

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 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 wastewater. A significant amount of carbon of the feed remains in partially converted products, such as phenols, ketones and alcohols. Part of such oxygenates and essentially all of CO will end up in the gaseous effluent (off-gas). The gaseous effluent is conventionally processed in amine adsorption and steam methane reforming (SMR). However, light oxygenates and high amounts of CO will make this processing scheme difficult to implement. Oxygenates will be partially dissolved in the amine solution causing degradation and foaming. CO is detrimental as the exotherm at SMR pre-treatment will become prohibitive already at low concentrations, even below few vol%. Furthermore, SMR cannot process higher hydrocarbons in the feed without a separate pre-reformer.

WO 2011038911 discloses new polymetallic catalysts supported on at least slightly basic materials and a process for the conversion of lignin to hydrocarbons, which uses said catalysts.

WO 2017050580 discloses a method for generating a hydrogen rich gas from pyrolysis of carbonaceous material, a system for upgrading tar oil from pyrolysis of carbonaceous material and a method for upgrading tar oil.

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
5 embodiments of the invention are disclosed in the dependent claims.

The invention is based on the surprising realization that conversion of carbonaceous feed to liquid hydrocarbons by catalytic hydroliquefaction can be optimized by utilization of conversion of off-gas hydrocarbons to syngas by partial oxidation
10 followed by shifting carbon monoxide to carbon dioxide and hydrogen. This allows efficient utilization of the off-gas components and thermally efficient overall process flow. The hydrogen recovery efficiency may be further maximized by its optimized recovery and recirculation.

BRIEF DESCRIPTION OF THE DRAWINGS

15 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.

DETAILED DESCRIPTION OF THE INVENTION

20 The present invention provides a method for the production of hydrocarbon composition, comprising
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
25 and off-gas comprising carbon monoxide (CO), carbon dioxide, (CO₂), hydrogen (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;
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),
30 light (C₁-C₃) hydrocarbons, and light oxygenates;

- iv) recovering at least part of H₂ from the first gaseous fraction (c-1) to obtain a H₂ depleted second gaseous fraction (c-2), and recirculating at least part, preferably all, of the recovered H₂ to step ii);
- v) subjecting at least part, preferably all, of the H₂ depleted second gaseous fraction (c-2) to partial oxygenation (POx) to convert at least part of the light hydrocarbons comprised in the H₂ depleted first gaseous fraction to syngas to obtain a third gaseous fraction (c-3) comprising syngas;
- vi) converting in the presence of water steam at least part of the carbon monoxide (CO) comprised in the third gaseous fraction (c-3) to carbon dioxide (CO₂) and hydrogen (H₂) to obtain a CO₂ and H₂ enriched third gaseous fraction (c-3e);
- vii) recovering at least part of H₂ from the CO₂ and H₂ enriched third gaseous fraction (c-3e) and recirculating at least part, preferably all, of the recovered H₂ to step ii); and
- viii) recovering the first liquid fraction (b-1) to 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 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%.

25 Feedstock, Step i)

The term "carbonaceous feedstock" refers to carbonaceous material which is intended to be converted by hydroprocessing into liquid hydrocarbons, such as renewable hydrocarbons or other valuable hydrocarbon products, such as valuable renewable 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.

10 The ^{14}C -isotope content can be used as evidence of the renewable or biological 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
15 by analyzing the ratio of ^{12}C and ^{14}C isotopes. Thus, a particular ratio of said 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
20 (2020). An example of how to apply ASTM D6866 to determine the renewable 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
25 using ASTM D6866.

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
30 EN228:2017, for paraffinic diesel EN15940:2023, and for aviation turbine fuel containing synthesized hydrocarbons D7566-22.

The carbonaceous feedstock contemplated herein typically comprises high amounts of carbon and oxygen but relatively low amounts of hydrogen in the 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 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 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 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 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:

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

- 5 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
10 wt%, more preferably at least 65 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
15 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,
20 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.

25 Prior to being fed to the hydroliquefaction step ii) the carbonaceous feedstock, such as 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.

30 **Step ii): Catalytic Hydroliquefaction of the Feedstock**

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

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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.
15 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
20 hydroliquefaction reactor is at least 5 MPa, such as from 5 to 26, 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
25 catalyst. Suitable catalysts for 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
30 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, 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 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. 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

- ii-1) subjecting the carbonaceous feedstock (a) to catalytic hydroliquefaction the biomass feedstock (a) to obtain an intermediate product mixture comprising partially treated biomass, 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 an off-gas fraction (c-o) comprising carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), light (C₁-C₃) hydrocarbons, and light oxygenates; and
- ii-3) subjecting the partially treated biomass comprised in the intermediate product mixture to catalytic hydroliquefaction in the presence of deoxygenated hydrocarbons and optionally off-gas produced in step ii-1) to obtain a product mixture comprising liquid hydrocarbons, 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).

5 Typically the consecutive catalytic hydroliquefaction stages are performed at essentially the same pressure, i.e. each stage typically 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, while the pressure of the first catalytic hydroliquefaction stage
10 determines the pressure of the following consecutive catalytic hydroliquefaction 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.

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Further, the consecutive catalytic hydroliquefaction stages are typically 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 for each consecutive stage within these ranges. Advantageously, the temperature of
20 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 temperature of step ii-3).

A person skilled in the art will be competent to adjust the residence time of the
25 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 sufficient.

Typically, the hydrogen partial pressure at the inlet of each catalytic
30 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 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.

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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.

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In an embodiment the catalytic hydroliquefaction step ii) comprises

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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;

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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

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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.

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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.

5 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.

10 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.

15 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 to separation of the liquid hydrocarbons and the off-gas.

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

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In step iii) the liquid hydrocarbons and the off-gas are separated 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.

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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 separation step iii).

30 After the first high temperature and high pressure separation, the separation in step iii) may comprise one or more, preferably one, further separation stage(s), each performed in lower temperature than the previous separation stage while the pressure typically remains essentially the same, to separate further condensables,

such as condensable hydrocarbon and/or water, from the first gaseous fraction. The condensables separated in the further separation stages of step iii) may be combined to the first liquid fraction (b-1)

- 5 Thus, typically the separation step iii) 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 skilled person will be competent to select a pressure for each consecutive stage within these ranges keeping in mind that preferably the last preceding catalytic
- 10 hydroliquefaction stage determines the pressure of the following separation step. Further, typically the first stage of 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 for each consecutive stage within these ranges, keeping in mind that preferably the last
- 15 preceding catalytic hydroliquefaction stage determines the temperature of the following first separation stage and the optional further separation stages are performed at a lower temperature.

- The separation in step iii) may be accomplished by any unit operation suitable for
- 20 separation of a gaseous phase and a liquid phase and wherein the indicated 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 hydrogen recovery.

- 25 The first liquid fraction (b-1) comprising liquid hydrocarbons may be recovered 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.

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Step iv): Hydrogen recovery

In step iv) at least part, such as 50 to 80 %, preferably essentially all, of H₂ comprised in the first gaseous fraction (c-1) separated in step iii) is recovered to obtain a H₂ depleted second gaseous fraction (c-2), and at least part, preferably all, of the recovered H₂ is recirculated to step ii).

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

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

Thus, typically the hydrogen recovery step iv) is carried out at a pressure at least 6
20 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 preferably the preceding step determines the pressure of the following hydrogen recovery step.

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Typically, the hydrogen recovery step iv) is carried out at a temperature from 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.

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After the removal of at least part of, such as 50 to 80 %, preferably essentially all, of the hydrogen present in the first gaseous fraction (c-1), at least part, preferably

all, of the H₂ depleted second gaseous fraction (c-2) is subjected to partial oxidation in step v)

Step v): Partial oxygenation

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In step v) at least part, preferably all, of the H₂ depleted second gaseous fraction (c-2) produced in the step iv) is subjected to partial oxygenation (POx) to convert at least part of the light hydrocarbons comprised in the H₂ depleted first gaseous fraction to syngas to obtain a third gaseous fraction (c-3) comprising syngas.

10 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.

15 Advantageously, essentially all, such as 95 to 100 %, typically 95 to 98 %, of the hydrocarbons present in the treated second gaseous fraction is converted to CO and H₂ by the end of the partial oxidation step.

Typically partial oxidation step v) 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).

25

Typically, partial oxidation step v) 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.

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The residence time in the partial oxidation 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
5 hourly space velocity (GHSV) in conversion step v) 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 v) 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.
10 After partial oxidation in step v) the obtained third gaseous fraction is subjected to conversion of carbon monoxide to carbon dioxide and hydrogen in the presence of water vapor.

Step vi): Water-Gas Shift

15 In step vi) at least part, preferably at least 50%, such as 80 to 98% of the carbon monoxide (CO) comprised in the third gaseous fraction (c-3) is converted to carbon dioxide (CO₂) and hydrogen (H₂) to obtain a CO₂ and H₂ enriched third gaseous fraction (c-3e). The conversion is achieved in the presence of water vapor (H₂O) by
20 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 comprised in the off-gas and/or brought into the WGS step and thus reduce the need for external hydrogen.

25 The conversion in step vi) is typically carried out at a temperature from 180 to 500 °C, such as from 300 to 450 °C for high temperature conversion or from 220 to 270 °C for medium temperature conversion or from 180 to 250 °C for low temperature conversion, preferably from 220 to 450 °C, more preferably from 300 to 400 °C,
30 more preferably from 350 to 370 °C. A skilled person will be competent to select a temperature within these ranges keeping in mind that the equilibrium is such that reaction is more on H₂+CO₂ side at low temperatures. Kinetics will slow down so

there is a practical low limit. Reaction is exothermic so two-stage operation with cooling in between is sometimes used.

5 The conversion in step vi) is 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 keeping in mind that preferably the pressure of the previous steps is suitably maintained in the conversion step vi).

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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
15 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.

The conversion step is performed in the presence of at least one catalyst. The third gaseous fraction (c-3) typically contains hydrogen sulfide. Because of this, so-called
20 clean shift catalysts cannot be used. Suitable catalysts for the conversion step 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. Examples of suitable supports include silica and/or alumina. Preferably
25 the catalyst is unsupported. 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 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 %.

30 The conversion in step vi) 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 conversion step vi) is advantageously performed in continuous mode. Examples of suitable reactors include, but are not

limited to, fluidized bed reactors, such as ebullated bed reactors, bubble column reactors, fixed bed reactors, such as percolation reactors with liquid circulation, tubular reactors, such as multitubular reactors, continuous stirred tank reactor (CSTR).

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Typically, the third gaseous fraction (c-3) has a sufficient amount of water vapor to drive the WGS reaction. The relative amount of water vapor controls the H_2/CO ratio of the produced CO_2 and H_2 enriched first gaseous fraction via WGS reaction. Preferably the ratio of H_2O 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 vi).

10

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

15

It is appreciated that the conditions described above in general for the conversion step vi) apply to all conversion stages, such as first conversion step and second conversion step, comprised in the conversion sequence of step vi).

20

Typically, the consecutive conversion stages are performed at essentially the same pressure, i.e. each stage 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, while the pressure of the first conversion stage determines the pressure of the following consecutive conversion stages. As an example, the pressure of the first conversion step and the second conversion step is the same.

25

Further, the consecutive conversion stages are typically carried out at a temperature from 180 to 500 °C, such as from 300 to 450 °C for high temperature conversion or from 220 to 270 °C for medium temperature conversion or from 180 to 250 °C for low temperature conversion, preferably from 220 to 450 °C, more 250 to 400 °C, preferably from 300 to 400 °C, more preferably from 350 to 370 °C. A skilled person

30

will be competent to select a temperature for each consecutive stage within these ranges. Advantageously, the temperature of the following stage will be lower than the temperature of the preceding stage. As an example, the temperature of the first conversion step may be 10 to 60 °C lower than the temperature of the second conversion step.

After conversion step vi) at least part, preferably all, of the CO₂ and H₂ enriched third gaseous fraction (c-3e) produced in step vi) is subjected to hydrogen recovery.

10 **Step vii): Hydrogen Recovery**

In step vii) at least part, preferably essentially all, of H₂ comprised in the third gaseous fraction (c-3) produced in step vi) is recovered and at least part, preferably all, of the recovered H₂ is recirculated to step ii).

15

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 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.

25

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

30

Thus, typically the hydrogen recovery step vii) is carried out at a temperature from 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
5 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 preferably the preceding step determines the pressure of the H₂ recovery step.

10

Before the hydrogen removal from the third gaseous fraction (c-3), the third gaseous fraction (c-3) may be subjected to purification of the gas stream to remove undesired oxygen, and/or sulfur containing gases, such as CO₂, and/or H₂S. Should there remain any nitrogen containing gases, such as NH₃, in the third gaseous fraction,
15 also those may be removed here. Examples of suitable purification methods include, but are not limited to, physical and/or chemical absorption, membrane separation, pressure swing adsorption, hydrocarbon absorption, and/or cryogenic separation. Preferably the third gaseous fraction (c-3) is subjected to physical or chemical absorption, more preferably to amine absorption, before hydrogen recovery,
20 whereby the hydrogen recovery is preferably accomplished by hydrogen separation membrane.

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

25

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
30 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 recovery 30 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 as discussed herein for step iv). The thus obtained H₂ depleted second gaseous fraction 22 is then subjected to conversion step 40 comprising partial oxidation of at least part of the light hydrocarbons comprised in the H₂ depleted second gaseous fraction 22 to syngas to obtain a third gaseous fraction (not shown) comprising syngas as discussed herein for step v) and then converting in the presence of water steam at least part of the carbon monoxide comprised in the third gaseous fraction to carbon dioxide (CO₂) and hydrogen (H₂) by water gas shift reaction to obtain a CO₂ and H₂ enriched third gaseous fraction 23 as discussed herein for step vi). The CO₂ and H₂ enriched third gaseous fraction 23 is then subjected to recovery 50 of H₂ 94 and a H₂ depleted second gaseous fraction 24 is further obtained. At least part, preferably all, of the recovered H₂ is recirculated 93 back to catalytic hydroliquefaction 10, typically as part of the inlet hydrogen.

20

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 recovery 30 of H₂ 92 and at least part, preferably all, of the recovered H₂ is recirculated (not shown) back to catalytic hydroliquefaction 10 as part of the inlet hydrogen as discussed herein for step iv). The thus obtained H₂ depleted second gaseous fraction 22 is the subjected conversion step 40 comprising partial oxidation of at least part of the light hydrocarbons comprised in the H₂ depleted second gaseous fraction 22 to syngas to obtain a third gaseous fraction (not shown) comprising syngas as discussed herein for step v) and then converting in the presence of water steam at least part of the carbon monoxide comprised in the third gaseous fraction to carbon dioxide (CO₂) and hydrogen (H₂) by water gas shift reaction to obtain a CO₂ and H₂ enriched third gaseous fraction 23 as discussed herein for step vi). The CO₂ and H₂ enriched third gaseous fraction 23 is then subjected to recovery 50 of H₂ 94 and a H₂ depleted second gaseous fraction 24 is further obtained. 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.

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.

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

The obtained liquid hydrocarbon composition thus may be subjected to e.g.
5 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 stream and a middle distillate stream, the fractions derived from the fractionation may comprise a gas stream and a distillation bottom. The fractionation may
10 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 valuable hydrocarbon products with reduced oxygen and sulfur content as
15 compared to corresponding products obtained with comparative conventional methods not utilizing intermediate partial oxidation of light hydrocarbons 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 and 2, the first liquid fraction is recovered 60 to provide a liquid hydrocarbon composition 62 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 valorization, e.g. fractionating to provide at least a
25 gasoline fraction and a middle distillate fraction, 70 to obtain one or more valorized liquid hydrocarbons 63 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).

30

CLAIMS

1. A method for the production of hydrocarbon composition, comprising

5 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
10 (H₂), water vapor (H₂O), light (C₁-C₃) hydrocarbons, and light oxygenates;

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),
15 light (C₁-C₃) hydrocarbons, and light oxygenates;

iv) recovering at least part of H₂ from the first gaseous fraction (c-1) to obtain a H₂ depleted second gaseous fraction (c-2), and recirculating at least part, preferably all, of the recovered H₂ to step ii);
20

v) subjecting at least part, preferably all, of the H₂ depleted second gaseous fraction (c-2) to partial oxygenation (POx) to convert at least part of the light hydrocarbons comprised in the H₂ depleted first gaseous fraction to syngas to obtain a third gaseous fraction (c-3) comprising syngas;
25

vi) converting in the presence of water steam at least part of the carbon monoxide (CO) comprised in the third gaseous fraction (c-3) to carbon dioxide (CO₂) and hydrogen (H₂) to obtain a CO₂ and H₂ enriched third gaseous fraction (c-3e);

vii) recovering at least part of H₂ from the CO₂ and H₂ enriched third gaseous fraction (c-3e) and recirculating at least part, preferably all, of the recovered H₂ to step ii);
30 and

viii) recovering the first liquid fraction (b-1) to provide a liquid hydrocarbon composition;

wherein the carbonaceous feedstock comprises lignocellulosic biomass feedstock.

5

2. The method as claimed in claim 1, 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.

25

3. The method as claimed in claim 1 or 2, wherein recovering in step viii) comprises upgrading and distillation.

4. The method as claimed in any one of claims 1 to 3, 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.

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5. The method as claimed in any one of claims 1 to 4, 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.

5

6. The method as claimed in any of claims 1 to 5, wherein the carbonaceous feedstock consists of lignocellulosic biomass feedstock.

7. The method as claimed in any of claims 1 to 6, wherein essentially all, such as
10 95 to 100 %, typically 95 to 98 %, of the hydrocarbons present in the treated second gaseous fraction is converted to CO and H₂ by the end of the partial oxidation step.

8. The method as claimed in any of claims 1 to 7, wherein partial oxidation step v) is accomplished at a temperature from 800 to 1600 °C, preferably from 1100 to 1500
15 °C, more preferably from 1200 to 1400 °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, preferably from 2 to 8 MPa, more preferably from 4 to 8 MPa, given as gauge pressure.

9. The method as claimed in any of claims 1 to 8, wherein the gas hourly space
20 velocity (GHSV) in conversion step v) is typically from 1500 to 15000 h⁻¹, preferably from 2000 to 10000, more preferably from 3000 to 5000 h⁻¹.

10. The method as claimed in any of claims 1 to 9, wherein the carbonaceous feedstock comprises at least 10 wt%, preferably at least 20 wt%, more preferably at
25 least 30 wt%, oxygen on a dry basis, measured as elemental oxygen.

11. The method as claimed in any of claims 1 to 9, wherein the carbonaceous feedstock comprises from 45 to 55 wt%, carbon, and less than 10 wt%, such as from
30 5 to 8 wt%, hydrogen on a dry basis, measured as elemental carbon and hydrogen, respectively.