temperature within these ranges.

Further, typically the hydrogen recovery step iv) is carried out at a pressure at least 6 MPa, such as from 6 to 30 Mpa, preferably at least 7 MPa, such as from 7 to 16
25 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 preferably the preceding step determines the pressure of the H₂ recovery step.

After the recovery of at least part of the recovered H₂, preferably all of the recovered
30 H₂, is recirculated to step ii).

Figure 1 illustrates a first exemplary process flow of the present method.

Referring to Figure 1, a carbonaceous feedstock, preferably comprising or consisting of biomass feedstock such as lignocellulosic biomass 1 is subjected to catalytic hydroliquefaction 10 in the presence of hydrogen 91 to obtain a product mixture 11 comprising liquid hydrocarbons, and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), light (C₁-C₃) hydrocarbons, and light oxygenates, as discussed herein for step ii). The product mixture 11 is then subjected to separation 20 of the liquid hydrocarbons and the off-gas to obtain a first liquid fraction 61 comprising liquid hydrocarbons and a first gaseous fraction 21 comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates, as discussed herein for step iii). The first gaseous fraction 21 is then subjected to a conversion step 30 comprising converting in gas phase at least part of the light oxygenates (oxygen containing hydrocarbons) comprised in the first gaseous fraction (c-1) to deoxygenated hydrocarbons, carbon monoxide (CO) and carbon dioxide (CO₂), and water (H₂O), and converting in the presence of water steam at least part of the carbon monoxide (CO) comprised in the first gaseous fraction (c-1) and/or produced in step iv) to carbon dioxide (CO₂) and hydrogen (H₂) by water gas shift reaction to obtain a CO₂ and H₂ enriched first gaseous fraction 22 as discussed herein for step iv) and step v). The CO₂ and H₂ enriched first gaseous fraction 22 is then subjected to separation 40 of non-condensables to obtain a second gaseous fraction 23 comprising CO, CO₂, H₂, and light hydrocarbons and a second liquid fraction 62 comprising condensable deoxygenated hydrocarbons (and H₂O) as discussed herein for step vi). The second gaseous fraction 23 is then subjected to recovery 50 of H₂ 92 and at least part, preferably all, of the recovered H₂ is recirculated 93 back to catalytic hydroliquefaction 10 as part of the inlet hydrogen.

Figure 2 illustrates a second exemplary process flow of the present method.

Referring to Figure 2, a carbonaceous feedstock, preferably comprising or consisting of biomass feedstock such as lignocellulosic biomass 1 is subjected to a first catalytic hydroliquefaction 10a in the presence of hydrogen 91 to obtain an intermediate product mixture 12 comprising partially treated biomass, deoxygenated

liquid hydrocarbons, and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), light (C1-C3) hydrocarbons, and light oxygenates as discussed herein for step ii) and/ or step ii-a). The intermediate product mixture 12 is then subjected to a further catalytic hydroliquefaction step 10b in the presence of hydrogen 91 to obtain a product mixture 11 comprising liquid hydrocarbons, and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), light (C1-C3) hydrocarbons, and light oxygenates, as discussed herein for step ii). The product mixture 11 is then subjected to separation 20 of the liquid hydrocarbons and the off-gas to obtain a first liquid fraction 61 comprising liquid hydrocarbons and a first gaseous fraction 21 comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C1-C3) hydrocarbons, and light oxygenates, as discussed herein for step iii). The first gaseous fraction 21 is then subjected to a conversion step 30 comprising converting in gas phase at least part of the light oxygenates (oxygen containing hydrocarbons) comprised in the first gaseous fraction 21 to deoxygenated hydrocarbons, carbon monoxide (CO) and carbon dioxide (CO₂), and water (H₂O), and converting in the presence of water steam at least part of the carbon monoxide (CO) comprised in the first gaseous fraction and/or produced in step iv) to carbon dioxide (CO₂) and hydrogen (H₂) by water gas shift reaction to obtain a CO₂ and H₂ enriched first gaseous fraction 22 as discussed herein for step iv) and step v). The CO₂ and H₂ enriched first gaseous fraction 22 is then subjected to separation 40 of non-condensables to obtain a second gaseous fraction 23 comprising CO, CO₂, H₂, and light hydrocarbons and a second liquid fraction 62 comprising condensable deoxygenated hydrocarbons (and H₂O) as discussed herein for step vi). The second gaseous fraction 23 is then subjected to recovery 50 of H₂ 92 and at least part, preferably all, of the recovered H₂ is recirculated (not shown) back to catalytic hydroliquefaction 10a and/or 10b as part of the inlet hydrogen.

1st Exemplary Embodiment of the Hydrogen Recovery

In an embodiment the recovery at least part of H₂ from the second gaseous fraction (c-2) and recirculating at least part of the recovered H₂ to step ii) of step vii) is accomplished by x) recovering H₂ from at least part of the second gaseous fraction (c-2) and recirculating at least part, preferably all, of the recovered H₂ to step ii);

partially oxygenating (POx) at least part of the H₂ depleted second gaseous fraction to convert at least part of the light hydrocarbons comprised in the H₂ depleted second gaseous fraction to syngas to further produce hydrogen and to increase CO₂:light hydrocarbon ratio of the second gaseous fraction obtain a H₂ and CO₂ enriched second gaseous fraction (c-2e);

xi) removing CO₂ from the H₂ and CO₂ enriched second gaseous fraction (c-2e) to obtain a CO₂ *depleted second* gaseous fraction (c-2t) comprising H₂ and CO; and
xii) recirculating at least part, preferably all, of the CO₂ depleted second gaseous fraction (c-2t) to step iv) and/or v).

Hydrogen may be recovered as defined herein in context of step vii). Preferably hydrogen is recovered from the second gaseous fraction (c-2) by hydrogen membrane diffusion. After the removal of at least part of H₂, such as 50 to 80 % , preferably essentially all, of the hydrogen present in the second gaseous fraction (c-2), at least part of the H₂ depleted second gaseous fraction (c-2) is subjected to partial oxidation in step x).

Partial oxygenation, Step x)

In step x) at least part of the H₂ depleted second gaseous fraction (c-2) produced in the step vii) is partially oxygenated (POx) to convert at least part of the light hydrocarbons comprised in the H₂ depleted second gaseous fraction to syngas to further produce hydrogen and to increase CO₂:light hydrocarbon ratio of the second gaseous fraction to obtain a H₂ and CO₂ enriched second gaseous fraction (c-2e). Utilization of partial oxidation for provision of further hydrogen allows the utilization of lower-quality second gaseous fraction (c-2) as compared to e.g. steam reforming.

Term “syngas” as used herein refers to a gas mixture comprising CO, H₂, CO₂, and methane in any ratio. Syngas may further comprise water vapor (H₂O).

Term “partial oxidation” as used herein refers to oxidation of hydrocarbons to carbon monoxide and hydrogen in the presence of a substoichiometric amount of oxygen.

Advantageously 95 to 100 % of the hydrocarbons present in the second gaseous fraction is converted to lighter products, such as CO and H₂, by the end of the partial oxidation step.

Typically partial oxidation in step x) is accomplished at a temperature from 800 to 1600 °C, preferably from 1100 to 1500 °C, more preferably from 1200 to 1400 °C. A skilled person will be competent to select a temperature within these ranges, considering that the temperature is dictated by equilibrium and kinetics (higher is better) and balanced by reduced yield as more material needs to be combusted and limitations due to materials of construction (lower is better).

Typically partial oxidation in step x) is accomplished at a pressure from 0.5 to 30 MPa, such as from 0.5 to 15 MPa or 0.5 to 10 MPa, preferably from 2 to 8 MPa, more preferably from 4 to 8 MPa, given as gauge pressure. A skilled person will be competent to select a pressure within these ranges. Higher pressure will reduce compression costs as feed is already at high pressure and product (hydrogen) is to be used at high pressure. Also lower equipment volumes are required at high pressures. On the other hand high pressure requires thicker equipment walls.

The residence time in the partial oxidation step x) may be from a fraction of a second up to a minute 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 a shorter residence time is sufficient. The gas hourly space velocity (GHSV) in conversion step vi) is typically from 1500 to 15000 h⁻¹, preferably from 2000 to 10000, more preferably from 3000 to 5000 h⁻¹.

Partial oxidation in step x) may be carried out either in the absence of a catalyst or in the presence of a catalyst. Catalysts are not required due to the high temperature.

After partial oxidation in step x) the obtained H₂ and CO₂ enriched second gaseous fraction (c-2e) is subjected to removal and/recovery of CO₂ to obtain a CO₂ depleted second gaseous fraction.

Step xi)

In step xi) CO₂ is removed from the H₂ and CO₂ enriched second gaseous fraction (c-2e) to obtain a CO₂ depleted second gaseous fraction (c-2t) comprising H₂ and CO. Optionally the removed CO₂ is recovered.

5 The removal of CO₂ from the H₂ and CO₂ enriched second gaseous fraction (c-2e) may be accomplished by any method known by a skilled person. Preferably it is accomplished by chemical adsorption or chemical scrubbing, such as amine adsorption or amine scrubbing.

10 In the absence of higher hydrocarbons also physical solvent absorption would be feasible and less energy intensive than chemical adsorption processes like amine scrubbing. Amine scrubbing is the best option between separator vi) and hydrogen recovery x) for minimizing hydrocarbon solubility.

Preferably the removal of CO₂ is accomplished by conventional amine scrubbing.

15 In case of amine scrubbing, the removal of CO₂ is typically achieved in temperatures where amine is not boiling and at high pressure. It is preferred that the pressure conditions of the partial oxidation step is essentially maintained in step xii).

Thus typically the removal of CO₂ in step xii) is accomplished at a temperature below 100 °C such as from 20 to 100 °C, preferably below 80 °C, such as from 30 to 80 °C, more preferably below 60 °C, such as from 40 to 60 °C. A skilled person will be competent to select a temperature within these ranges.

20 Typically the removal of CO₂ in step xii) is accomplished at a pressure from 0.5 to 30 MPa, such as from 0.5 to 15 MPa or 0.5 to 10 MPa, preferably from 2 to 8 MPa, more preferably from 4 to 8 MPa, given as gauge pressure. A skilled person will be competent to select a pressure within these ranges, considering that the pressure conditions of the preceding steps are preferably maintained.

25 The thus obtained CO₂ depleted second gaseous fraction (c-2t) comprises CO and H₂. The CO₂ depleted second gaseous fraction may further comprise minor amounts of light hydrocarbons not converted in step x). The CO₂ depleted second gaseous fraction (c-2t) may then be recirculated at least in part, preferably in full, to step v), directly and/or via step iv), to undergo GWS reaction to generate more hydrogen
30 and carbon dioxide. The thus generated further hydrogen will be then recovered

though separation of non-condensables of step vi) and hydrogen recovery of step vii).

Step xii): Recirculation

Accordingly in step xii) at least part, preferably all, of the CO₂ depleted second
5 treated gaseous fraction (c-2t) is recirculated to step iv) and/or v).

Figure 3 illustrates a third exemplary process flow of the present method.

Referring to Figure 3, a carbonaceous feedstock 1, preferably comprising or consisting of biomass feedstock such as lignocellulosic biomass, is subjected to catalytic hydroliquefaction 10 in the presence of hydrogen 91 to obtain a product
10 mixture 11 comprising liquid hydrocarbons, and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates, as discussed herein for step ii). The product mixture 11 is then subjected to separation 20 of the liquid hydrocarbons and the off-gas to obtain a first liquid fraction 61 comprising liquid hydrocarbons and a first
15 gaseous fraction 21 comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates, as discussed herein for step iii). The first gaseous fraction 21 is then subjected to a conversion step 30 comprising converting in gas phase at least part of the light oxygenates comprised in the first gaseous fraction 21 to deoxygenated
20 hydrocarbons, carbon monoxide (CO) and carbon dioxide (CO₂), and water vapor (H₂O), and converting in the presence of water steam at least part of the carbon monoxide (CO) comprised in the first gaseous fraction 21 and/or produced in step iv) to carbon dioxide (CO₂) and hydrogen (H₂) by water gas shift reaction to obtain a CO₂ and H₂ enriched first gaseous fraction 22 as discussed herein for step iv) and
25 step v). The CO₂ and H₂ enriched first gaseous fraction 22 is then subjected to separation 40 of non-condensables to obtain a second gaseous fraction 23 comprising CO, CO₂, H₂, and non-condensable hydrocarbons and a second liquid fraction 62 comprising condensable hydrocarbons and H₂O as discussed herein for step vi). The second gaseous fraction 23 is then subjected, preferably by membrane
30 separation, to recovery 50 of H₂ 92 and to further obtain H₂ depleted second gaseous fraction 24. At least part, preferably all, of the recovered H₂ is recirculated

(not shown) back to catalytic hydroliquefaction 10, typically as part of the inlet hydrogen. At least part, preferably all, of the H₂ depleted second gaseous fraction 24 is then subjected to partial oxidation 80 to convert non-condensable hydrocarbons comprised in the H₂ depleted second gaseous fraction 24 to syngas
5 to obtain a H₂ and CO₂ enriched second gaseous fraction 25 as discussed herein for step x). The H₂ and CO₂ enriched second gaseous fraction 25 is then subjected to removal and/or recovery of CO₂ to obtain a CO₂ depleted second gaseous fraction 26 and optionally recovered CO₂ (not shown). At least part, preferably all, of the CO₂ depleted second gaseous fraction 26 is then recirculated to conversion step
10 30 to undergo WGS reaction to further generate hydrogen which will be then recovered through separation of non-condensables 40 and hydrogen recovery 50.

2nd Exemplary Embodiment of the Hydrogen Recovery

In an alternative embodiment the recovery at least part of H₂ from the second gaseous fraction (c-2) and recirculating at least part of the recovered H₂ to step ii)
15 of step vii) is accomplished by

xiii) subjecting the second gaseous fraction (c-2) to steam reforming to convert at least part of the non-condensable hydrocarbons comprised in the second gaseous fraction (c-2) to hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂); and

20 xiv) converting in the presence of water vapor at least part of the carbon monoxide (CO) comprised in the second gaseous fraction (c-2) and/or produced in step xiii) to carbon dioxide (CO₂) and hydrogen (H₂);

to obtain a CO₂ and H₂ enriched second gaseous fraction (c-2r); and recovering at least part, preferably all, of the H₂, and optionally CO₂, comprised in the CO₂ and H₂
25 enriched second gaseous fraction (c-2r) and recirculating at least part of the recovered H₂ to step ii).

At least part of, such as 50 to 80 %, preferably essentially all, of the hydrogen comprised in the CO₂ and H₂ enriched second gaseous fraction (c-2r) may be recovered as defined herein in context of step vii). Preferably hydrogen is recovered

from the CO₂ and H₂ enriched second gaseous fraction (c-2r) by hydrogen membrane diffusion.

Steps xiii) and xiv): Steam reforming and water-gas shift

5 In step xiii) at least part, preferably essentially all, of the non-condensable hydrocarbons comprised in the second gaseous fraction (c-2) are converted to hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂). Conversion is desired as presence of hydrocarbons complicates the hydrogen recovery process while hydrogen will be generated from said hydrocarbons and thus reduce the need for external hydrogen.

10 Advantageously 85 to 99 % of the non-condensable hydrocarbons present in the second gaseous fraction is converted to carbon monoxide, carbon dioxide, and hydrogen by the end of the conversion step.

The conversion in steps xiii) may be performed in any suitable reactor(s) wherein the indicated conditions may be achieved. A fixed bed reactor is preferred.

15 The conversion in step xiii) is typically carried out at an inlet temperature from 300 to 380 °C, such as from 310 to 360 °C, preferably from 320 to 340 °C. A skilled person will be competent to select a temperature within these ranges keeping in mind that typically temperature rise in the reactor will be 50 to 100 °C.

20 The conversion in step xiii) is typically carried out at a pressure from 0.5 to 10 MPa, preferably from 2 to 8 MPa, more preferably from 4 to 8 MPa, given as gauge pressure. A skilled person will be competent to select a pressure within these ranges keeping in mind that preferably the pressure of the previous steps is suitably maintained in the conversion step xiii).

25 The residence time in the conversion step may be from a fraction of a second up to a minute 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. The gas hourly space velocity (GHSV) in conversion step vi) is typically from 1500 to 15000 h⁻¹, preferably from 2000 to 10000, more preferably from 3000 to 5000 h⁻¹. Typically
30 the residence time is from 0.10 second to 1.

Typically the second gaseous fraction (c-2) has a sufficient amount of water vapor to drive the reaction. Preferably the ratio of H₂O to CO in the WGS is at least 2, preferably from 4 to 30, more preferably from 15 to 20. If required the ratio can be controlled by adding water steam to step xiii).

- 5 The conversion in steps xiii) and xiv) are performed in the presence of at least one catalyst. Examples of suitable sulfided heterogeneous metal catalysts include, but are not limited to, mixed metal oxide catalysts, such as mixed Fe-Cr-oxide catalysts.

- Further in step xiv) at least part, preferably at least 70 %, such as 80 to 98%, of the carbon monoxide (CO) comprised in the second gaseous fraction (c-2) and/or
10 produced in step xiii) is converted to carbon dioxide (CO₂) and hydrogen (H₂). The conversion is achieved in the presence of water vapor (H₂O) by water-gas shift (WGS) reaction. Conversion of CO to CO₂ is desired as CO₂ can be more easily removed from the hydrogen recycle loop and further, while converting CO to CO₂ with a water gas shift reaction, hydrogen can be generated from water vapor
15 comprised in the off-gas and/or brought into the WGS step and thus reduce the need for external hydrogen.

As a result of conversion steps xiii) and xiv) a CO₂ and H₂ enriched second gaseous fraction (c-2r) comprising CO₂, H₂, and water vapor (H₂O) is obtained. The generated hydrogen reduces the need for external hydrogen.

- 20 Figure 4 illustrates a fourth exemplary process flow of the present method.

- Referring to Figure 4, a carbonaceous feedstock 1, preferably comprising or consisting of biomass feedstock such as lignocellulosic biomass, is subjected to catalytic hydroliquefaction 10 in the presence of hydrogen 91 to obtain a product mixture 11 comprising liquid hydrocarbons, and off-gas comprising carbon
25 monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), light (C1-C3) hydrocarbons, and light oxygenates, as discussed herein for step ii). The product mixture 11 is then subjected to separation 20 of the liquid hydrocarbons and the off-gas to obtain a first liquid fraction 61 comprising liquid hydrocarbons and a first gaseous fraction 21 comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water
30 vapor (H₂O), light (C1-C3) hydrocarbons, and light oxygenates, as discussed herein

for step iii). The first gaseous fraction 21 is then subjected to a conversion step 30 comprising converting in gas phase at least part of the light oxygenates comprised in the first gaseous fraction (c-1) to deoxygenated hydrocarbons, carbon monoxide (CO) and carbon dioxide (CO₂), and water (H₂O), and converting in the presence of water steam at least part of the carbon monoxide (CO) comprised in the first gaseous fraction (c-1) and/or produced in step iv) to carbon dioxide (CO₂) and hydrogen (H₂) by WGS reaction to obtain a CO₂ and H₂ enriched first gaseous fraction 22 as discussed herein for step iv) and step v). The CO₂ and H₂ enriched first gaseous fraction 22 is then subjected to separation 40 of non-condensables to obtain a second gaseous fraction 23 comprising CO, CO₂, H₂, and non-condensable hydrocarbons and a second liquid fraction 62 comprising condensable hydrocarbons and H₂O as discussed herein for step vi). The second gaseous fraction 23 is then subjected to steam reforming 55 to convert at least part of the non-condensable hydrocarbons comprised in the second gaseous fraction (c-2t) to carbon dioxide (CO₂) and hydrogen (H₂) to obtain an intermediate CO₂ and H₂ enriched second gaseous fraction 27 as discussed herein for step xiii). The intermediate CO₂ and H₂ enriched second gaseous fraction 27 is then subjected to converting 56 at least part, preferably all, of the carbon monoxide (CO) comprised in the first CO₂ and H₂ enriched treated gaseous fraction to carbon dioxide (CO₂) and hydrogen (H₂) to obtain a CO₂ and H₂ enriched second gaseous fraction 28 comprising CO₂ and H₂ as discussed herein for step xiv). The CO₂ and H₂ enriched second gaseous fraction is then subjected to recovery 50 of H₂ 92 and to further obtain H₂ depleted second gaseous fraction 24. At least part, preferably all, of the recovered H₂ is recirculated 93 back to catalytic hydroliquefaction 10, typically as part of the inlet hydrogen.

Step viii): Recovery of liquid hydrocarbon composition

In step viii) the first liquid fraction (b-1) and/or the second liquid fraction (b-2) are recovered to provide a liquid hydrocarbon composition. The liquid hydrocarbon composition can then be utilized as such and/or after further valorization as fuels, fuel components, and/or other valuable hydrocarbon products, in particular renewable fuels, renewable fuel components, and/or other valuable renewable hydrocarbon products.

The obtained hydrocarbon composition comprises a mixture of linear, branched, and cyclic hydrocarbons having from 4 to 90 carbon atoms, referred here as C₄-C₉₀ hydrocarbons.

5 The hydrocarbon composition can preferably be further treated to produce valorized products.

The obtained liquid hydrocarbon composition thus may be subjected to e.g. fractionating to provide at least a gasoline fraction and a middle distillate fraction. These fractions are the most valuable for transportation fuels and thus separating these fractions from less valuable fractions is favorable. In addition to a gasoline
10 stream and a middle distillate stream, the fractions derived from the fractionation may comprise a gas stream and a distillation bottom. The fractionation may comprise any suitable distillation means, including distillation at normal pressure or distillation or evaporation under reduced pressure.

The present method allows the production of fuels, fuel components, and/or other
15 valuable hydrocarbon products with reduced oxygen and sulfur content as compared to corresponding products obtained with comparative conventional methods not utilizing intermediate gas-phase deoxygenation of light oxygenates and shifting carbon monoxide to carbon dioxide as described herein. Further, the obtained products may have an improved cloud point and aromatics content.

20 Referring to Figures 1 to 4, the first liquid fraction 61 and/or the second liquid fraction 62 may be recovered 60 to provide a liquid hydrocarbon composition 63 which may then be utilized as such as fuels, fuel components, and/or other valuable hydrocarbon products, in particular renewable fuels, renewable fuel components, and/or other valuable renewable hydrocarbon products, or subjected to further
25 valorization, e.g. fractionating to provide at least a gasoline fraction and a middle distillate fraction, 70 to obtain one or more valorized liquid hydrocarbons (not shown) which may be utilized as fuels, fuel components, and/or other valuable hydrocarbon products, in particular renewable fuels, renewable fuel components, and/or other valuable renewable hydrocarbon products as discussed herein for step viii).

CLAIMS

1. A method for the production of liquid hydrocarbon composition, comprising
- i) providing carbonaceous feedstock (a);
 - ii) subjecting the carbonaceous feedstock (a) to catalytic hydroliquefaction (10) in the presence of hydrogen to obtain a product mixture comprising liquid hydrocarbons and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;
 - iii) separating (20) the liquid hydrocarbons and the off-gas to obtain a first liquid fraction (b-1) comprising liquid hydrocarbons and a first gaseous fraction (c-1) comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;
 - iv) converting (30) in gas phase at least part of the light oxygenates comprised in the first gaseous fraction (c-1) to deoxygenated hydrocarbons, carbon monoxide (CO), carbon dioxide (CO₂), and water vapor (H₂O), and
 - v) converting in the presence of water steam at least part of the carbon monoxide (CO) comprised in the first gaseous fraction (c-1) and/or produced in step iv) to carbon dioxide (CO₂) and hydrogen (H₂) by water gas shift reaction, to obtain a CO₂ and H₂ enriched first gaseous fraction (c-1e), wherein steps iv) and v) are preferably accomplished in the same reactor step-up, more preferably in a fixed bed reactor; and
 - vi) separating (40) non-condensables from the CO₂ and H₂ enriched first gaseous fraction (C-1e) to obtain a second gaseous fraction (c-2) comprising CO, CO₂, H₂, and non-condensable hydrocarbons and a second liquid fraction (b-2) comprising condensable hydrocarbons;
 - vii) recovering (50) at least part, such as 50 to 80 %, preferably essentially all, of H₂ from the second gaseous fraction (c-2) and recirculating (93) at least part, preferably all, of the recovered H₂ to step ii);

viii) recovering the first liquid fraction (b-1) and/or the second liquid fraction (b-2) to provide a liquid hydrocarbon composition.

2. The method as claimed in claim 1, wherein step vii) is accomplished by

x) recovering H_2 from at least part of the second gaseous fraction (c-2) and
5 recirculating at least part, preferably all, of the recovered H_2 to step ii) and partially oxygenating (POx) at least part of the H_2 depleted second gaseous fraction to convert at least part of the light hydrocarbons comprised in the H_2 depleted second gaseous fraction to syngas to further produce hydrogen and to increase CO_2 :light hydrocarbon ratio of the second gaseous fraction to obtain a H_2 and CO_2 enriched
10 second gaseous fraction (c-2e);

xi) removing CO_2 from the H_2 and CO_2 enriched second gaseous fraction (c-2e) to obtain a CO_2 depleted second gaseous fraction (c-2t) comprising H_2 and CO; and

xii) recirculating at least part, preferably all, of the CO_2 depleted second gaseous fraction (c-2t) to steps iv) and/or v).

15 3. The method as claimed in claim 2, wherein step vii) is accomplished by

xiii) subjecting the second gaseous fraction (c-2) to steam reforming to convert at least part of the non-condensable hydrocarbons comprised in the second gaseous fraction (c-2) to carbon dioxide (CO_2) and hydrogen (H_2); and

xiv) converting in the presence of water vapor at least part of the carbon monoxide
20 (CO) comprised in the second gaseous fraction (c-2) and/or produced in step xiii) to carbon dioxide (CO_2) and hydrogen (H_2);

to obtain a CO_2 and H_2 enriched second gaseous fraction (c-2r) and recovering at least part, preferably all, of the H_2 , and optionally CO_2 , comprised CO_2 and H_2 enriched second gaseous fraction (c-2r) and recirculating at least part of the
25 recovered H_2 to step ii).

4. The method as claimed in any of claims 1 to 3, wherein step ii) is accomplished by

ii-1) subjecting the carbonaceous feedstock (a) to catalytic hydroliquefaction in the presence of hydrogen to obtain an intermediate product mixture comprising partially treated carbonaceous material, deoxygenated liquid hydrocarbons, and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;

ii-2) optionally separating and removing at least part of the non-hydrogen gases comprised in the off-gas formed in step ii-1 from the intermediate product mixture to obtain a hydrogen enriched off-gas fraction (c-h) and a second off-gas fraction (c-o) comprising carbon monoxide (CO), carbon dioxide (CO₂), light (C₁-C₃) hydrocarbons, and light oxygenates;

ii-3) subjecting the intermediate product mixture to catalytic hydroliquefaction in the presence of hydrogen and optionally the hydrogen enriched off-gas fraction (c-h) resulting from step ii-2) to obtain a product mixture comprising liquid hydrocarbons and off-gas comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates.

5. The method as claimed in any one of claims 1 to 4, wherein recovering in step viii) comprises upgrading and distillation.

6. The method as claimed in any one of claims 1 to 5, wherein the catalytic hydroliquefaction in step ii) is carried out at a temperature 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.

7. The method as claimed in any of claims 1 to 6, wherein the catalytic hydroliquefaction in step ii) is carried out at a pressure of at least 6 MPa, such as 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.

8. The method as claimed in any of claims 1 to 7, wherein the catalyst in the catalytic hydroliquefaction step is selected from sulfided heterogeneous metal catalysts, preferably from sulfided NiMo, sulfided CoMo, and sulfided Mo based catalysts.

9. The method as claimed in any of claims 1 to 8, wherein the carbonaceous feedstock comprises or consists of, preferably consists of, biomass feedstock, such as lignocellulosic biomass feedstock.
10. The method as claimed in any of claims 1 to 9, wherein the carbonaceous
5 feedstock comprises at least 10 wt%, preferably at least 20 wt%, more preferably at least 30 wt%, oxygen on a dry basis, measured as elemental oxygen.
11. The method as claimed in any of claims 1 to 10, wherein the carbonaceous feedstock comprises from 45 to 55 wt%, carbon, and less than 10 wt%, such as from 5 to 8 wt%, hydrogen on a dry basis, measured as elemental carbon and hydrogen,
10 respectively.
12. The method as claimed in any of claims 1 to 11, wherein the conversions in steps vi) and v) are carried out at a temperature from 200 to 500 °C, such as from 250 to 400 °C, preferably from 300 to 350 °C, more preferably from 310 to 320 °C and at a pressure from 0.5 to 30 MPa, such as from 0.5 to 15 MPa or 0.5 to 10 MPa,
15 preferably from 2 to 8 MPa, more preferably from 4 to 8 MPa, given as gauge pressure.
13. The method as claimed in any of claim 1 to 12, wherein the gas hourly space velocity (GHSV) in conversion steps iv) and v) is from 1500 to 15000 h⁻¹, preferably from 2000 to 10000, more preferably from 3000 to 5000 h⁻¹.