

(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 2013296143 B2**

(54) Title
A method of hydrotreatment and a hydrotreatment system

(51) International Patent Classification(s)
C10G 1/06 (2006.01) **C10G 49/04** (2006.01)
C10G 45/06 (2006.01) **C10L 1/02** (2006.01)
C10G 47/02 (2006.01)

(21) Application No: **2013296143** (22) Date of Filing: **2013.07.24**

(87) WIPO No: **WO14/015380**

(30) Priority Data

(31)	Number	(32)	Date	(33)	Country
	2012903196		2012.07.25		AU

(43) Publication Date: **2014.01.30**

(44) Accepted Journal Date: **2018.03.15**

(71) Applicant(s)
Curtin University of Technology

(72) Inventor(s)
Li, Chun-Zhu;Gunawan, Richard;Gholizadeh, Mortaza;Chaiwat, Weerawut

(74) Agent / Attorney
Griffith Hack, GPO Box 1285, Melbourne, VIC, 3001, AU

(56) Related Art
WO 2012/082401 A2
US 2010228062 A1
US 2011119994 A1
US 4795841 A
US 2010043279 A1
US 4347122 A
WO 2010/049075 A2
US 2009163744 A1



(51) International Patent Classification:

C10G 1/06 (2006.01) *C10G 49/04* (2006.01)
C10G 45/06 (2006.01) *C10L 1/02* (2006.01)
C10G 47/02 (2006.01)

(21) International Application Number:

PCT/AU2013/000825

(22) International Filing Date:

24 July 2013 (24.07.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2012903196 25 July 2012 (25.07.2012) AU

(71) Applicant: CURTIN UNIVERSITY OF TECHNOLOGY [AU/AU]; Kent Street, Bentley, Western Australia 6102 (AU).

(72) Inventors: **LI, Chun-Zhu**; c/- Curtin University of Technology, Kent Street, Bentley, Western Australia 6102 (AU). **GUNAWAN, Richard**; c/- Curtin University of Technology, Kent Street, Bentley, Western Australia 6102 (AU). **GHOLIZADEH, Mortaza**; c/- Curtin University of Technology, Kent Street, Bentley, Western Australia 6102 (AU). **CHAIWAT, Weerawut**; c/- Curtin University of Technology, Kent Street, Bentley, Western Australia 6102 (AU).

(74) Agent: GRIFFITH HACK; Level 19, 109 St Georges Terrace, Perth, Western Australia 6000 (AU).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

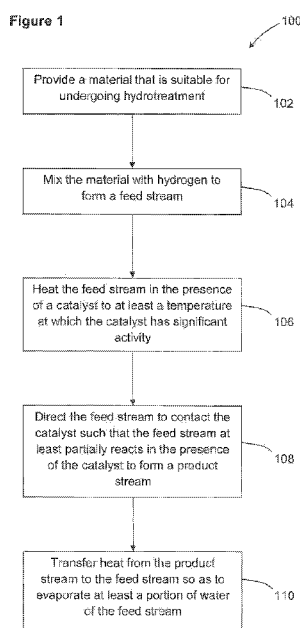
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: A METHOD OF HYDROTREATMENT AND A HYDROTREATMENT SYSTEM

Figure 1



(57) Abstract: A method of hydrotreatment is provided. The method comprises the steps of providing a material that is suitable for undergoing hydrotreatment; mixing the material with a hydrogenation agent to form a feed stream; and heating the feed stream to break chemical bonds of the material in the presence of a catalyst. The feed stream is heated to at least a temperature at which the catalyst can provide activated hydrogen to react with the broken bonds within the material so as to minimise coke formed from the material. A system for conducting the method is also provided.

A METHOD OF HYDROTREATMENT AND A HYDROTREATMENT SYSTEM

Field of the Invention

- 5 The present invention relates to a method of hydrotreatment and a hydrotreatment system.

Background of the Invention

- 10 Biomass can be pyrolysed to form bio-crude, which can in turn be hydrotreated to form biofuel. However, the composition of bio-crude produced from pyrolysing biomass presents particular challenges when undergoing hydrotreatment.

- 15 In particular, bio-crude typically contains high concentrations of oxygen-containing functionalities making the bio-crude highly reactive, polar, acidic and corrosive. This can lead to the formation of coke on a catalyst's surface, including an internal surface of the catalyst, when bio-crude is hydrotreated, which in turn can deactivate the catalyst.

- 20 Further, bio-crude typically has a relatively high concentration of water, which can reduce the energy efficiency of hydrotreating the bio-crude. For example, under typical hydrotreatment conditions, water is likely to be in the gaseous state and therefore a large amount of energy is used in evaporating water from the bio-crude.

25

Summary of the Invention

In accordance with a first aspect of the present invention, there is provided a method of hydrotreatment, the method comprising the steps of:

providing a material comprising a bio-crude that is suitable for undergoing hydrotreatment;

mixing the material with a hydrogen to form a feed stream comprising a mixture of the material and the hydrogen; and

5 heating the feed stream to break chemical bonds of the material in the presence of a catalyst, the feed stream being heated to at least a temperature at which the catalyst can provide activated hydrogen to react with the broken bonds within the material so as to minimise coke formed from the material,

wherein

10 the feed stream is fed directly into a reaction region of a reactor, wherein the reaction region is at a temperature sufficient for the reaction between the material and the hydrogen to occur in the presence of the catalyst to facilitate matching bond-breaking within the material with activated hydrogen provided by the catalyst; and

15 prior to heating the feed stream in the presence of the catalyst, the feed stream is maintained below a predefined temperature at which an amount of coke formed from the material would substantially reduce activity of the catalyst.

Throughout this specification, the term 'hydrogenation agent' is used for hydrogen
20 or any suitable compound that can provide hydrogen for hydrotreatment of the material.

The step of heating the feed stream typically comprises heating the feed stream to a temperature at which the catalyst has significant activity.

25

The feed stream may be heated upon contact with the catalyst, the catalyst having been heated to at least the temperature at which the catalyst has significant activity.

Prior to heating the feed stream in the presence of the catalyst, the feed stream is maintained below a predefined temperature at which an amount of coke formed from the material would substantially reduce activity of the catalyst.

- 5 Heating the feed stream in the presence of the catalyst may provide the advantage of substantially minimising coke formed from the material prior to the material having access to activated hydrogen.

The predefined temperature depends on the material to be hydrotreated; this may
10 be preferably below 150°C for bio-crude (e.g. bio-oil) to be hydrotreated.

In one embodiment, the feed stream is maintained below the predefined temperature by mixing the hydrogenation agent with the material such that the feed stream has a linear velocity sufficient to reduce a residence time of the
15 material in a first region, which may be at or above the predefined temperature, prior to contacting the catalyst in a second region. The first and second regions may be in a hydrotreating reactor.

Reducing the residence time of the material in the first region may have the
20 advantage of limiting the temperature of the material to below the predefined temperature prior to contacting the catalyst.

Further, or alternatively, the feed stream can be maintained below the predefined temperature by directing the feed stream directly into the second region. In one
25 embodiment, the feed stream is directed through a passage that is provided with a feed stream outlet from which the feed stream can flow, the feed stream outlet being arranged at or adjacent the second region such that at least a portion of the feed stream flowing from the feed stream outlet flows directly into the second region.

Directing the feed stream directly into the second region may assist in preventing the material from being heated and undergoing reactions that result in coke formation prior to the feed stream contacting the catalyst. Preventing coke formation prior to the feed stream contacting the catalyst may assist in preventing
5 coke formation on the catalyst, thereby maintaining relatively high catalyst activity.

In one embodiment, a fluid dispersing device is provided at the feed stream outlet so as to disperse or atomise the feed stream as the feed stream flows through the feed stream outlet. Providing a fluid dispersing device may provide the advantage
10 of dispersing the feed stream in such a way so as to promote contact between the feed stream and the catalyst compared to if the fluid dispersing device were not provided. This may facilitate rapid heating of the material to be hydrotreated. The fluid dispersing device may be a distributor or an atomizer.

15 The method may further comprise the steps of:
directing the feed stream to contact the catalyst such that the feed stream at least partially reacts in the presence of the catalyst to form a product stream; and
transferring heat from the product stream to the feed stream.

20 In one embodiment, a hydrogen stream is used to transfer heat from the product stream to the feed stream. The hydrogen stream can be directed such that at least a portion of the hydrogen stream obtains heat from a heat exchanger through which the product stream flows. Heat obtained by the hydrogen stream can then be transferred to the feed stream. In one embodiment, the heat obtained by the
25 hydrogen stream is transferred to the feed stream by mixing the hydrogen stream with the feed stream. The hydrogen stream may also be used in the reaction in the presence of the catalyst, such as by directing the hydrogen towards a region in which the catalyst is located.

If the feed stream comprises water, transferring heat from the product stream to the feed may facilitate evaporating at least a portion of the water of the feed stream.

- 5 The heat exchanger may be a heat exchange coil or other appropriate heat exchange design familiar to those skilled in the field.

In one embodiment, the feed stream passes through a first region to react in a second region, and the resulting product stream is directed to the first region
10 where heat is transferred from the product stream to the feed stream. In one embodiment, the first and second regions are internal to a reactor. In an alternative embodiment, at least a portion of the first region is external to the reactor, and the second region is internal to the reactor. In one embodiment, the product stream is directed to the first region via the second region.

15

The material may be bio-crude. The material may be a biological material, a pharmaceutical material, or any material that can be hydrotreated but that can undergo undesirable reactions in the absence of activated hydrogen provided by a catalyst. The green bio-crude may be obtained from the pyrolysis or hydrothermal
20 treatment or liquefaction of biomass using a variety of ways known to those skilled in the field.

It will be appreciated that the hydrogen may be provided as a gas stream containing hydrogen. One such example is the synthesis gas (mainly CO and H₂)
25 from the gasification/reforming of a solid or liquid fuel.

A variety of hydrotreatment catalysts, known now or in the future, may be used. In one embodiment, the catalyst is a nickel-based catalyst or a cobalt-based catalyst. In one particular example, the catalyst is a NiMo catalyst pre-sulphided or
30 sulphided in situ. In another example, the catalyst is a CoMo catalyst pre-sulphided

or sulphided in situ. In another embodiment, the catalyst (or catalyst mixture) contains catalytic species that can catalyse the *in situ* formation of activated hydrogen from the feed material and/or hydrogenation agent including a hydrogen-containing gas stream. It may be advantageous if the catalytic species can

5 catalyse the formation of activated hydrogen at low temperature. One such example is the catalytic species that can catalyse the water-gas-shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$) in the forward and/or backward directions.

In accordance with an embodiment, there is provided a method of hydrotreatment,

10 the method comprising the steps of:

directing a feed stream to contact a catalyst such that the feed stream at least partially reacts in the presence of the catalyst to form a product stream, the feed stream comprising a material that is suitable for undergoing hydrotreatment and a hydrogenation agent; and

15 transferring heat from the product stream to the feed stream.

The hydrogenation agent may be hydrogen or a hydrogen-containing reactant.

Transferring heat from the product stream to the feed stream may increase an

20 energy efficiency of the method compared to if the heat transfer did not occur. If the feed stream comprises water, transferring heat from the product stream to the feed may facilitate evaporating at least a portion of the water of the feed stream.

Further, transferring heat from the product stream to the feed stream may facilitate

25 quenching the product stream, thereby minimising decomposition of the product stream.

The feed stream may pass through a first region to a second region in which the catalyst is located, the second region being at at least a temperature at which the

30 catalyst has significant activity.

In one embodiment, a hydrogen stream is used to transfer heat from the product stream to the feed stream. It will be appreciated that the hydrogen stream that is used to transfer heat from the product stream to the feed stream may be a stream
5 of hydrogen that is different from the hydrogen of the feed stream. The hydrogen stream can be directed such that at least a portion of the hydrogen stream obtains heat from a heat exchanger through which the product stream flows. Heat obtained by the hydrogen stream may then be transferred to the feed stream. In one
10 embodiment, the heat obtained by the hydrogen stream is transferred to the feed stream by mixing the hydrogen stream with the feed stream. The hydrogen stream may also be used in the reaction in the presence of the catalyst, such as by directing the hydrogen to the second region.

The heat exchanger may be a heat exchange coil or other appropriate heat exchange design familiar to those skilled in the field.

15

In one embodiment, the feed stream passes through the first region to react in the second region, and the resulting product stream is directed to the first region where heat is transferred from the product stream to the feed stream. In one
embodiment, the first and second regions are internal to a reactor. In an alternative
20 embodiment, at least a portion of the first region is external to the reactor, and the second region is internal to the reactor. In one embodiment, the product stream is directed to the first region from or via the second region.

The method may further comprise the step of heating the feed stream to break
25 chemical bonds of the material in the presence of a catalyst, the feed stream being heated to at least a temperature at which the catalyst can provide activated hydrogen to react with the broken bonds within the material so as to minimise coke formed from the material.

The feed stream may be heated upon contact with the catalyst, the catalyst having been heated to at least the temperature at which the catalyst has significant activity.

- 5 In one embodiment, the method comprises the step of, prior to heating the feed stream in the presence of the catalyst, maintaining the feed stream below a predefined temperature at which an amount of coke formed from the material would substantially reduce activity of the catalyst.
- 10 The predefined temperature depends on the material to be hydrotreated; this may be preferably below 150°C for bio-crude (e.g. bio-oil) to be hydrotreated.

- In one embodiment, the feed stream is maintained below the predefined temperature by mixing the hydrogen with the material such that the feed stream
- 15 has a linear velocity sufficient to reduce a residence time of the material in a first region prior to contacting the catalyst in a second region.

- Further, or alternatively, the feed stream can be maintained below the predefined temperature by directing the feed stream directly into the second region. In one
- 20 embodiment, the feed stream is directed through a passage that is provided with a feed stream outlet from which the feed stream can flow, the feed stream outlet being arranged at or adjacent the second region such that at least a portion of the feed stream flowing from the feed stream outlet flows directly into the second region.

25

In one embodiment, a fluid dispersing device is provided at the feed stream outlet so as to disperse or atomise the feed stream as the feed stream flows through the feed stream outlet. The fluid dispersing device may be a distributor or an atomizer.

The material may be bio-crude. The material may be a biological material, a pharmaceutical material, or any material that can be hydrotreated but that can undergo undesirable reactions in the absence of activated hydrogen provided by a catalyst. The green bio-crude may be obtained from the pyrolysis or hydrothermal
5 treatment or liquefaction of biomass using a variety of ways known to those skilled in the field.

It will be appreciated that the hydrogen may be provided as a gas stream containing hydrogen. One such example is the synthesis gas (mainly CO and H₂)
10 from the gasification/reforming of a solid or liquid fuel.

A variety of hydrotreatment catalysts, known now or in the future, may be used. In one embodiment, the catalyst is a nickel-based catalyst or a cobalt-based catalyst. In one particular example, the catalyst is a NiMo catalyst pre-sulphided or
15 sulphided in situ. In another example, the catalyst is a CoMo catalyst pre-sulphided or sulphided in situ. In another embodiment, the catalyst (or catalyst mixture) contains catalytic species that can catalyse the *in situ* formation of activated hydrogen from the feed material and/or hydrogenation agent including a hydrogen-containing gas stream. It may be advantageous if the catalytic species can
20 catalyse the formation of activated hydrogen at low temperature. One such example is the catalytic species that can catalyse the water-gas-shift reaction (CO + H₂O = H₂ + CO₂) in the forward and/or backward directions.

In accordance with another aspect of the present invention, there is provided a
25 hydrotreatment system comprising:

- a reaction region in which a catalyst is located;
- a first input for providing a material comprising a bio-crude that is suitable for undergoing hydrotreatment;

a second input for providing a hydrogen stream for forming a feed stream when mixed with the material, the feed stream comprising a mixture of the material and the hydrogen;

5 a feed stream passage arranged to receive the material and the hydrogen stream, the feed stream passage further being arranged to direct the resulting feed stream to the reaction region in which the catalyst is located;

a heat source for providing heat to the reaction region so as to heat the feed stream to break chemical bonds of the material in the presence of the catalyst, the feed stream being heated to at least a temperature at which the catalyst can
10 provide activated hydrogen to react with the broken bonds within the material so as to minimise coke formed from the material; and

an outlet stream passage for products and any unreacted components of the feed stream to exit the hydrotreatment system,

wherein the system is arranged so that:

15 the feed stream is fed directly into the reaction region of a reactor, wherein the reaction region is at a temperature sufficient for the reaction between the material and the hydrogenation to occur in the presence of the catalyst to facilitate matching bond-breaking within the material with activated hydrogen provided by the catalyst; and

20 prior to heating the feed stream in the presence of the catalyst, the feed stream is maintained below a predefined temperature at which an amount of coke formed from the material would substantially reduce activity of the catalyst.

The hydrogenation agent is hydrogen or a hydrogen-containing reactant.

25

It will be appreciated that the heat source may be provided by exothermic reactions that occur during hydrotreatment of the material.

In accordance with an embodiment, there is provided a hydrotreatment system
30 comprising:

a reaction region in which a catalyst is located;

a feed stream passage arranged to direct a feed stream to contact the catalyst located in the reaction region such that the feed stream at least partially reacts in the presence of the catalyst to form a product stream, the feed stream comprising a material that is suitable for undergoing hydrotreatment and a hydrogenation agent;

a heat exchanger arranged to receive the product stream and to transfer heat from the product stream to the feed stream; and

an outlet stream passage for products and any unreacted components of the feed stream to exit the hydrotreatment system.

The hydrogenation agent may be hydrogen or a hydrogen-containing reactant.

The material of the system may be bio-crude. The material of the system may be a biological material, a pharmaceutical material, or any material that can be hydrotreated but that can undergo undesirable reactions in the absence of activated hydrogen provided by a catalyst. The green bio-crude may be obtained from the pyrolysis or hydrothermal treatment or liquefaction of biomass using a variety of ways known to those skilled in the field.

A variety of hydrotreatment catalysts, known now or in the future, may be used. In one embodiment, the catalyst is a nickel-based catalyst or a cobalt-based catalyst. In one particular example, the catalyst is a NiMo catalyst pre-sulphided or sulphided in situ. In another example, the catalyst is a CoMo catalyst pre-sulphided or sulphided in situ. In another embodiment, the catalyst (or catalyst mixture) contains catalytic species that can catalyse the *in situ* formation of activated hydrogen from the feed material and/or hydrogenation agent including a hydrogen-containing gas stream. It may be advantageous if the catalytic species can catalyse the formation of activated hydrogen at low temperature. One such

example is the catalytic species that can catalyse the water-gas-shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$) in the forward and/or backward directions.

It will be appreciated that the hydrogen may be provided as a gas stream
5 containing hydrogen. One such example is the synthesis gas (mainly CO and H_2) from the gasification/reforming of a solid or liquid fuel.

The system may be a standalone system, or the system may be a component of a further system, such as a petro-refinery system.

10

Brief Description of the Figures

Embodiments of the present disclosure will now be described, by way of example only, with reference to the accompanying figures, in which:

15

Figure 1 is a flow diagram of a method of hydrotreatment in accordance with an embodiment of the present disclosure; and

Figure 2 is a schematic diagram of a hydrotreatment system in accordance
20 with an embodiment of the present disclosure.

Detailed Description

Figure 1 shows a method 100 of hydrotreatment. The method 100 is generally
25 directed to reacting a material that is suitable for undergoing hydrotreatment with hydrogen in the presence of a catalyst. In the following description, the material is bio-crude from biomass pyrolysis, although it will be appreciated that the material may, for example, be green crude obtained from treating biomass in water, a biological material, a pharmaceutical material, or any material that can be
30 hydrotreated but that can undergo undesirable reactions in the absence of activated

hydrogen provided by a catalyst.

In this example, the method 100 particularly involves feeding a mixture of the material and hydrogen (also referred to as a feed stream) directly into a reaction region of a reactor, wherein the reaction region is at a temperature sufficient for the reaction
5 between the material and the hydrogen to occur in the presence of a hydrotreating catalyst.

Feeding the mixture of the material and hydrogen rapidly and directly into the
10 reaction region facilitates matching bond-breaking within the material with active hydrogen provided by the hydrotreating catalyst. This can prevent the material from forming coke on the catalyst (including its internal surface), which in turn prevents an activity level of the catalyst from being reduced.

15 In contrast, conventional hydrotreatment methods typically comprise heating the material to a level at which coke may form prior to the material having access to the activated hydrogen.

After the material has reacted with the hydrogen in the presence of the catalyst, a
20 resulting product stream, which is at a relatively high temperature after passing through the reaction region, is directed to a heat exchanger. The heat exchanger facilitates removing heat from the product stream, such as by condensing the product stream, and transfers heat removed from the product stream to the feed stream.

25 Removing heat from the product stream can facilitate reducing the temperature of the product stream, thereby preventing products formed from the hydrotreatment process undergoing any further undesirable thermal reactions that may degrade the quality of the products. In a conventional hydrotreatment system, heat may be removed from the product stream from inside the reactor to a region external to the reactor. Given
30 that the reactor may be a high pressure reactor having a relatively thick wall, heat

transfer across the wall may be slower than desired and may be a rate-limiting step.

Transferring heat from the product stream to the feed stream as per the method 100 facilitate the relatively rapid removal of heat from the product stream.

5

Transferring heat to the feed stream can also facilitate increasing the energy efficiency of the method of hydrotreatment 100. For example, if the material has a relatively high concentration of water, then under hydrotreatment conditions the water is likely to be in the gaseous state as the temperature may be a relatively high temperature at which the catalyst can provide activated hydrogen, such as 375°C or higher. Therefore, in heating up the material to this temperature, the water contained in the material will evaporate, requiring a large amount of energy. In some cases, the latent heat of evaporation for water (approximately 2258 kJ/kg) can be greater than the sensible heat (approximately 4.18 kJ/kg °C) required to heat the water to the reaction temperature. As mentioned above, the reactor will typically have a relatively thick wall, and therefore supplying energy across the reactor wall to heat up the feed bio-crude and evaporate its water may become a rate-limiting step.

10

15

20

In the embodiment of the method 100, heat transferred from the product stream to the feed stream can facilitate evaporating water of the material, and in heating the feed stream close to the reaction temperature generally. This reduces an amount of heat that is required to be supplied from a heat source, such as a heat source external to the reactor.

25

Specific steps of the method 100 will now be described. In the example illustrated in Figure 1, the method 100 comprises a first step 102 of providing a material that is suitable for undergoing hydrotreatment. As mentioned, the material in this example is bio-crude, although it will be appreciated that the material may be any material that is desired to undergo hydrotreatment.

30

In a second step 104, the material is mixed with hydrogen to form a feed stream. The feed stream is then, in a third step 106, heated in the presence of a catalyst to at least a temperature at which the catalyst has significant activity.

5

The feed stream is directed in a fourth step 108 to contact the catalyst such that the material and hydrogen of the feed stream at least partially react in the presence of the catalyst to form a product stream.

10 It will be appreciated that steps 106 and 108 may be combined into one step.

In a fifth step 110, heat is transferred from the product stream to the feed stream so as to evaporate at least a portion of water of the feed stream and also to heat up the feed stream.

15

An example hydrotreatment system 200 that is arranged to conduct the method of hydrotreatment 100 is illustrated in Figure 2 and will now be described.

20 The hydrotreatment system 200 comprises a reactor 202 in which a material that is suitable for undergoing hydrotreatment reacts with hydrogen (or hydrogen-containing reactants such as a mixture containing mainly CO and H₂) in the presence of a catalyst. As mentioned, in this example the material is bio-crude.

25 A catalyst 204 is located within a reaction region 206 of the reactor 202. In this example the catalyst 204 is a pre-sulphided NiMo catalyst, although it will be appreciated that the catalyst 204 may be any appropriate catalyst (or a catalyst mixture) for the reaction between the bio-crude and the hydrogen. For example, the catalyst may be a nickel-based catalyst or a cobalt-based catalyst. In one particular example, the catalyst is a NiMo catalyst pre-sulphided or sulphided in
30 situ. In another example, the catalyst is a CoMo catalyst pre-sulphided or

5 sulphided *in situ*. Mixed catalysts may also be used. In another example, the catalyst (or catalyst mixture) contains catalytic species that can catalyse the *in situ* formation of activated hydrogen from the feed material and/or hydrogenation agent including a hydrogen-containing gas stream. It will be advantageous if the catalytic species can catalyse the formation of activated hydrogen at low temperature. One such example is the catalytic species that can catalyse the water-gas-shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$) in the forward and/or backward directions.

10 In this example, the bio-crude is input, corresponding to step 102 of the method 100, into the hydrotreatment system 200 via a first input 208. The hydrogen is input as a first hydrogen stream via a second input 210.

15 The bio-crude and the first hydrogen stream are mixed (step 104) to form a feed stream as they enter a feed stream passage 212. The feed stream passage 212 functions to direct the feed stream through a heat exchange region 214 of the reactor 202 to be dispersed through an outlet 216. A further catalyst may be arranged in the heat exchange region 214. Alternatively, the heat exchange region 214 may be at least partially filled with an inert solid or may be empty apart from other functional components of the system 200.

20 The outlet 216 is a fluid dispersing device arranged to disperse or atomise the feed stream as the feed stream flows through the outlet 216 and may be a distributor or an atomizer. The outlet 216 disperses the feed stream into the reaction region 206 of the reactor 202.

25 A second stream of hydrogen is input to the hydrotreatment system 200 via a third input 218. The second stream of hydrogen is then directed via a hydrogen stream passage 219 through the heat exchange region 214 to the reaction region 206 of the reactor 202. The second stream of hydrogen functions, amongst other things, to transfer heat (step 110) from a product stream produced by the hydrotreatment

30

system 200 to the feed stream. This process will be described in more detail later.

The second stream of hydrogen mixes with the feed stream in the reaction region 206 of the reactor 202, and provides additional hydrogen for hydrogenation so as to
5 react with the bio-crude in the method of hydrotreatment 100.

The feed stream, the general direction of flow of which is indicated by arrows 220, is heated (step 106) to at least a temperature at which the catalyst 204 has significant activity. In this example, the heat is provided by a heat source 222 arranged to supply
10 heat to the reaction region 206. The feed stream may be heated indirectly by the heat source 222 when the feed stream comes into contact with the catalyst 204.

The feed stream is directed (step 108) to contact the catalyst 204 such that the bio-crude and the hydrogen of the feed stream react in the presence of the catalyst 204
15 to form a product stream.

Upon contacting the catalyst 204, which in this example is at an elevated temperature, the bio-crude and hydrogen are heated up rapidly to the reaction temperature. The fluid of bio-crude and hydrogen mixture will then flow along a
20 length of the reactor 202 while the bio-crude is continuously hydrotreated to form the product stream.

The product stream, a direction of which is indicated by arrows 224, is directed into a product stream passage (or a bank of passages) 226 that is of a relatively small diameter. The product stream passage 226 directs the product stream to a heat
25 exchange coil 228. The heat exchange coil 228 is located in the heat exchange region 214 and is arranged to facilitate condensing the product stream to a liquid, thereby removing heat from the product stream. Taking the reaction product stream through the relatively small diameter product stream passage 226 and heat
exchange coil 228 directly from the hot reaction region 206 and quenching the
30 product stream rapidly facilitates preventing thermal decomposition of the

hydrotreated products, which would tend to degrade the quality of the products.

The heat is transferred (step 110) to the second hydrogen stream as the second hydrogen stream flows through the heat exchange region 214. The second hydrogen stream is then able to transfer heat obtained from the heat exchange coil 228 to the feed stream, for example when the second hydrogen stream mixes with the feed stream.

The second hydrogen stream provides a number of functions in the method of hydrotreatment 100. As the second hydrogen stream flows through the hydrogen stream passage 219, the second hydrogen stream will flow around an outside of the feed stream passage 212 carrying the bio-crude – hydrogen mixture. This can facilitate preventing the feed stream mixture from being heated to an elevated temperature before the feed stream mixture comes into contact with the catalyst 204. Otherwise, excess coke formation could result.

Further, and as mentioned, the second hydrogen stream will flow around the heat exchange coil 228. With its high heat conductivity, the second hydrogen stream will effectively cool down the hydrotreated product stream flowing inside the heat exchange coil 228, and transfer heat from the product stream to the reaction region 206 inside the reactor 202 where the bio-crude and hydrogen mixture contact the catalyst 204. This is the region of high heat demand where the bio-crude is heated up and the bio-crude's water is evaporated.

The second hydrogen stream will also mix with the feed stream of bio-crude and hydrogen to become part of hydrogen required by the hydrotreating reactions.

The now condensed and cooled product stream then flows from the hydrotreatment system 200 via a product stream outlet 230 and the product stream can be processed further or used as a bio-fuel.

As described above, the method 100 and the system 200 provide the advantages of reducing coke formation and increasing the energy efficiency of hydrotreatment process.

5

With respect to minimising coke formation, experiments using some features of the system 200 illustrated in Figure 2 have been carried out for the hydrotreatment of bio-crude at various scales in the laboratory.

- 10 Using a pre-sulphided NiMo catalyst, the system 200 has been shown to effectively minimise the coke formation on the catalyst surface by matching the bond-breaking with the supply of active hydrogen.

15 Firstly, the system 200 can effectively prevent the bio-crude from being heated up to elevated temperatures before it comes into contact with the catalyst 204 that can supply active hydrogen. As is shown in Figure 2, the bio-crude feed is mixed with hydrogen gas at room (or relatively low) temperature. The addition of hydrogen to the bio-crude feed is to increase the linear velocity (and thus to decrease its residence time) of bio-crude inside the feed stream passage 212 to prevent the bio-crude from being heated up to elevated temperatures before coming into contact with the catalyst.

20 Secondly, the bio-crude will be heated up rapidly only when it is in contact with the catalyst – hydrogen system. This means that free radicals formed from the breakdown of bio-crude molecules will have immediate access to active hydrogen generated at/on the catalyst surface. As was discussed above, this effectively minimises the formation of coke. With this arrangement, the catalyst 204 can be heated and maintained at relatively high temperatures. For example the pre-sulphided NiMo catalyst could be maintained up to 375°C and higher, at which the catalyst is sufficiently active to generate abundant active hydrogen (e.g. hydrogen atoms) to stabilise the radicals, without significant coke formation.

25

30

With respect to increasing energy efficiency of the hydrotreatment process, as shown in Figure 2, the hot hydrotreatment product stream will flow through the heat exchange coil 228 to be cooled down before exiting the system 200. The second
5 stream of hydrogen, which is relatively cold, flows outside the heat exchange coil 228. The heat released from the condensation of steam in the product stream and that released from the cooling down of the hot products will be transferred to the catalyst or inert solid or flowing gas in region 214, which will then be transferred to the catalyst 204 in a region of the reactor 202 where relatively cold bio-crude comes
10 in. Through this arrangement of an internal heat exchange system, a substantial fraction of the heat released from the product stream is used to heat up the feed steam as well as to evaporate the water in the feed stream. This represents an effective management of heat supply and demand within the hydrotreatment system 200, thereby increasing its energy efficiency.

15

The method 100 and system 200 can facilitate overcoming some problems encountered in the hydrotreatment of bio-crude, particularly the aforementioned issues of coke formation on the catalyst's surface and energy efficiency. It is with this method 100 and system 200 that a commercially available sulphided NiMo catalyst
20 can be used to hydrotreat bio-crude to produce liquid "drop-in" biofuels that are miscible with petrol/gasoline and/or diesel. This is advantageous in the field of biorefining, contributing to making liquid biofuels commercially competitive.

In addition to the bio-crude from the pyrolysis of biomass, there are many other
25 thermally instable materials that require thermochemical treatment/processing at elevated temperatures. For example, green crude produced from the treatment of biomass in supercritical/subcritical water could also be hydrotreated using the method 100 and system 200 described herein.

30 The method 100 and system 200 may also find applications for the thermochemical

treatment of biological/pharmaceutical materials or any other heat-sensitive materials, which is prone to form coke or undergo other side reactions in the absence of another reactant such as hydrogen.

- 5 Numerous variations and modifications will suggest themselves to persons skilled in the relevant art, in addition to those already described, without departing from the basic inventive concepts. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the foregoing description.

10

For example, it will also be appreciated that, although the transfer of heat from the product stream to the feed stream has been described as occurring internal to the reactor 202, the system 200 may be arranged such that at least a portion of the heat transfer process occurs external to the reactor. For example, the heat exchange coil
15 228 may be located external to the reactor 202, and at least a portion of the second hydrogen stream may flow around the heat exchange coil 228 to obtain heat therefrom before being directed into the reaction region 206 where the second hydrogen stream can transfer heat to the feed stream.

- 20 In the description of the invention, except where the context requires otherwise due to express language or necessary implication, the words "comprise" or variations such as "comprises" or "comprising" are used in an inclusive sense, i.e. to specify the presence of the stated features, but not to preclude the presence or addition of further features in various embodiments of the invention.

Claims:

1. A method of hydrotreatment, the method comprising the steps of:
providing a material comprising bio-crude that is suitable for undergoing
5 hydrotreatment;
mixing the material with a hydrogen to form a feed stream comprising a
mixture of the material and the hydrogen; and
heating the feed stream to break chemical bonds of the material in the
presence of a catalyst, the feed stream being heated to at least a temperature at
10 which the catalyst can provide activated hydrogen to react with the broken bonds
within the material so as to minimise coke formed from the material,
wherein:
the feed stream is fed directly into a reaction region of a reactor, wherein the
reaction region is at a temperature sufficient for the reaction between the material
15 and the hydrogen to occur in the presence of the catalyst to facilitate matching
bond-breaking within the material with activated hydrogen provided by the catalyst;
and
prior to heating the feed stream in the presence of the catalyst, the feed
stream is maintained below a predefined temperature at which an amount of coke
20 formed from the material would substantially reduce activity of the catalyst.
2. The method of claim 1, wherein the feed stream is heated upon contact with
the catalyst, the catalyst having been heated to at least the temperature at which
the catalyst can provide activated hydrogen to react with the broken bonds within
25 the material so as to minimise coke formed from the material.
3. The method of claim 1 or claim 2, wherein the feed stream is maintained
below the predefined temperature by mixing the hydrogen with the material such
that the feed stream has a linear velocity sufficient to reduce a residence time of

the material in a first region, which is at or above the predefined temperature, prior to contacting the catalyst in the reaction region.

4. The method of claim 3, wherein the feed stream is directed through a
5 passage that is provided with a feed stream outlet from which the feed stream can flow, the feed stream outlet being arranged at or adjacent the reaction region such that at least a portion of the feed stream flowing from the feed stream outlet flows directly into the reaction region.

10 5. The method of claim 4, wherein a fluid dispersing device is provided at the feed stream outlet so as to disperse or atomise the feed stream as the feed stream flows through the feed stream outlet.

6. The method of any one of the preceding claims further comprising the steps
15 of:
directing the feed stream to contact the catalyst such that the feed stream at least partially reacts in the presence of the catalyst to form a product stream; and transferring heat from the product stream to the feed stream.

20 7. The method of claim 6, wherein a hydrogen stream is used to transfer heat from the product stream to the feed stream.

8. The method of claim 7, wherein the hydrogen stream is directed such that at least a portion of the hydrogen stream obtains heat from a heat exchanger through
25 which the product stream flows.

9. The method of claim 7 or claim 8, wherein heat obtained by the hydrogen stream is transferred to the feed stream by mixing the hydrogen stream with the feed stream.

10. The method of any one of claims 7 to 9, wherein the hydrogen stream is used in the reaction in the presence of the catalyst.

11. The method of any one of claims 6 to 10, wherein the feed stream passes
5 through the first region to react in the reaction region, and the resulting product stream is directed to the first region where heat is transferred from the product stream to the feed stream.

12. The method of claim 11, wherein the first and reaction regions are internal
10 to a reactor.

13. The method of claim 11, wherein at least a portion of the first region is external to a reactor, and the reaction region is internal to the reactor

14. The method of any one of claims 11 to 13, wherein the product stream is
15 directed to the first region via the reaction region.

15. The method of any one of the preceding claims, wherein the catalyst is a nickel-based catalyst or a cobalt-based catalyst.
20

16. The method of claim 15, wherein the catalyst is a NiMo catalyst pre-sulphided or sulphided in situ, or a CoMo catalyst pre-sulphided or sulphided in situ.

17. The method of claim 16, wherein the catalyst contains catalytic species that
25 can catalyse the *in situ* formation of activated hydrogen from the feed material and/or hydrogen.

18. A hydrotreatment system comprising:
30 a reaction region in which a catalyst is located;

a first input for providing a material comprising bio-crude that is suitable for undergoing hydrotreatment;

a second input for providing a hydrogen stream for forming a feed stream when mixed with the material, the feed stream comprising a mixture of the material
5 and the hydrogen;

a feed stream passage arranged to receive the material and the hydrogen stream, the feed stream passage further being arranged to direct the resulting feed stream to the reaction region in which the catalyst is located;

a heat source for providing heat to the reaction region so as to heat the feed
10 stream to break chemical bonds of the material in the presence of the catalyst, the feed stream being heated to at least a temperature at which the catalyst can provide activated hydrogen to react with the broken bonds within the material so as to minimise coke formed from the material; and

an outlet stream passage for products and any unreacted components of
15 the feed stream to exit the hydrotreatment system,

wherein the system is arranged so that:

the feed stream is fed directly into the reaction region of a reactor, wherein the reaction region is at a temperature sufficient for the reaction between the material and the hydrogenation to occur in the presence of the catalyst to facilitate
20 matching bond-breaking within the material with activated hydrogen provided by the catalyst; and

prior to heating the feed stream in the presence of the catalyst, the feed stream is maintained below a predefined temperature at which an amount of coke formed from the material would substantially reduce activity of the catalyst.

25

19. The system of claim 18, wherein the heat source is provided by exothermic reactions that occur during hydrotreatment of the material.

20. The system of claim 18 or claim 19, wherein the catalyst is a NiMo catalyst pre-sulphided or sulphided in situ, or the catalyst is a CoMo catalyst pre-sulphided or sulphided in situ.
- 5 21. The system of claim 20, wherein the catalyst contains catalytic species that can catalyse the *in situ* formation of activated hydrogen from the feed material and/or hydrogen.
22. The system of any one of claims 18 to 21, wherein the system is a
10 component of a further system, such as a petro-refinery system.

1 / 2

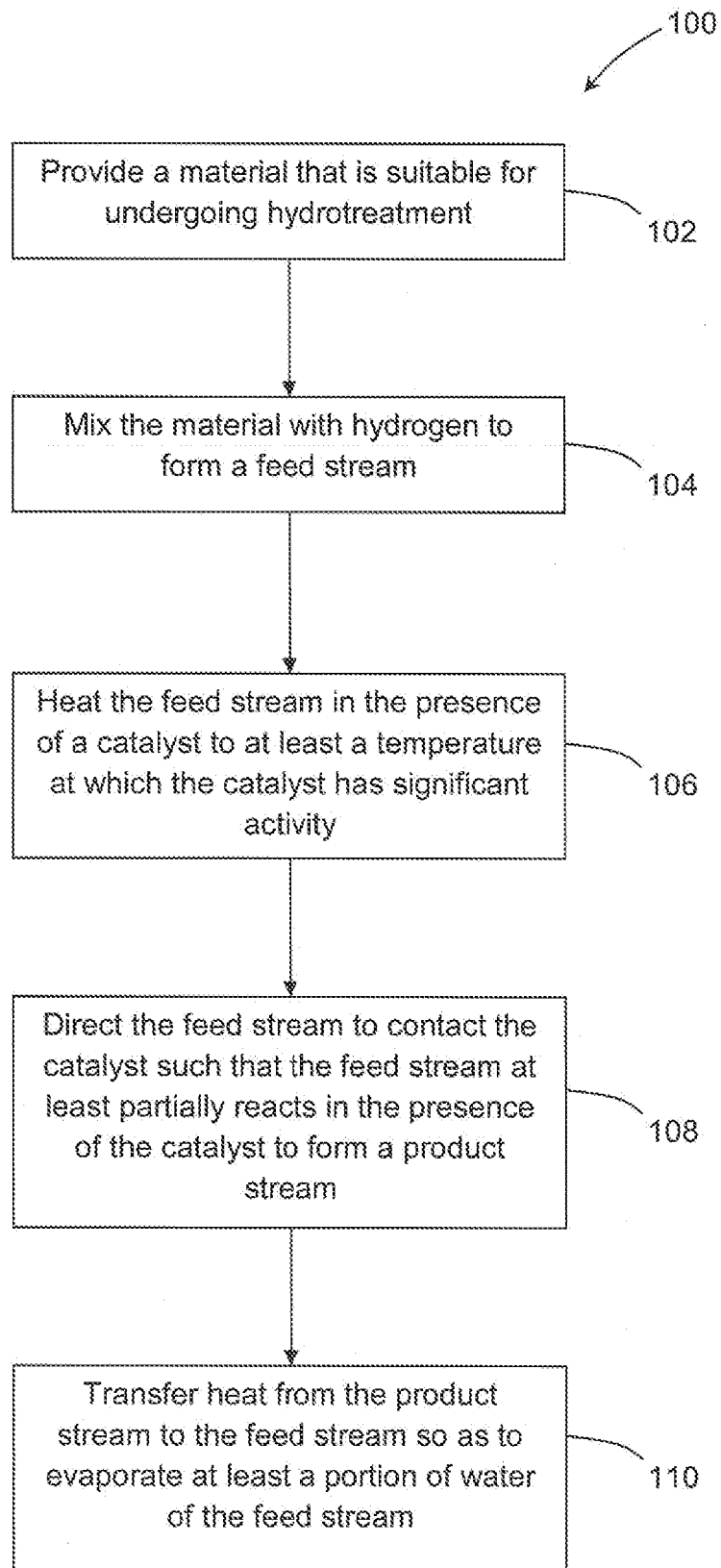


Figure 1

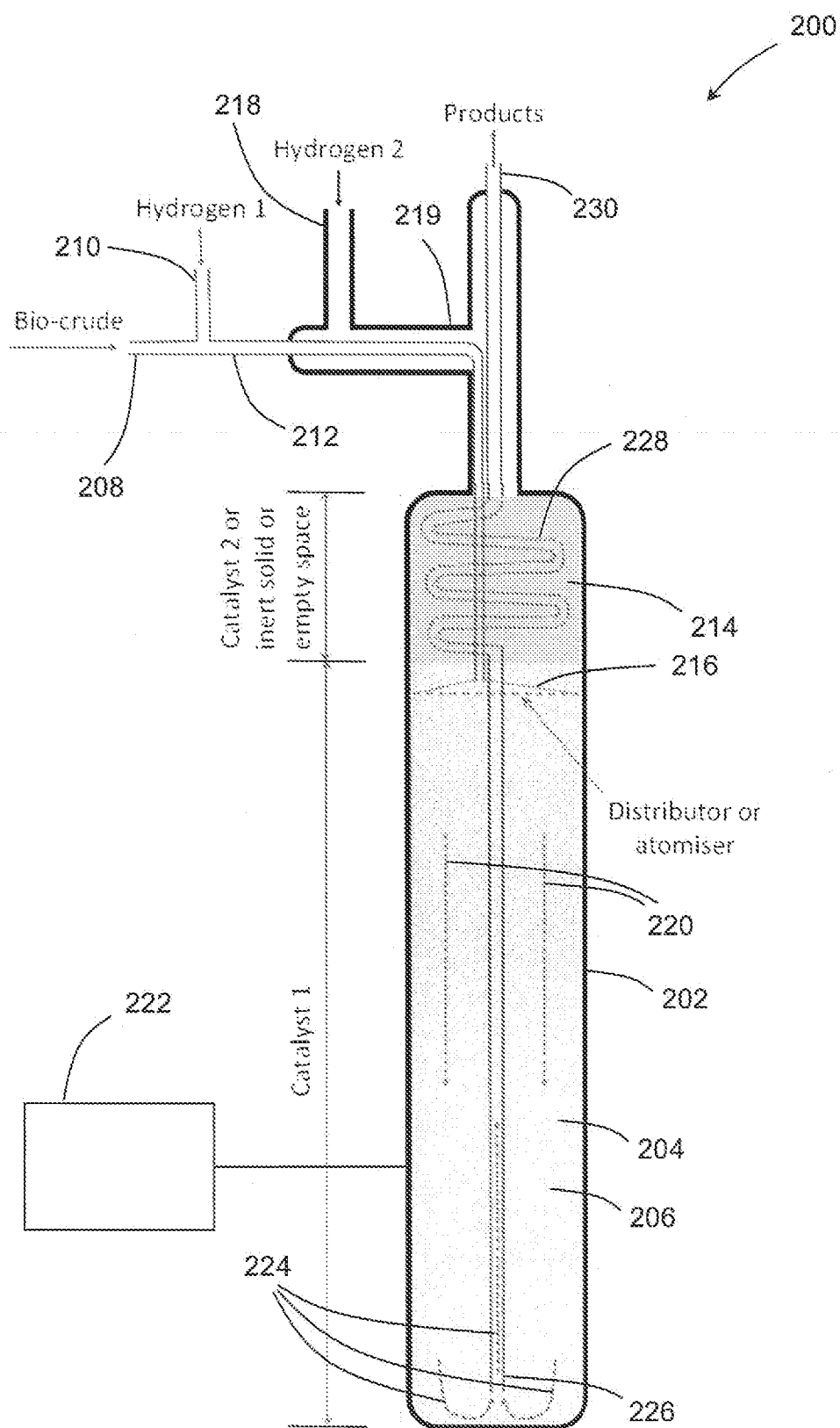


Figure 2