

PHASED HYDROGEN FEED IN CATALYST HYDROLIQUEFACTION

FIELD OF THE INVENTION

The present invention relates to a method of processing biomass feeds for the purpose of liquefaction. More particularly the present invention relates to a method of preparing a biomass feed and preheated with the use of a preheater prior to liquefying the biomass feed.

BACKGROUND OF THE INVENTION

Liquefaction of biomaterial has attracted increased attention in recent years. Such liquefaction processes are generally known in the art. For example, WO2022058128 A1 discloses direct hydrogenation of lignocellulosic material using an unsupported NiMo catalyst. US 2011/0167713 A1 also discloses direct hydrogenation of lignocellulosic material.

One problem associated with liquefaction of slurry biomass feeds is that they are difficult materials to heat up as the decomposition of biomass will generate char, coke and tar. These reactions are known to cause fouling in the equipment, and heat transfer surfaces are especially prone to fouling. Typically, the best way of controlling unwanted thermal reactions, i.e., fouling and coke formation, when heating slurry biomass feed, is by limiting the final temperature. However, this is not the best solution when considering liquefaction of biomass; catalytic hydroliquefaction reactions have commercially meaningful performance in temperatures higher than 300 °C but the solid biomass materials in the slurry biomass feed start to decompose in significantly lower temperatures. For example, wood starts to decompose already at around 170 °C.

The purpose of the present invention is to offer a solution to overcome the problems described above by providing a method for preheating biomass before liquefaction of said biomass.

BRIEF DESCRIPTION OF THE INVENTION

An object of the present invention is thus to provide a method so as to solve the above problem. 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 current invention thereby provides a method of processing a slurry biomass feed for liquefaction, said method comprising

- i) providing a slurry biomass feed comprising solid biomass, a liquid

carrier medium, an active catalyst and a hydrogen source,

ii) transferring the slurry biomass feed to a liquefaction reactor via a preheater to obtain a preheated slurry biomass feed, wherein the residence time of the slurry biomass feed containing hydrogen in the preheater is in the range of about 1 second to about 5 minutes, and

iii) liquefying the preheated slurry biomass feed in the liquefaction reactor.

General benefits of the method are the combination of enriching the slurry biomass feed with hydrogen and a certain type of catalyst that is either activated or can be active without thermal activation and transferring said slurry biomass feed to a liquefaction reactor via a preheater. The composition of the slurry biomass feed in the present invention allows for preheating in a preheater without suffering from high formation of char, coke and tar that would normally form as the side product of a thermal reaction when biomass is subjected to high temperatures. By avoiding fouling occurring in the equipment, liquefaction of biomass can then take place in a continuous mode without interruptions.

BRIEF DESCRIPTION OF THE DRAWINGS

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

Figure 1 depicts one possible embodiment of the current method.

Figure 2 depicts one possible embodiment of the current method.

DETAILED DESCRIPTION OF THE INVENTION

In conventional liquefaction process, the biomass to be liquefied is subjected to preheating with the use of a feed heater. With the use of preheating, there is then a lesser demand to heat up the feedstock to reach the required liquefaction temperature in the liquefaction reactor, in particular when liquefaction is taking place in a continuous mode. However, as there is no catalyst in the feed heater, only thermal reactions are taking place. Key thermal reaction is coke formation i.e., fouling, and the best way of controlling it is by limiting the heating temperatures.

The present invention relates to a method for processing and treating biomass feeds before liquefaction of said biomass feeds. The method comprises providing a slurry biomass feed, providing an active catalyst, introducing a hydrogen source to the slurry biomass feed, transferring the slurry biomass containing hydrogen and at least one active catalyst to a liquefaction reactor via a preheater,

and subsequently liquefying the slurry biomass in the liquefaction reactor at elevated temperatures. The slurry biomass feed is obtained by mixing solid biomass, active catalyst and hydrogen source in a liquid carrier medium. An active catalyst can be introduced to the slurry biomass feed either before or during the introduction of the hydrogen source to the slurry biomass feed.

The invention is based on the surprising realisation that the combined presence of an active catalyst and hydrogen in preheater and during pre-heating of the slurry biomass feed, reduces formation of coke and therefore decreases the amount of fouling in the equipment. It has been observed that when hydrogen or an active catalyst is missing from the slurry biomass, there is substantial coke formation during pre-heating while with the addition of both hydrogen and the active catalyst in the biomass feed prevents formation of such solid components.

When solid biomass suspended in a liquid carrier medium, for example oil, is preheated in the presence of an active catalyst, for example an active hydrogenation catalyst, and hydrogen, one or more of the following reactions can occur; including, but not limited to any one or more of deoxygenation, such as decarbonylation, decarboxylation, and hydrodeoxygenation (HDO), hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM), hydrodearomatization (HDA), hydrogenation, and hydrocracking. The oil product comprises oxygenates and hydrocarbons. These reactions are beneficial in comparison to preheating a feed containing solid biomass in a carrier medium without the presence of an active catalyst and hydrogen because they enable reduced formation of coke and fouling in the equipment.

The term “**biomass**” used herein includes, but is not limited to, algae, lignocellulosic biomass including lignocellulosic biomass components such as cellulose, hemicellulose and/or lignin. The process contemplated herein is particularly suitable and optimized for lignocellulosic biomass and its components. Lignocellulosic biomass is essentially made up of three natural polymers: cellulose, hemicellulose and lignin.

The lignocellulosic starting material in the present invention can be of any type of lignocellulosic material. A non-exhaustive list of examples of the lignocellulosic material includes wood chips and/or saw dust which may have a dry content of 50 wt.-% or more; forestry residue chosen from bark, and/or roots, and/or branches which may have a dry content of 50 wt.-% or more; wood having been subjected to drying; lignocellulose from agriculture like for example straw from crops like oats, wheat, barley and rye, corn stover, grasses and herbs, forage

crops, oat husks, rice husks, construction waste containing at least 50 wt.-% originating from lignocellulosic matter; and mixtures thereof. Prior to being fed to the hydrol liquefaction step the biomass feedstock, may be grinded and/or dried as found suitable by a skilled person by any conventional means found suitable for the purpose to render it processable in the hydrol liquefaction step.

The term “**carrier medium**” used herein refers to a liquid medium into which biomass is added. It can be of renewable based and/or fossil based. A non-exhaustive list of examples of renewable based liquid medium includes vegetable oils and fats, a liquefaction product or fraction thereof, etc. A non-exhaustive list of examples of fossil based liquid medium include VGO, middle distillate, etc.

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

The term “**slurry biomass feed**” used herein refers to a slurry comprising solid biomass, a liquid carrier medium, an active catalyst, and a hydrogen source. The slurry biomass feed is obtained by mixing the solid biomass, the active catalyst and the hydrogen source into the liquid carrier medium in any particular order before being fed to the preheater. For illustration, the active catalyst can be mixed into the liquid carrier medium before the solid biomass, together with the

solid biomass or after the solid biomass has been mixed into the liquid carrier medium. The active catalyst can be mixed into the liquid carrier medium before the hydrogen source is mixed into the liquid carrier medium or together with the hydrogen source. The hydrogen source can be mixed into the liquid carrier medium simultaneously with the solid biomass and the active catalyst or it can be mixed into the liquid carrier medium in which solid biomass and the active catalyst have already been mixed into.

In one embodiment of the invention the slurry biomass feed is obtained by first mixing the solid biomass and the active catalyst into the liquid carrier medium and by then introducing the hydrogen source to the mixture.

In one embodiment of the invention the slurry biomass feed is obtained by simultaneously mixing the solid biomass, the active catalyst and the hydrogen source into the liquid carrier medium.

In one embodiment of the invention the slurry biomass feed is obtained by first mixing the active catalyst into the liquid carrier medium, then mixing the solid biomass into the mixture comprising the active catalyst and the liquid carrier medium, and then introducing the hydrogen source into the mixture.

The terms “**active catalyst**” and “**activated catalyst**” used herein refer to a catalyst in its active form such that it is available for use without the need for any activation steps. In one embodiment the active or activated catalyst is a solid catalyst comprising or composed of one or more metals from IUPAC group 6, 8, 9 and/or 10 of the Periodic Table of Elements. In one embodiment the active or activated catalyst is a solid catalyst comprising or composed of one or more metals from IUPAC group 6, 8 and/or 10 of the Periodic Table of Elements. Preferably the active catalyst is unsupported. The active catalyst can be in a particulate form and is insoluble in a carrier medium such that the active catalyst can be suspended in the carrier medium to form a slurry biomass feed when dispersed in the carrier medium together with the solid biomass material. Unsupported active catalyst can be sulphided catalyst particles suspended in a liquid. Examples of the active catalyst can be a sulphided catalyst comprising at least one of NiMo, CoMo, NiW, NiMoW, Mo and W, and optionally has a median particle size (D50, based on particle size distribution determined by laser diffraction) in the range of from 0.01 μm to 100.00 μm , such as 0.10 μm to 50.00 μm , or 1.00 μm to 50.00 μm .

In one embodiment the active catalyst present in the hydroliquefaction step is an active, sulphided catalyst of NiMo, CoMo, Mo and/or any combination thereof.

In one embodiment the active catalyst present in the hydroliquefaction step is an active hydrogenation catalyst.

The term **“hydrogen source”** refers to any suitable source of hydrogen that can be added to the feed. The hydrogen source can, for example, be a gaseous hydrogen stream or a hydrogen carrier solvent, for example, any known suitable hydrogen donor solvent.

Hydrogen source is introduced to the liquid medium carrier to obtain slurry biomass feed. The introduction of the hydrogen source to the feed is performed before the feed is transferred to a liquefaction reactor via a preheater to prevent formation of coke and/or fouling inside the preheater. Introduction of the hydrogen source can be performed during or after mixing the active catalyst and/or the solid biomass into the liquid carrier medium.

Hydrogen saturated slurry biomass refers to a slurry biomass which contains solid biomass, carrier medium, such as oil, H₂ and active catalyst, such as hydrogenation catalyst, in which the hydrogen content is in the range of about 0.05 wt% to about 15 wt%, preferably the hydrogen content is less than about 10 wt%, more preferably the hydrogen content is less than about 5 wt%.

In an embodiment hydrogen is dissolved into the carrier medium and the obtained slurry biomass feed is a hydrogen saturated slurry biomass feed.

In an embodiment, the slurry biomass feed has a hydrogen content in the range between about 0.05 wt% to 15 wt%.

In an embodiment, the slurry biomass feed has a hydrogen content of less than about 10 wt%.

In an embodiment, the slurry biomass feed has a hydrogen content of less than about 5 wt%.

In an embodiment of the invention the dissolution of hydrogen into the slurry biomass feed is performed by means of a mixer and flashing with gaseous hydrogen.

In an embodiment, the slurry biomass feed is saturated with hydrogen and gaseous hydrogen is separated from the feed flow to minimize equipment sizes and to avoid issues related to flow regimes.

In another embodiment, the slurry biomass feed is to be mixed with gaseous hydrogen.

In an embodiment hydrogen carrier solvent is added to the feed to eliminate the need for gaseous hydrogen altogether.

The term “**preheater**” used herein refers to any equipment suitable for preheating and transferring the slurry biomass feed containing hydrogen and active catalyst to a liquefaction reactor. A person skilled in the art is capable of choosing an arrangement suitable to be used as a preheater.

In an embodiment of the invention, the method further comprises a pre-heating step, wherein the slurry biomass feed containing hydrogen is subjected to a pre-heating step in the preheater. Preferably the pre-heating step is performed by the means of at least one heating step.

In one embodiment the pre-heating step comprises multi-stage heating conducted in respective individual heaters.

In embodiment the temperature of the slurry biomass feed is in the range of about 100 °C to about 300 °C after the pre-heating step. Preferably the temperature of the slurry biomass feed is in the range of about 150 °C to about 250 °C after the pre-heating step.

The term “**residence time**” herein refers to the time the slurry biomass feed containing hydrogen and catalyst stays inside the preheater prior to being transferred to the liquefaction reactor. The residence time according to the invention is from about 1 second to about 5 minutes, preferably from about 2 second to about 1 minute, more preferably from about 3 seconds to about 45 seconds.

The term “**liquefaction reactor**” used herein refers to any reactor suitable for liquefying slurry biomass. For example, liquefaction reactor can be a hydrocracking reactor. Biomass liquefaction is previously known in the art and a person skilled in the art is capable of designing a liquefaction reactor suitable for liquefying slurry biomass feeds.

The method of the present invention can be performed so that slurry biomass feed is processed and/or liquefied in continuous mode.

Figure 1 depicts an embodiment of the invention wherein solid biomass (1) and liquid carrier medium (2) are mixed (3) to obtain slurry biomass feed (10), after which hydrogen source (20) and active catalyst (11) are introduced to the slurry biomass feed (10). This is followed by preheating (30) the slurry biomass feed (10) containing hydrogen and active catalyst (11), which then is followed by liquefaction (40) of the preheated slurry biomass containing hydrogen and catalyst.

Figure 2 depicts an embodiment of the invention, wherein solid biomass (1), liquid carrier medium (2) and active catalyst (11) are mixed (3) to obtain a slurry biomass feed (10) containing active catalyst. A hydrogen source (20) is

then introduced to the slurry biomass feed (10) containing the active catalyst to obtain a slurry biomass feed containing hydrogen. After this the slurry biomass feed containing hydrogen is subjected to preheating (30) followed by liquefaction (40) of the preheated slurry biomass feed containing hydrogen.

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

CLAIMS

1. A method of processing a slurry biomass feed for liquefaction, said method comprising

i) providing a slurry biomass feed comprising solid biomass, a liquid carrier medium, an active catalyst and a hydrogen source,

ii) transferring the slurry biomass feed to a liquefaction reactor via a preheater to obtain a preheated slurry biomass feed, wherein the residence time of the slurry biomass feed containing hydrogen in the preheater is in the range of about 1 second to about 5 minutes, and

iii) liquefying the preheated slurry biomass feed in the liquefaction reactor,

wherein the temperature of the preheated slurry biomass feed is in the range of about 100 °C to about 300 °C.

2. The method according to claim 1, wherein the residence time in ii) is in the range of about 2 seconds to about 1 minute.

3. The method according to any one of the preceding claims, wherein the residence time in ii) is in the range of about 3 seconds to about 45 seconds.

4. The method according to any one of the preceding claims, wherein the active catalyst comprises one or more metals from IUPAC group 6, 8, 9 and/or 10 of the Periodic Table of Elements.

5. The method according to any one of the preceding claims, wherein the active catalyst is an unsupported sulphided NiMo, CoMo, Mo, W and/or any combination thereof.

6. The method according to any one of the preceding claims, wherein the hydrogen source is a gaseous stream.

7. The method according to any one of the preceding claims, wherein the slurry biomass feed is a hydrogen saturated slurry biomass feed.

8. The method according to any one of the preceding claims, wherein the hydrogen content of the slurry biomass feed is in the range of about 0.05 wt% to about 15 wt%, preferably the hydrogen content is less than about 10 wt%, more preferably the hydrogen content is less than about 5 wt%.

9. The method according to any one of the preceding claims, wherein the hydrogen source has been mixed to the slurry biomass feed by the means of a mixer and flashing with gaseous hydrogen.

10. The method according to any one of the preceding claims, wherein the slurry biomass feed is subjected to a pre-heating step in the preheater to

provide the preheated slurry biomass feed.

11. The method according to claim 10, wherein the pre-heating step is performed by means of at least one heating step.

12. The method according to claim 11, wherein the pre-heating step comprises multi-stage heating conducted in respective individual heaters.

13. The method according to any one of the preceding claims, wherein the temperature of the preheated slurry biomass feed is in the range of about 150 °C to about 250 °C.

14. The method according to any one of the preceding claims, wherein the method further comprises feeding additional hydrogen independently into the liquefaction reactor.

15. The method according to any one of the preceding claims, wherein the slurry biomass feed is processed and/or liquefied in continuous mode.

16. The method according to any one of the preceding claims, wherein the active catalyst is an active hydrogenation catalyst.

17. The method according to any one of the preceding claims, wherein the solid biomass is selected from or comprises algae, lignocellulosic biomass, such as wood chips, saw dust, forestry residue, bark, roots, branches, wood, lignocellulose from agriculture, straw, corn stover, grasses and herbs, forage crops, oat husks, rice husks, construction waste, and/or mixtures thereof.

18. The method according to any one of the preceding claims, wherein a liquefied biomass product is obtained by the method.

19. A method for producing a liquefied biomass product wherein the method comprises the method steps according to any one of the claims 1 to 18.