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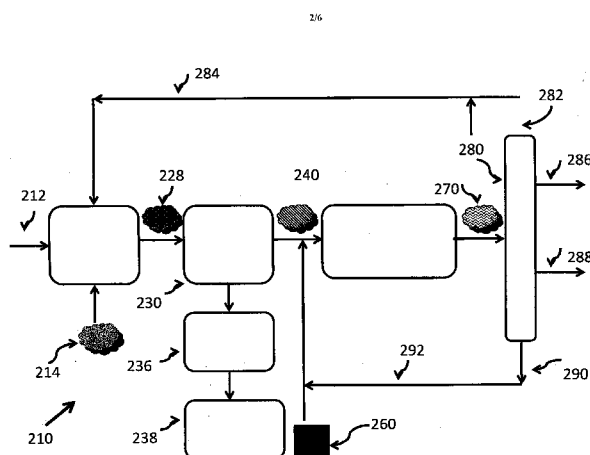
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(54) Title: A PROCESS FOR INTEGRATION OF A METHANOL PLANT AND AN OIL HYDROPROCESSING PLANT



(57) Abstract: The invention relates to a system for integrating methanol production and hydroprocessing of oil feedstock comprising: a first feedstock comprising hydrocarbons that is fed to a steam reformer to produce synthesis gas comprising carbon monoxide and excess hydrogen; a methanol reactor configured to produce methanol from the synthesis gas, an oil hydroprocessing reactor configured to receive the excess hydrogen; a second feedstock comprising an oil that is fed to the hydroprocessing reactor and mixed with the excess hydrogen for use in hydroprocessing reactions to produce a hydrocarbon product from the oil.

***A process for integration of a methanol plant and an oil
hydroprocessing plant***

Incorporation by cross-reference

- 5 [0001] This application claims priority from NZ provisional application no. 577464 filed on 8 June 2009, NZ provisional application no. 578435 filed 16 July 2009, and NZ provisional application no. 580652 filed on 27 October 2009, each of which is incorporated herein by cross-reference in its entirety.

10 **Technical field**

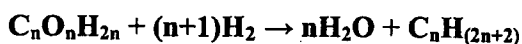
- [0002] The present invention relates generally to the field of fuel production and in particular renewable fuel production. More specifically, the invention relates to a process for integrating an oil hydroprocessing plant with a methanol processing plant for the improved generation of fuel products. In particular, the present invention relates to recycling hydrogen produced by a steam reformer of a methanol processing plant into an oil hydroprocessing plant for the catalytic hydroprocessing of oils and/or recycling hydrocarbon products produced by an oil hydroprocessing plant into the steam reformer for the production of methanol.

20 **Background**

- [0003] The current market value of transportation fuels, such as diesel and jet fuel, is high due to the depletion of accessible fossil fuel supplies. Fossil fuels, such as world crude oil reserves, are being rapidly depleted raising global concerns regarding the future supply or potential shortages of such fuel sources. Furthermore, reduced fossil fuel supply is likely to have an economic impact by leading to further increases in the cost of such fuel. In addition, the combustion of transportation fuels produced by the refining of crude oil releases carbon dioxide into the atmosphere, which is known as a "green house" gas (GHG), and is considered to be contributing to the global climate change. Crude oil contains sulfur and nitrogen-containing compounds that also adversely affect the environment.

- 30 [0004] In recent years there has been increased interest in processes for producing bio-fuels from renewable animal and/or plant sources. Transportation grade bio-fuels are generally refined from bio-oils generated from renewable biomass sources such as trees, forestry waste, corn waste, algae, crops, landfill gas, garbage, vegetable oils (e.g. palm oil) and waste products from animal processing (e.g. tallow).

[0005] In a conventional refinery based on a crude oil feedstock a hydroprocessing step is used to remove sulphur and hydrogenate aromatic structures to produce a high quality transportation fuel. However, most bio-oils and coal-oils contain relatively high concentrations of oxygen containing hydrocarbons and low levels of sulfur containing structures. Thus, the hydroprocessing step required for a bio-oil or coal oil feedstock is a catalytic hydrodeoxygenation step to remove the oxygen from the hydrocarbon structures. The following is an example of a hydrodeoxygenation reaction:



Large amounts of hydrogen are consumed in the hydrodeoxygenation step making this process expensive. In addition, aromatic hydrocarbon structures also exist in many bio-oil and coal-oil feedstocks which need to be hydrogenated to improve the transportation fuel quality.

[0006] There have been a number of patents describing processes to produce bio-fuels or fuel additives from animal or plant oils in recent times.

[0007] For example, United States patent publication no. 2006/0207166 (Herskowitz et al.) describes a process for producing a bio-fuel from vegetable and/or animal oil using a single step hydrodeoxygenation and hydroisomerisation reaction.

[0008] United States patent publication no. 2008/0050792 (Zmierczak et al.) describes the catalytic conversion of lignin to a liquid bio-fuel. The process involves producing an intermediate partially hydrodeoxygenated product which is then subsequently reacted to reduce or eliminate the reactor plugging and the catalyst coking.

[0009] The processes described in the above patent applications suffer the disadvantage of requiring a significant amount of hydrogen to facilitate hydrodeoxygenation reactions, thus increasing cost.

[0010] Although hydrogen may be produced in oil refineries as a by-product of catalytic reforming of naphtha to produce gasoline, most refineries suffer from a shortage of hydrogen due to the increasing demands to hydroprocess heavy crude oil and the increasingly low sulphur requirements of transportation fuel products. The reduction in world crude oil supplies is also likely to exacerbate the current shortage of hydrogen. The production of hydrogen by processes such as catalytic steam reforming can lead to high levels of carbon emissions which are harmful to the environment.

[0011] Accordingly, current processes for refining bio-oils into fuel products generally require the input of high levels of hydrogen (for catalytic hydrodeoxygenation) increasing costs and/or carbon emissions. Moreover, current processes for generating fuels and chemicals from hydrocarbon feedstocks also emit significant amounts of greenhouse

gases in many cases. For example, the production of methanol from natural gases, naphtha or similar hydrocarbon feedstocks releases gaseous byproducts which reduce atmospheric levels of hydroxyl radicals and increase the lifetime of greenhouse gases such as methane.

- 5 [0012] The present invention aims to provide an improved process for generating fuel products from oils that alleviates at least one of the aforementioned disadvantages. Preferably, the improved process generates at least one product that may be recycled for use in an integrated process to produce additional product(s).

10 Summary of the invention

- [0013] The applicant has surprisingly found that the production of fuel products in an oil hydroprocessing plant can be improved by integration with a methanol processing plant. In particular, the integration of an oil hydroprocessing plant and a steam reformer of a methanol processing plant can be used to improve generation of fuel products in the oil hydroprocessing plant and/or methanol production in the methanol plant. Co-product(s) 15 generated by the integrated methanol plant may be used as feed material in the integrated oil hydroprocessing plant to improve the generation of fuel products. In addition, co-product(s) from the integrated oil hydroprocessing plant can be used as an additional feedstock to the integrated methanol processing plant, improving the production of methanol and/or synthesis gas. Component(s) of the synthesis gas may be recycled to the 20 oil hydroprocessing plant and/or be used to facilitate the improved production of methanol.

[0014] In a first aspect, the invention provides a system for integrating methanol production and hydroprocessing of oil feedstock comprising:

- 25 a first feedstock comprising hydrocarbons that is fed to a steam reformer to produce synthesis gas comprising carbon monoxide and excess hydrogen;
a methanol reactor configured to produce methanol from the synthesis gas,
an oil hydroprocessing reactor configured to receive the excess hydrogen;
a second feedstock comprising an oil that is fed to the hydroprocessing reactor
30 and mixed with the excess hydrogen for use in hydroprocessing reactions to produce a hydrocarbon product from the oil.

[0015] In one embodiment of the first aspect, the system comprises a component for separating the mixed hydrocarbon product into different groups according to carbon atom number.

[0016] In one embodiment of the first aspect, the excess hydrogen is separated from methanol produced by the methanol reactor and supplied to the oil hydroprocessing reactor.

[0017] In another embodiment of the first aspect, the excess hydrogen is supplied
5 directly from the steam reformer to the oil hydroprocessing reactor.

[0018] In a further embodiment of the first aspect, C₁ to C₄ hydrocarbons are separated from the hydrocarbon product and recycled to the first feedstock.

[0019] In another embodiment of the first aspect, C₁ to C₂ hydrocarbons are separated from the hydrocarbon product and recycled to the first feedstock

10 [0020] In an additional embodiment of the first aspect, C₃ to C₄ hydrocarbons are separated from the hydrocarbon product as LPG fuel.

[0021] In a further embodiment of the first aspect, hydrocarbons of C₁₇ or greater are separated from the hydrocarbon product and recycled to the second feedstock.

[0022] In another embodiment of the first aspect, C₅ to C₁₆ hydrocarbons are separated
15 from the hydrocarbon product as fuels.

[0023] In one embodiment of the first aspect, the fuels comprise naphtha and diesel, and are further processed to produce upgraded fuels.

[0024] In a further embodiment of the first aspect, the naphtha is upgraded in a catalytic reformer step to a gasoline.

20 [0025] In one embodiment of the first aspect, the diesel is upgraded in a hydroisomerisation step to a jet fuel.

[0026] In another embodiment of the first aspect, the second feedstock comprises bio-oil.

[0027] In one embodiment of the first aspect, the second feedstock comprises crude oil.

25 [0028] In a further embodiment of the first aspect, the feedstock comprises coal oil.

[0029] In one embodiment of the first aspect, the feedstock comprises a mixture of a bio-oil, crude oil, and/or coal oil.

[0030] In a further additional embodiment of the first aspect, the second feedstock comprises 1% to 100% oil and 0% to 99% highly paraffinic gas condensate.

30 [0031] In one embodiment of the first aspect, the second feedstock comprises 1% to 100% bio-oil and 0% to 99% coal oil.

[0032] In another embodiment of the first aspect, the second feedstock comprises 1% to 100% bio-oil and 0% to 99% crude oil.

[0033] In one embodiment of the first aspect, the second feedstock comprises a
35 detergent.

[0034] In one embodiment of the first aspect, a catalyst is used in the catalytic hydroprocessing reactions.

[0035] In an additional embodiment of the first aspect, the hydroprocessing reactions are catalytic hydroprocessing reactions utilising a catalyst comprising an active metal or a combination of active metals.

[0036] In another embodiment of the first aspect, the catalyst comprises at least one group VIB metal, at least one metal group VIII metal, or a combination thereof.

[0037] In one embodiment of the first aspect, the catalyst is at least one of a cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW) type catalyst.

[0038] In one embodiment of the first aspect, the catalyst is a low activity hydrodeoxygenation catalyst.

[0039] In another embodiment of the first aspect, the low activity hydrodeoxygenation catalyst is a single metal such as Mo or W supported on gamma alumina.

[0040] In an additional embodiment of the first aspect, the low activity hydrodeoxygenation catalyst is a combination of metals such as Ni/Mo or Ni/W supported on gamma alumina.

[0041] In one embodiment of the first aspect, the hydroprocessing reactor is a multi-bed hydroprocessing reactor.

[0042] In one embodiment of the first aspect, the hydroprocessing reactor is a series flow hydroprocessing reactor.

[0043] In an additional embodiment of the first aspect, the hydroprocessing reactor is a two stage hydroprocessing reactor.

[0044] In a second aspect, the invention provides a hydrocarbon product produced in accordance with the system of the first aspect.

[0045] In a third aspect, the invention provides a methanol product produced in accordance with the system of the first aspect.

[0046] In one embodiment of the second or third aspect, the product is at least a 20% renewable bio-fuel product.

[0047] In another embodiment of the second or third aspect, the product is at least a 50% renewable bio-fuel product.

[0048] In a fourth aspect, the invention provides a process for integrating a methanol plant with an oil hydroprocessing plant comprising feeding a hydrogen co-product from the methanol plant to the oil hydroprocessing plant to provide a hydrogen source for catalytic hydroprocessing reactions in the hydroprocessing plant.

[0049] In one embodiment of the fourth aspect, the hydrogen is separated from methanol produced by the methanol plant and fed to the oil hydroprocessing plant.

[0050] In another embodiment of the fourth aspect, the hydrogen is fed to the oil hydroprocessing plant directly from a steam reformer.

5 [0051] In one embodiment of the fourth aspect, a co-product of C₁ to C₄ hydrocarbons produced by the oil hydroprocessing plant is recycled for use as a feedstock for the methanol plant.

[0052] In a fifth aspect, the invention provides a process for producing a fuel product comprising:

10 feeding a first feedstock comprising hydrocarbons into a steam reformer of a methanol plant to produce a synthesis gas comprising carbon monoxide and excess hydrogen;

 feeding the excess hydrogen from the methanol plant into an oil hydroprocessing reactor configured to receive excess hydrogen from the methanol plant; and

15 feeding a second feedstock comprising an oil into the oil hydroprocessing reactor for use with said excess hydrogen in hydroprocessing reactions to produce a hydrocarbon product from the oil.

[0053] In one embodiment of the fifth aspect, the excess hydrogen is fed to the oil hydroprocessing reactor directly from the steam reformer.

20 [0054] In another embodiment of the fifth aspect, the synthesis gas is converted to a methanol product in a methanol synthesis reactor and the excess hydrogen is fed to the oil hydroprocessing reactor from the methanol synthesis reactor.

[0055] In an additional embodiment of the fifth aspect, C₁ to C₄ hydrocarbons are separated from the hydrocarbon product and recycled to the first feedstock.

25 [0056] In another embodiment of the fifth aspect, the hydroprocessing reactions utilize a catalyst comprising an active metal or a combination of active metals.

[0057] In a sixth aspect, the invention provides a fuel product produced in accordance with the process of the fifth aspect.

30 [0058] In a seventh aspect, the invention provides a methanol product produced in accordance with the process of the fifth aspect.

[0059] In one embodiment of the sixth or seventh aspect, the product is at least a 20% renewable product.

[0060] In one embodiment of the sixth or seventh aspect, the product is at least a 50% renewable product.

[0061] In another embodiment of the sixth or seventh aspect, the product is a renewable LPG product, a renewable naphtha product, a renewable diesel product, or a renewable gasoline product.

[0062] In an eighth aspect, the invention provides an integrated methanol processing and oil hydroprocessing plant comprising:

a steam reformer configured to produce a synthesis gas comprising carbon monoxide and excess hydrogen by reaction of steam with a first feedstock comprising hydrocarbons;

a methanol reactor configured to produce methanol from the synthesis gas, wherein the excess hydrogen is separated from the methanol;

an oil hydroprocessing reactor configured to produce a fuel product of mixed hydrocarbons from a second feedstock comprising an oil by catalytic hydroprocessing reactions utilising said excess hydrogen; and

a component for size-based separation of the fuel products produced by the hydroprocessing reactor;

wherein the hydroprocessing reactor is configured to receive excess hydrogen produced by the methanol reactor and the steam reformer is configured to receive a separated C₁ to C₄ hydrocarbon product produced by the hydroprocessing reactor.

[0063] A further aspect of the invention relates to a process of reducing the carbon footprint of a methanol plant by integrating the methanol plant with an oil hydroprocessing plant wherein the excess hydrogen produced from a steam reformer of the methanol plant is feed to a catalytic hydroprocessing reaction in the oil hydroprocessing plant and the light gaseous hydrocarbon products produced by the oil hydroprocessing plant are recycled to the steam reformer of the methanol plant. Preferably the heavy hydrocarbon products produced from the oil hydroprocessing plant are recycled as a further feedstock to the catalytic hydroprocessing reaction. Preferably the hydroprocessing reaction is a catalytic hydrodeoxygenation reaction.

[0064] A further aspect of the invention relates to methanol produced from an integrated methanol plant and oil hydroprocessing plant such that the methanol produced is formed in part from a renewable source of light gaseous hydrocarbons, preferably C₁ to C₂ or C₁-C₄ hydrocarbons.

[0065] A further aspect of the invention relates to a transportation fuel composition derived from an integrated methanol and oil hydroprocessing plant of the invention, the composition comprising a mixture of C₅ to C₂₀ hydrocarbons, preferably C₅ to C₁₆

hydrocarbons. Preferably at least a portion of the fuel composition is a renewable bio-fuel composition.

[0066] Further aspects of the invention relate to a renewable LPG product, a renewable naphtha product, a renewable diesel product, a renewable gasoline product and a
5 renewable jet fuel product produced according to the system of the invention.

[0067] Other aspects, features and advantages of the invention will become apparent from the following detailed description when taken in conjunction with the accompanying drawings, which are a part of this disclosure and which illustrate, by way of example, embodiments of this invention.

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Brief description of the drawings

[0068] The following figures are used to illustrate the preferred embodiments of the invention and in no way are to be considered limiting.

[0069] Figure 1 shows a schematic of a methanol processing plant according to the prior
15 art.

[0070] Figure 2 shows a schematic of a methanol plant integrated with an oil hydroprocessing plant according to an embodiment of the invention.

[0071] Figure 3 shows a schematic of a methanol processing plant according to an embodiment of the invention showing where the hydrogen is taken off for use in the oil
20 hydroprocessing plant.

[0072] Figure 4 shows a schematic of a single stage oil hydroprocessing plant according to an embodiment of the invention.

[0073] Figure 5 shows a schematic of a series flow oil hydroprocessing plant according to an embodiment of the invention.

25 [0074] Figure 6 shows a schematic of a two-stage oil hydroprocessing plant according to an embodiment of the invention.

Definitions

[0075] In describing and claiming the invention the following terminology will be used.

30 [0076] As used herein, the singular forms of "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example "a step" includes references to one or more steps.

[0077] As used herein, the term "bio-fuel" is to be understood to refer to any fuel, fuel additive, aromatic, and/or aliphatic compound derived from at least a portion of bio-oil
35 material.

[0078] As used herein, the term “bio-oil” will be understood to be a reference to any mixture of liquid organic materials obtained by conversion of biomass (e.g. by thermal, hydrothermal and/or catalytic conversion or by any other means).

[0079] As used herein, the term “coal” is to be understood to refer to any form of coal that may be used to produce coal oil, for example anthracite, bituminous, subbituminous, lignite and any other forms of coal.

[0080] As used herein, the term “coal oil” is to be understood to refer to any oil product derived partially or wholly from the treatment of coal (e.g. by pyrolysis or any other means).

[0081] As used herein, the term “oil hydroprocessing plant” will be understood encompass any hydroprocessing plant capable of refining oil, including for example, bio-oil, coal-oil, crude oil, and any combination thereof.

[0082] As used herein, the terms “integrated oil hydroprocessing plant” and “integrated hydroprocessing plant” will be understood to be a reference to an oil hydroprocessing plant integrated with a methanol plant.

[0083] As used herein, the terms “methanol processing plant” and “methanol plant” will be understood to be a reference to a methanol processing plant comprising a steam reformer and a methanol synthesis reactor.

[0084] As used herein, the terms “integrated methanol processing plant” and “integrated methanol plant” will be understood to be a reference to a methanol processing plant integrated with an oil hydroprocessing plant. The methanol processing plant may be integrated with the oil hydroprocessing plant by virtue of an integrated steam reformer component and/or by virtue of an integrated methanol reactor component.

[0085] As used herein, the term “steam reformer” encompasses any apparatus used for generating a synthesis gas (“syngas”) comprising hydrogen and carbon monoxide by treatment of a hydrocarbon feedstock with steam in the presence of a catalyst.

[0086] As used herein, the term “reaction” is to be understood to cover any single or multi-step reactions, which may be direct reactions of reactants to products or may include one or more intermediate products, which can be stable or transient.

[0087] As used herein, the term “comprising” is to be understood in its “open” sense, that is, in the sense of “including”, and thus not limited to its “closed” sense, that is the sense of “consisting only of”. A corresponding meaning is to be attributed to the corresponding words “comprise, comprised and comprises” where they appear.

Detailed description

[0088] The present invention provides a system and process for integrating an oil hydroprocessing plant with methanol processing plant. Also provided is an integrated plant for fuel and/or methanol production comprising an oil hydroprocessing plant integrated with a methanol processing plant. The methanol processing plant may be a fully functional plant, or, a semi-functional plant in which the steam reformer is functional but the methanol synthesis reactor is not.

[0089] In accordance with the invention, co-product(s) from the integrated methanol processing plant (e.g. hydrogen) may be used as an input feedstock to the oil hydroprocessing processing plant for the improvement of fuel generation processes. The co-product(s) may be sourced from the methanol synthesis reactor of the methanol processing plant. Additionally or alternatively, the co-products may be sourced from the steam reformer of the methanol processing plant.

[0090] Co-products from the integrated oil hydroprocessing plant (e.g. gaseous light hydrocarbons) can be used as additional feedstock for the methanol processing plant for improved synthesis gas production, and hence improved methanol production in the case of a fully functioning integrated methanol plant.

[0091] Integration of the methanol processing plant with the oil hydroprocessing plant allows utilization of the excess hydrogen waste stream produced by the steam reformer to be used as a hydrogen source for the oil hydroprocessing plant. This provides significant cost savings in sourcing hydrogen by reducing the requirement of an additional catalytic reformer for the oil hydroprocessing plant to provide the required hydrogen. This may reduce the emission of GHG such as carbon dioxide (CO₂) that are released from catalytic reformers utilized to produce hydrogen in a traditional oil hydroprocessing plant.

[0092] Hydrogen provided to the integrated oil hydroprocessing plant may be sourced from the steam reformer of the integrated methanol plant, from the methanol synthesis reactor of the integrated methanol plant, or both. Additionally or alternatively, hydrogen provided to the integrated oil hydroprocessing plant may be derived from other different sources.

[0093] For example, an integrated methanol processing plant in accordance with the invention may be a fully functional plant in which case co-product(s) such as hydrogen may be accessed directly from the steam reformer or any other component of the methanol plant from which the co-product(s) (e.g. hydrogen) can be accessed including, for example, the methanol synthesis reactor. Alternatively, in the case where the methanol processing plant is only semi-functional as may be the case, for example, when the

methanol synthesis reactor is not in operation, the co-product(s) (e.g. hydrogen) may be accessed from the steam reformer.

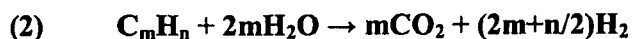
[0094] In alternative embodiments of the present invention a steam reformer may be integrated with an oil hydroprocessing plant, wherein the steam reformer is not a component of a methanol processing plant. The steam reformer may generate a synthesis gas comprising hydrogen from a hydrocarbon-containing feedstock, the hydrogen being recycled as a feedstock for the integrated oil hydroprocessing plant. Additionally or alternatively, light gaseous hydrocarbons produced by the integrated oil hydroprocessing plant may be recycled to the integrated steam reformer.

[0095] An integrated methanol processing plant in accordance with the invention may synthesize methanol from a hydrocarbon-containing feedstock (also referred to hereinafter as "methanol hydrocarbon feedstock") such as, for example, natural gas, naphtha or similar feedstocks. There is no particular limitation regarding the particular type or form of a methanol processing plant utilized in accordance with the invention.

[0096] For example, a suitable apparatus and process for manufacturing methanol is described in United States patent no. 4,219,492 (Konoki et al.) the entire contents of which are incorporated herein by cross-reference.

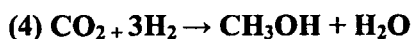
[0097] Reference is made to **Figure 1** of the present application which provides an exemplary flow diagram outlining a process for producing methanol in a methanol plant according to the prior art.

[0098] The methanol plant comprises a steam reformer reactor 7 in which the methanol hydrocarbon feedstock 1 is reacted with steam 4 at high temperatures to convert the hydrocarbons into synthesis gas, CO and H₂, and CO₂ as indicated by reactions (1) and (2) below:



[0099] The above reactions may be performed under high pressure and in the presence of a catalyst such as, for example, a nickel containing catalyst. The methanol hydrocarbon feedstock and steam may be pre-heated, for example, using heat exchangers 3 and 5 respectively, before entering the steam reformer reactor 7. Heat for the reactions may be provided to the steam reformer reactors 7 by burners 9. Reactions (1) and (2) above are performed in the steam reformer reactors 7. The gaseous mixture produced by the steam

reformer reactors may be cooled by transferring heat to a series of pre-heaters 10, 11, 12 and/or a cooler 13. The cooled gaseous mixture may then be fed into a condensate separator 14 to primarily remove condensed water. The remaining synthesis gas mixture may be supplied to the methanol synthesis reactor 19 via circulator 16 and pipe 18 where
5 catalytic reactions (3) and (4) below are carried out.



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[00100] Reactions (3) and (4) are generally performed under elevated pressures, for example 2.9×10^6 to 4.9×10^6 N/m² (29 to 49 bar). The methanol containing gaseous mixture produced by the methanol synthesis reactor 19 may then be cooled via pre-heaters 20, 21 and cooler 22 and fed to a crude methanol separator 23 to remove the
15 gaseous stream from the crude methanol. The gaseous stream may be recycled using pipe 17 back to the methanol synthesis reactor 19 for further processing. The crude methanol can be piped via pipe 25 and may be further purified. Excess hydrogen produced in the methanol plant may be removed by burning the hydrogen off.

[00101] In accordance with the present invention, a methanol processing plant may be
20 integrated with an oil hydroprocessing plant. There is no particular limitation regarding the particular type or form of an integrated oil hydroprocessing plant utilized in accordance with the invention.

[00102] Any oxygen containing hydrocarbon source can be used as part of the feedstock in the integrated hydroprocessing plant, non-limiting examples of which include bio-oil, coal-oil, crude oil, and combinations thereof.
25

[00103] Bio-oils for use in the integrated oil hydroprocessing plant may be produced from a variety of sources, non-limiting examples of which include plant oils, lignocellulosic biomass, tallow and other renewable biomass sources. The bio-oil may be produced by any method known in the art.

[00104] For example, bio-oil may be produced from biomass by a fast pyrolysis reaction. A fast pyrolysis reaction requires heating the biomass material in an oxygen-reduced atmosphere, sometimes with steam, for a generally short time period, e.g. several seconds. This reaction breaks down the biomass into a large number of relatively small molecules. The mixture is then quickly cooled to prevent further reaction and produces the dark oily
35 liquid called bio-oil. For example, a bio-oil may be produced from biomass using the

pyrolysis method described in PCT publication no. WO 1988/000935 (Wisenhunt and Scott) (also issued as European patent no. 0316355), the entire contents of which are incorporated herein by cross-reference.

[00105] Additionally or alternatively, bio-oil for use in the integrated oil hydroprocessing plant may be produced from biomass by a thermochemical reaction. This generally requires treating the biomass with a supercritical liquid (e.g. supercritical water) for a moderate period of time (e.g. several minutes) resulting in the hydrolysis of biomass and forming a light stable bio-oil. Non-limiting examples of suitable thermochemical reaction methods are provided in PCT publication no. WO2009/015409 (Humphreys), and United States patent no. 6,180,845 (Catallo et al.), each of which is incorporated herein by cross-reference in its entirety.

[00106] Coal-oils for use in the integrated oil hydroprocessing plant may be produced from a variety of sources, non-limiting examples of which include anthracite, bituminous, subbituminous, lignite and any other forms of coal. The coal oil may be produced by any method known in the art.

[00107] For example, the coal oil may be produced by pyrolysis of coal or thermochemical processing of coal.

[00108] Suitable coal to coal oil conversion processes may include, for example, liquefaction of coal by hydrogenation as described in United States patent no. 4,243,509 (Sinor) and/or by thermochemical conversion of coal to coal oil as described in International patent application WO2009/015409 (Humphreys), United States patent no. 3,850,738 (Stewart, Jr., et al.), and/or United States patent no. 4,485,003 (Coenen et al.), each of which is incorporated herein by cross-reference in its entirety. The total coal oil produced by such processes may be used as a feedstock to the hydroprocessing plant or a suitable distilled fraction of the coal oil. Coal oil production processes such as those described in the aforementioned documents may produce a coal oil comprising oxygen containing compounds that can be readily hydrodeoxygenated in the oil hydroprocessing plant to produce high quality hydrocarbon transportation fuels.

[00109] The present invention provides a system and process for integrating a methanol processing plant with an oil hydroprocessing plant for the improved production of methanol and/or hydrocarbon fuel products. In certain embodiments, the integrated plant may decrease the cost associated with generating product(s) (e.g. hydrocarbon product(s) and/or methanol products) and/or reduce the environmental impact of generating such product(s) (e.g. reduced carbon footprint and/or reduced consumption of non-renewable resources).

[00110] Hydrocarbon fuel products produced in the integrated oil hydroprocessing plant include, but are not limited to, short, medium and long chain hydrocarbon-containing products. Preferably, light gaseous hydrocarbon products (e.g. C₁₋₄ hydrocarbon products) produced in the integrated oil hydroprocessing plant may be recycled back to the integrated methanol processing plant for use as a feedstock. The recycled light gaseous hydrocarbon products may be used as a stand alone feedstock in the integrated methanol processing plant, although it is preferable that it be combined with other methanol hydrocarbon feedstocks.

[00111] Recycling of light gaseous hydrocarbon products from the integrated oil hydroprocessing plant for use as a feedstock in the integrated methanol processing plant comprising a steam reformer facilitates the production of methanol from a renewable feedstock resulting in a renewable methanol. For example, the use of a high percentage of renewable oil (e.g. bio-oil) in the feedstock for the integrated oil hydroprocessing plant may make more light gaseous hydrocarbon products available for utilization as an alternative (renewable) feedstock to the methanol processing plant and reduce the level of non-renewable feedstocks (e.g. natural gas) required. This reduction in the use of non-renewable feedstocks may significantly reduce the environmental impact of producing methanol.

[00112] The production of synthesis gas in the integrated methanol processing plant may result in the production of hydrogen gas. The hydrogen gas may be recycled back to the integrated oil hydroprocessing plant and used to drive catalytic hydrodeoxygenation of oxygenated hydrocarbons in the oil feedstock and/or hydrogenate aromatic hydrocarbon structures. The recycling of hydrogen to the integrated oil hydroprocessing plant may therefore reduce or remove the need to independently produce hydrogen for fuel production in the integrated oil hydroprocessing plant reducing costs and/or adverse environmental consequences arising from hydrogen production.

[00113] **Figure 2** shows an outline of an exemplary integrated plant according to an embodiment of the invention. The integrated plant 210 arises from the integration of an oil hydroprocessing plant with a methanol processing plant. The integrated plant 210 facilitates the use of a hydrogen co-product produced from the methanol processing plant 230 in the oil hydroprocessing plant 250. The integrated plant 210 comprises a hydrocarbon feedstock 212 that may be feed to a steam reformer 220 together with steam 214 to produce synthesis gas 228. The synthesis gas 228 may then be fed to the methanol synthesis reactor 230. The crude methanol 236 produced from the methanol plant 230 may be separated and processed for further purification 238 and the gaseous stream by-

product containing hydrogen 240 may be piped to the oil hydroprocessing plant 250 as an input to the hydroprocessing reaction. The utilization of the hydrogen from the methanol processing plant or directly from the steam reformer from a methanol processing plant (not shown) to the hydroprocessing plant provides significant cost savings in obtaining the required hydrogen for the hydroprocessing reactions.

[00114] In the hydroprocessing plant 250 an oil feedstock 260 may be mixed with the hydrogen 240 from the methanol plant 230 in a hydroprocessing reactor in the presence of a catalyst. The hydroprocessing reaction can be performed under appropriate reaction conditions in the hydroprocessing reactor 250 as outlined below. The hydrocarbon products 270 produced may then be separated into the different product groups using any suitable apparatus such as, for example, a distillation column 280. In a preferred embodiment the light gaseous such as C_{1-2} or C_{1-4} hydrocarbon products 282 may be recycled back, via a pipe, as feed to the steam reformer reactor 220 as indicated by arrow 284. Alternatively, as in a traditional hydroprocessing plant the liquid petroleum gas (LPG) component of the light gaseous hydrocarbon products, C_3-C_4 , may be extracted and the remaining light gaseous hydrocarbon products, C_1-C_2 , used as a fuel for the burners and heaters in the integrated processing plant (not shown). The heavy hydrocarbon products 290, for example, C_{17} products or greater, may be optionally recycled back as a feed to the hydroprocessing reactor 250 as indicated by arrow 292. Hydrocarbon products C_{5-20} , preferably C_{5-16} such as naphtha 286 and diesel 288 may be collected and may be further processed, for example, to produce upgraded bio-fuels such as gasoline and jet fuel.

[00115] In a certain embodiments of the invention oil feedstock provided to the integrated oil hydroprocessing plant may be comprised of a mixture of bio-oil together with fossil oil, such as crude oil, coal oil and/or a mixture of bio-oil and gas condensate. The bio-oil may be optionally mixed in the hydroprocessing plant with 0% to 99% by weight of fossil oil, coal oil and/or gas condensate. For example, if x% of bio-oil is utilized in the feedstock to the hydroprocessing reactor then both the gaseous and liquid hydrocarbon products, such as C_1-C_2 , LPG, naphtha, gasoline, diesel and jet fuel etc, will be considered x% renewable bio-fuel products. It is acknowledged that the coal oil feedstock may also be mixed with crude oil and/or a gas condensate.

[00116] Coal oil may be combined with bio-oil as a feedstock to the hydroprocessing plant to enable a coal oil feedstock to produce a partially renewable transportation fuel. Advantageously there are large global reserves of coal compared to crude oil thus

providing a very large potential reserve of coal oil derived feedstock for a hydroprocessing plant to produce at least partly renewable transportation fuels.

[00117] In a certain embodiments of the invention oil feedstock may be provided to the integrated oil hydroprocessing plant in a mixture comprising a hydrocarbon gas condensate which may reduce the overall hydrogen requirement for the hydroprocessing plant. Preferably, the condensate is a highly paraffinic gas condensate.

[00118] The high concentration of oxygen-containing molecules in oils such as bio-oil and coal oil are believed to increase the rate of the hydrodeoxygenation reactions in the hydroprocessing reactors and may cause coke formation on the catalyst. Without limitation to a particular mechanism, a highly paraffinic gas condensate may dilute the concentration of the oxygen-containing molecules in the bio-oil and/or coal oil and may enhance the rate of the hydrodeoxygenation reactions. The highly paraffinic gas condensate may assist in reducing the rate of catalyst deactivation, for example, by setting up a hydrogen-equilibrium on the surface of the catalysts which may assist in preserving the life of the catalysts. Furthermore, the dilution of the concentration of oxygen-containing molecules in the mixture of oil and paraffinic gas condensate may improve the heat distribution from the exothermic hydrodeoxygenation reactions over the whole reactor and reduce the amount of coke formation on the catalyst, thus further improving the life of the catalyst. Optionally, in one embodiment a detergent may also be added to the oil feedstock to facilitate the mixing of the hydrophilic oil with the hydrophobic gas condensate.

[00119] The paraffinic gas condensate may be $C_2 - C_{30}$, preferably $C_3 - C_{20}$, and more preferably $C_4 - C_{15}$. Additionally or alternatively, the paraffinic gas condensate may have a hydrogen to carbon ratio of about 1.5-2.0. Additionally or alternatively, the paraffinic gas condensate may have an oxygen content of less than about 1%, preferably less than about 0.5%, and more preferably less than about 0.1%. Additionally or alternatively, the paraffinic gas condensate may have a sulfur content of less than about 2%, preferably less than about 1%, and more preferably less than about 0.5%. Additionally or alternatively, the paraffinic gas condensate may have a nitrogen content of less than about 2%, preferably less than about 1%, and more preferably less than about 0.5%.

[00120] **Figure 3** shows an exemplary upgraded methanol plant according to an embodiment of the invention, indicating where the hydrogen is taken from after the methanol reactor for utilization in the hydroprocessing plant. The components of the methanol plant are identified and referred to using the same reference numbers as those used to describe the prior art methanol plant shown in **Figure 1**. Hydrogen 40 may be

taken off from the gaseous stream pipe 17 as indicated by the arrow and piped under pressure to the hydroprocessing plant. Additionally or alternatively, the hydrogen may be sourced from the steam reformer 7 of the methanol plant and piped to the hydroprocessing plant. This may be preferable, for example, if the methanol reactor of the methanol plant is shut down or not working.

[00121] An oil hydroprocessing plant in accordance with the invention includes any known oil hydroprocessing plant configurations or combinations thereof. Suitable oil hydroprocessing plant configurations are described, for example, in "*Hydrocracking Science and Technology*", by Julius Scherzer and A.J. Gruia. Macell Dekker, (1996), p 13-71. Single stage or multi-bed oil hydroprocessing plants may be employed including, but not limited to, any one or more of those described below.

[00122] **Figure 4** shows an exemplary single stage reactor oil hydroprocessing plant according to one embodiment of the invention. Hydrogen 340 used in the oil hydroprocessing plant 300 may be sourced from an integrated methanol plant. The hydrogen 340 may be added to the oil feedstock 360 prior to introducing the oil into the hydroprocessing reactor 350. Additionally or alternatively, hydrogen 340 may be added independently to the hydroprocessing reactor 350. The hydrogen 340 from the integrated methanol plant may optionally be compressed to the required reaction pressure in a makeup compressor 342 prior to use in the hydroprocessing reactions. Pressurised hydrogen 340 from the makeup compressor 342 may be fed to the hydroprocessing plant under pressure and mixed with the oil feedstock 360. Alternatively, the hydrogen 340 may be fed directly to the hydroprocessing reactor 350 without pressurisation (not shown).

[00123] Hydrogen 340 may be provided to the reactor 350 at any suitable flow rate. For example, the flow of hydrogen 340 into the hydroprocessing reactor 350 may preferably be maintained above about 1 kg hydrogen/bbl feed (420 s.c.f./bbl) of feed and more preferably in the range 2 to 20 kg hydrogen/bbl feed (840 to 8400 s.c.f./bbl.). In general, at least sufficient hydrogen may be provided to facilitate hydrodeoxygenation of oxygenated hydrocarbon structures in the oil feedstock, and to compensate for incidental hydrogenation of nitrogen and sulfur compounds, while maintaining a significant excess of hydrogen partial pressure. Excess hydrogen may be removed from the treated oil, and fed back as indicated by arrow 346 to the reactor 350 and optionally to compressor 342 to increase the pressure of the hydrogen.

[00124] Hydrogen 340 may be provided to the reactor 350 at any suitable pressure. Preferably, hydrogen 340 may be provided to the reactor 350 at a pressure of about 2 x

10^6 N/m^2 to about $20 \times 10^6 \text{ N/m}^2$ (about 20 to 200 bar) and more preferably at a pressure of about $4 \times 10^6 \text{ N/m}^2$ to about $8 \times 10^6 \text{ N/m}^2$ (about 40 to 80 bar). The oil feedstock may be preheated to an appropriate initial reaction temperature using the heater 352 before entering the hydroprocessing reactor 350. It will be understood that the hydroprocessing reactor 350 may comprise multiple reactor beds (as described, for example, below). The reactor beds may be packed with appropriate catalysts to assist in performing the hydroprocessing reactions.

[00125] The hydroprocessing reactor 350 may be a fixed bed reactor with downflow of liquid and gas. The reactor may be packed with several beds in series with quenching of the mixture between the beds to control the temperature of the reactors 350 as the hydroprocessing reactions are highly exothermic.

[00126] Hydrodeoxygenation reactions in the hydroprocessing reactor 350 may be performed at any suitable temperature. Typically, the hydrodeoxygenation reactions may be performed at a reaction temperature of between about 200°C and about 500°C , and preferably between about 250°C and about 400°C . However, the skilled addressee will recognise that the particular temperature used in the reaction may vary depending upon the oil feedstock and/or particular catalyst used in the reactions.

[00127] Hydrodeoxygenation reactions in the hydroprocessing reactor 350 may be performed at any suitable pressure. Typically, the hydrodeoxygenation reactions may be performed at pressures of between about $2 \times 10^6 \text{ N/m}^2$ (20 bar) and about $20 \times 10^6 \text{ N/m}^2$ (200 bar), and preferably at pressures of between about $4 \times 10^6 \text{ N/m}^2$ (40 bar) and about $12 \times 10^6 \text{ N/m}^2$ (120 bar).

[00128] For a fixed bed hydroprocessing reactor the weight hourly space velocity (WHSV) may be typically in the range of 0.1 to 10 hr^{-1} and preferably 0.5 to 5.0 hr^{-1} . As for temperature, the particular pressure or WHSV used in the reaction may vary depending on the particular feedstock and catalyst used in the reaction.

[00129] Any suitable catalyst or combination of different catalysts may be used in the hydroprocessing reactions. Preferred catalysts for the hydroprocessing reactions may be comprised of a combination of one or more (e.g. two) active metals wherein at least one metal is from group VIB and/or at least one metal from group VIII of the periodic table of elements. Suitable combinations include those comprising the cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) and nickel-tungsten (NiW) type/s. Combinations may also include monometallic catalysts (e.g. Co, Mo, W sulfides). Non-limiting examples of suitable catalysts include Pt/ $\text{Al}_2\text{O}_3/\text{SiO}_2$, Pd/ $\text{Al}_2\text{O}_3/\text{SiO}_2$, Ni/ $\text{Al}_2\text{O}_3/\text{SiO}_2$, NiO/ MoO_3 , CoO/ MoO_3 , NiO/ WO_2 and mixtures thereof.

[00130] Preferably each of the active metals is incorporated onto a metal oxide support, such as alumina, amorphous silica alumina and/or zeolites, such as zeolite Y, in an amount, for example, of from about 0.1 percent to about 20 percent by weight of the total catalyst. The alumina support of the catalyst may be the gamma form thereof. In some cases, the alumina support may include silica (for example, up to 10% silica). The single stage reactor configuration may contain a single catalyst or more than one catalyst in different catalyst beds.

[00131] The single stage reactor may, for example, contain a catalyst at the top of the bed with a relatively low activity for hydrodeoxygenation. This may avoid or reduce rapid reaction rates leading to local hot spots and coking of the catalyst causing rapid deactivation. Low activity hydrodeoxygenation catalysts may comprise, for example, a single metal such as Mo or W or combinations of metals such as Ni/Mo or Ni/W supported on gamma alumina, preferably with relatively low metal loadings in the range of 0.1-15%wt.

[00132] For series flow and two-stage hydroprocessing configurations different catalysts are typically deployed in each reactor stage although this is not a strict requirement. In certain embodiments, catalysts used in the single stage configuration or the first stage reactor of the series flow and two stage configurations may be based on an alumina support impregnated with cobalt-molybdenum (CoMo) or nickel-molybdenum (NiMo) as the active hydrogenation metals. In certain embodiments, catalysts used in the second stage reactor for series flow and two stage hydroprocessing configurations may be amorphous silica alumina and/or a zeolites, such as zeolite Y impregnated with cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW) to provide both a hydrogenation function and a cracking function for the catalyst.

[00133] In addition, for series flow and two stage hydroprocessing configurations a first catalyst in the first reactor may contain a low activity hydrodeoxygenation catalyst to avoid rapid reaction rates and fast catalyst deactivation due to coke formation. The low activity hydrodeoxygenation catalysts may comprise, for example, a single metal such as Mo or W or combinations of metals such as Ni/Mo or Ni/W supported on gamma alumina, preferably with relatively low metal loadings in the range of 0.1-15%wt.

[00134] Referring again to **Figure 4**, in certain embodiments the effluent mixture may be piped through heat exchangers to assist in preheating the feedstock 360 and cooling the effluent mixture (not shown). Wash water may also be mixed with the effluent mixture to assist in removing the impurities such as sulfur, nitrogen and oxygen, by converting the impurities to aqueous compounds. The effluent mixture may then be fed to a condenser

356 to condense the hydrocarbons in the effluent mixture. The condensed mixture may then be separated from the hydrogen gas present in the mixture in a separator 374. The hydrogen gas may be fed back as indicated by arrow 346 to the reactor and optionally to compressor 342 to increase the pressure of the hydrogen. The water soluble aqueous compounds containing the impurities may be removed as sour water.

[00135] The separated hydrocarbon mixture from the separator 374 may be fed to an appropriate apparatus to separate the different hydrocarbon components according to the number of carbon atoms such as, for example, distillation column 380. The lighter gas products 382, e.g. C₁-C₂, or C₁-C₄ may be piped back to the steam reformer of the methanol plant (not shown). The liquid hydrocarbon products such as naphtha 384 and diesel 388 may be collected for further refining into transportation fuels. The heavy hydrocarbon products 390 may be recycled back as an input to the hydroprocessing reactor 350 through recycle pump 394 and then pipe 392.

[00136] In certain embodiments of the invention, multi-bed hydroprocessing plants may be utilized to provide a higher level or more complete conversion of the oil feedstock into the desired hydrocarbon product(s). **Figure 5** shows an exemplary series flow hydroprocessing plant according to an embodiment of the invention. In the illustrated hydroprocessing plant configuration there is shown a first reactor 550 and a second reactor 551, although it is noted that there may be three, four, five, six or more reactors if desired. Each reactor 550, 551 may comprise the same or different catalyst beds. In a preferred arrangement the first reactor 550, or earlier reactors if more than two reactors are present, may comprise catalyst bed(s) adapted to remove oxygen and/or nitrogen and/or sulphur from oil feedstock 360. Thus the first reactor 550 may be preferably designed to perform hydrodeoxygenation reactions and/or hydrodenitrogenation and/or hydrodesulphurization reactions. Non-limiting examples of catalysts that may be included in catalyst beds of the first reactor 550 (or the earlier reactors) include transition metal sulfides on an appropriate support such as gamma-alumina or zeolite (e.g. sulfided CoMo and NiMo catalysts supported on γ -Al₂O₃).

[00137] To avoid rapid catalyst deactivation due to coking the first catalyst bed or beds in the first reactor may contain a relatively low activity hydrodeoxygenation catalyst. The low activity hydrodeoxygenation catalysts may comprise, for example, a single metal such as Mo or W, or combinations of metals such as Ni/Mo or Ni/W supported on gamma alumina, preferably with relatively low metal loadings in the range of 0.1-15%wt. In the case of series flow and two stage reactors the first reactor may preferably contain catalyst with the composition of Ni/Mo supported on gamma alumina and the second stage

catalyst may preferably contain Ni/W supported on gamma alumina or amorphous silica alumina and/or a zeolite, such as zeolite Y impregnated with cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW), to provide both a hydrogenation function and a cracking function for the catalyst.

5 [00138] The second or later reactors 551 may comprise catalyst beds adapted to break up the hydrocarbons present in the oil feedstock 360 by hydrocracking. In the illustrated hydroprocessing plant configuration the oil feedstock 360 and hydrogen 340 are initially fed via heater 352 into the first reactor 550 and then subsequently fed into the second reactor 551. This series flow configuration may provide improved control of the catalytic
10 reactions and spread the hydroprocessing reactions over more than one reactor. As for the single stage hydroprocessing reactor described in relation to **Figure 4** above the effluent mixture from the reactors may be processed through one or more separators such as a hot separator 574, high pressure separator 374 and/or low pressure separator 674. A number of heat exchangers 596 may be used to recycle the heat produced in the exothermic
15 reactions. The separated hydrocarbon mixture from separators 374, 574, 674 may be fed to an appropriate apparatus to separate the different hydrocarbon components according to the number of carbon atoms such as, for example, distillation column 380. The lighter gas products, e.g. C₁-C₂, or C₁-C₄ may optionally be recycled back to the steam reformer of the methanol plant (not shown). The liquid hydrocarbon products such as naphtha 384
20 and diesel 388 may be collected for further refining into transportation fuels. The heavy hydrocarbon products may be recycled back as an input to the hydroprocessing reactor 550 through recycle pipe 392.

[00139] **Figure 6** shows an exemplary two stage flow hydroprocessing plant according to an embodiment of the invention. In the illustrated hydroprocessing plant there is first
25 reactor 650 and a second reactor 651, each reactor comprising different catalyst beds. In a preferred arrangement the first reactor 650 comprises catalysts beds adapted to perform dehydrogenation reactions to remove oxygen and/or nitrogen and/or sulphur from the oil feedstock 360. Thus the first reactor 650 is preferably designed to perform hydrodeoxygenation reactions and/or hydrodenitrogenation reactions and optionally
30 desulphurisation reactions if required, although some hydrocracking reactions may also occur in the first reactor 650. Non-limiting examples of appropriate catalysts for these purposes are provided in the paragraphs above. The second or later reactors 651 comprise catalyst beds adapted to crack the hydrocarbons present in the feedstock 360 by performing hydrocracking reactions. The second reactor 651 generally comprises acidic
35 catalysts also with hydrogenation activity. In the illustrated two stage hydroprocessing

plant configuration the oil feedstock 360 and hydrogen 340 may be initially feed into the first reactor 650, the hydrogen 340 passing through heater 352. Effluent mixture from the first reactor 650 may be cooled at condenser 656 and then separated in one or more separators such as high pressure separator 374 and low pressure separator 674 and fed to the distillation column 380 to remove the produced hydrocarbon products, such as naphtha 384 and diesel 388. The remaining heavy hydrocarbon products 390 may be recycled via pipe 392 to the second reactor 651 where the majority of the hydrocracking reactions occur. The heat produced in these exothermic reactions may be cooled using a number of heat exchangers 696 to assist in controlling the temperature of the reactions.

10 The effluent mixture produced from the second reactor 651 may be mixed with the effluent from the first reactor 650 and again cooled at condenser 656 and then separated in one or more separators such as high pressure separator 374 and low pressure separator 674 and fed to the distillation column 380 to remove the produced hydrocarbon products, such as naphtha 384 and diesel 388. The remaining heavy hydrocarbon products 390 may again be recycled via pipe 392 to the second reactor 651 for further processing. This two-stage configuration may provide a more complete conversion of the oil feedstock into the desired hydrocarbon products due to the repeated recycling of the heavy products back to the second (or subsequent) reactor 651.

[00140] As discussed above, hydrocarbon products that are produced based on x% bio-oil feedstock are considered x% renewable products. These renewable hydrocarbon products may be further processed to upgrade the hydrocarbon product. For example the renewable naphtha may be processed in a catalytic reformer step to produce a renewable gasoline. Additionally or alternatively, the renewable diesel product may also be upgraded in a hydroisomerization step to produce a renewable jet fuel. The catalytic reforming and the hydroisomerization processes may be performed according to any process known in the art. For example the catalytic reforming process used may be that described in European patent publication no. 0567700 (Bauld) filed 1 May 1992. The hydroisomerization process used may be that according to the method described in United States patent no. 6,623,622 (Gupta) issued on 23 September 2003.

30 [00141] In a non-limiting example of an implementation of the invention, an existing methanol processing plant may be modified to allow integration with an oil hydroprocessing plant. To modify the existing methanol plant an oil hydroprocessing reactor may be built preferably in close proximity to the methanol plant to allow the utilization of co-product(s) produced from each plant to be piped to the other plant. For hydrogen collection from the methanol plant a pressurized piping system, optionally

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comprising a compressor, may be used to pipe the hydrogen to the oil hydroprocessing reactor.

[00142] In another non-limiting example of an implementation of the invention, an existing steam reformer may be modified to allow integration with an oil hydroprocessing plant. To modify the existing methanol plant an oil hydroprocessing reactor may be built preferably in close proximity to the steam reformer to allow co-product(s) produced from the steam reformer to be utilized in the oil hydroprocessing reactor, and to allow co-product(s) produced from the oil hydroprocessing reactor to be utilized in the steam reformer. For hydrogen collection from the steam reformer a pressurized piping system, optionally comprising a compressor, may be used to pipe the hydrogen to the oil hydroprocessing reactor.

[00143] In accordance with the present invention, green house gas (GHG) savings may be provided by reducing the emission of carbon waste products to the environment as they are recycled into the integrated methanol processing and/or the integrated oil hydroprocessing plant. Furthermore, as discussed above the utilization of the light gaseous hydrocarbon products produced from the integrated oil hydroprocessing plant may reduce the use of non-renewable feedstocks (e.g. natural gas) in the steam reformer/methanol plant and produce methanol formed in part from a renewable feedstock source resulting in less impact on the environment. Furthermore, the utilization of co-product(s) produced from alternative component(s) of the integrated plant may provide a reduction in operating costs for either or both plants.

[00144] While the invention has been described in connection with what are presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiments, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the invention.

CLAIMS:

1. A system for integrating methanol production and hydroprocessing of oil feedstock comprising:
 - 5 a first feedstock comprising hydrocarbons that is fed to a steam reformer to produce synthesis gas comprising carbon monoxide and excess hydrogen;
 - a methanol reactor configured to produce methanol from the synthesis gas,
 - an oil hydroprocessing reactor configured to receive the excess hydrogen;
 - a second feedstock comprising an oil that is fed to the hydroprocessing reactor
 - 10 and mixed with the excess hydrogen for use in hydroprocessing reactions to produce a hydrocarbon product from the oil.
2. The system according to claim 1, wherein the excess hydrogen is separated from methanol produced by the methanol reactor and supplied to the oil hydroprocessing reactor.
- 15 3. The system according to claim 1, wherein the excess hydrogen is supplied directly from the steam reformer to the oil hydroprocessing reactor.
4. The system according to any one of claims 1 to 3, wherein C_1 to C_4 hydrocarbons are separated from the hydrocarbon product and recycled to the first feedstock.
5. The system according to any one of claims 1 to 3, wherein C_1 to C_2 hydrocarbons
- 20 are separated from the hydrocarbon product and recycled to the first feedstock.
6. The system according to any one of claims 1 to 3, wherein C_3 to C_4 hydrocarbons are separated from the hydrocarbon product as LPG fuel.
7. The system according to any one of claims 1 to 6, wherein C_5 to C_{16} hydrocarbons are separated from the hydrocarbon product as fuels.
- 25 8. The system according to any one of claims 1 to 7, wherein hydrocarbons of C_{17} or greater are separated from the hydrocarbon product and recycled to the second feedstock.
9. The system according of claim 7, wherein the fuels comprise naphtha and diesel, and are further processed to produce upgraded fuels.
- 30 10. The system according to claim 9, wherein the naphtha is upgraded in a catalytic reformer step to a gasoline.
11. The system according to claim 9, wherein the diesel is upgraded in a hydroisomerisation step to a jet fuel.
12. The system according to any one of claims 1 to 11, wherein the second feedstock
- 35 comprises bio-oil.

13. The system according to any one of claims 1 to 12, wherein the second feedstock comprises crude oil.

14. The system according to any one of claims 1 to 13, wherein the second feedstock comprises coal oil.

5 15. The system according to any one of claims 1 to 14 wherein the second feedstock comprises 1% to 100% oil and 0% to 99% paraffinic gas condensate.

16. The system according to any one of claims 1 to 14 wherein the second feedstock comprises 1% to 100% bio-oil and 0% to 99% coal oil.

10 17. The system according to any one of claims 1 to 14 wherein the second feedstock comprises 1% to 100% bio-oil and 0% to 99% crude oil.

18. The system according to any one of claims 1 to 17, wherein the second feedstock comprises a detergent.

19. The system according to any one of claims 1 to 18, wherein the hydroprocessing reactions are catalytic hydroprocessing reactions utilising a catalyst comprising an active
15 metal or a combination of active metals.

20. The system according to claim 19, wherein the catalyst comprises at least one group VIB metal, at least one metal group VIII metal, or a combination thereof.

21. The system according to claim 19 or claim 20, wherein the catalyst is at least one of a cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW)
20 type catalyst.

22. The system according to any one of claims 1 to 21, wherein the hydroprocessing reactor is a single stage hydroprocessing reactor.

23. The system according to any one of claims 1 to 21, wherein the hydroprocessing reactor is a multi-bed hydroprocessing reactor.

25 24. The system according to claim 23, wherein the hydroprocessing reactor is a series flow hydroprocessing reactor.

25. The system according to claim 23, wherein the hydroprocessing reactor is a two stage hydroprocessing reactor.

26. A process for integrating a methanol plant with an oil hydroprocessing plant
30 comprising feeding a hydrogen co-product from the methanol plant to the oil hydroprocessing plant to provide a hydrogen source for catalytic hydroprocessing reactions in the hydroprocessing plant.

27. The process according to claim 26, wherein the hydrogen is separated from methanol produced by the methanol plant and fed to the oil hydroprocessing plant.

28. The process according to claim 26, wherein the hydrogen is fed to the oil hydroprocessing plant directly from a steam reformer.

29. The process according to claim 27 or claim 28, wherein a co-product of C₁ to C₄ hydrocarbons produced by the oil hydroprocessing plant is recycled for use as a feedstock
5 for the methanol plant.

30. A process for producing a fuel product comprising:

feeding a first feedstock comprising hydrocarbons into a steam reformer of a methanol plant to produce a synthesis gas comprising carbon monoxide and excess hydrogen;

10 feeding the excess hydrogen from the methanol plant into an oil hydroprocessing reactor configured to receive excess hydrogen from the methanol plant; and

feeding a second feedstock comprising an oil into the oil hydroprocessing reactor for use with said excess hydrogen in hydroprocessing reactions to produce a hydrocarbon product from the oil.

15 31. The process according to claim 30, wherein the excess hydrogen is fed to the oil hydroprocessing reactor directly from the steam reformer.

32. The process according to claim 31, wherein the synthesis gas is converted to a methanol product in a methanol synthesis reactor and the excess hydrogen is fed to the oil hydroprocessing reactor from the methanol synthesis reactor.

20 33. The process according to any one of claims 30 to 32, wherein C₁ to C₄ hydrocarbons are separated from the hydrocarbon product and recycled to the first feedstock.

34. The process according to any one of claims 30 to 33, wherein said hydroprocessing reactions utilize a catalyst comprising an active metal or a combination
25 of active metals.

35. A fuel product produced in accordance with the process of any one of claims 30 to 34.

36. A methanol product produced in accordance with the process claim 32.

37. The product according to claim 35 or claim 36, wherein the product is at least a
30 20% renewable product.

38. The product according to any one of claims 35 to 37, wherein the product is at least a 50% renewable product.

39. The product according to claim 37 or claim 38, wherein the product is a renewable LPG product, a renewable naphtha product, a renewable diesel product, or a
35 renewable gasoline product.

40. An integrated methanol processing and oil hydroprocessing plant comprising:

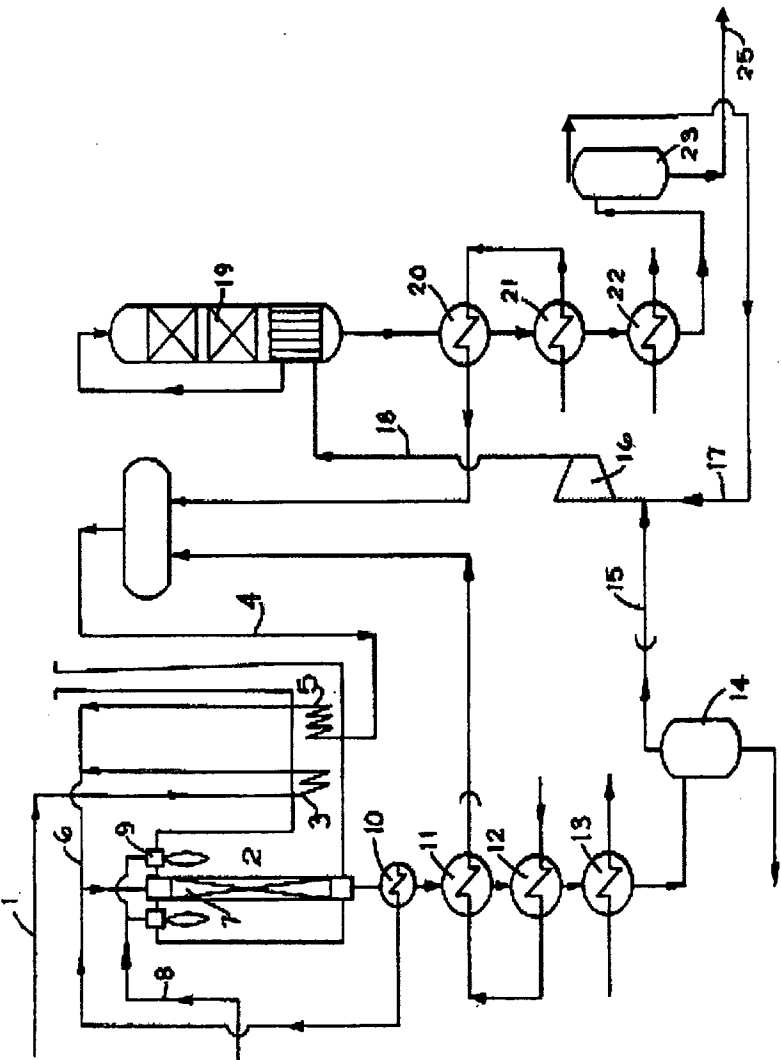
a steam reformer configured to produce a synthesis gas comprising carbon monoxide and excess hydrogen by reaction of steam with a first feedstock comprising hydrocarbons;

5 a methanol reactor configured to produce methanol from the synthesis gas, wherein the excess hydrogen is separated from the methanol;

an oil hydroprocessing reactor configured to produce a fuel product of mixed hydrocarbons from a second feedstock comprising an oil by catalytic hydroprocessing reactions utilising said excess hydrogen; and

10 a component for size-based separation of the fuel products produced by the hydroprocessing reactor;

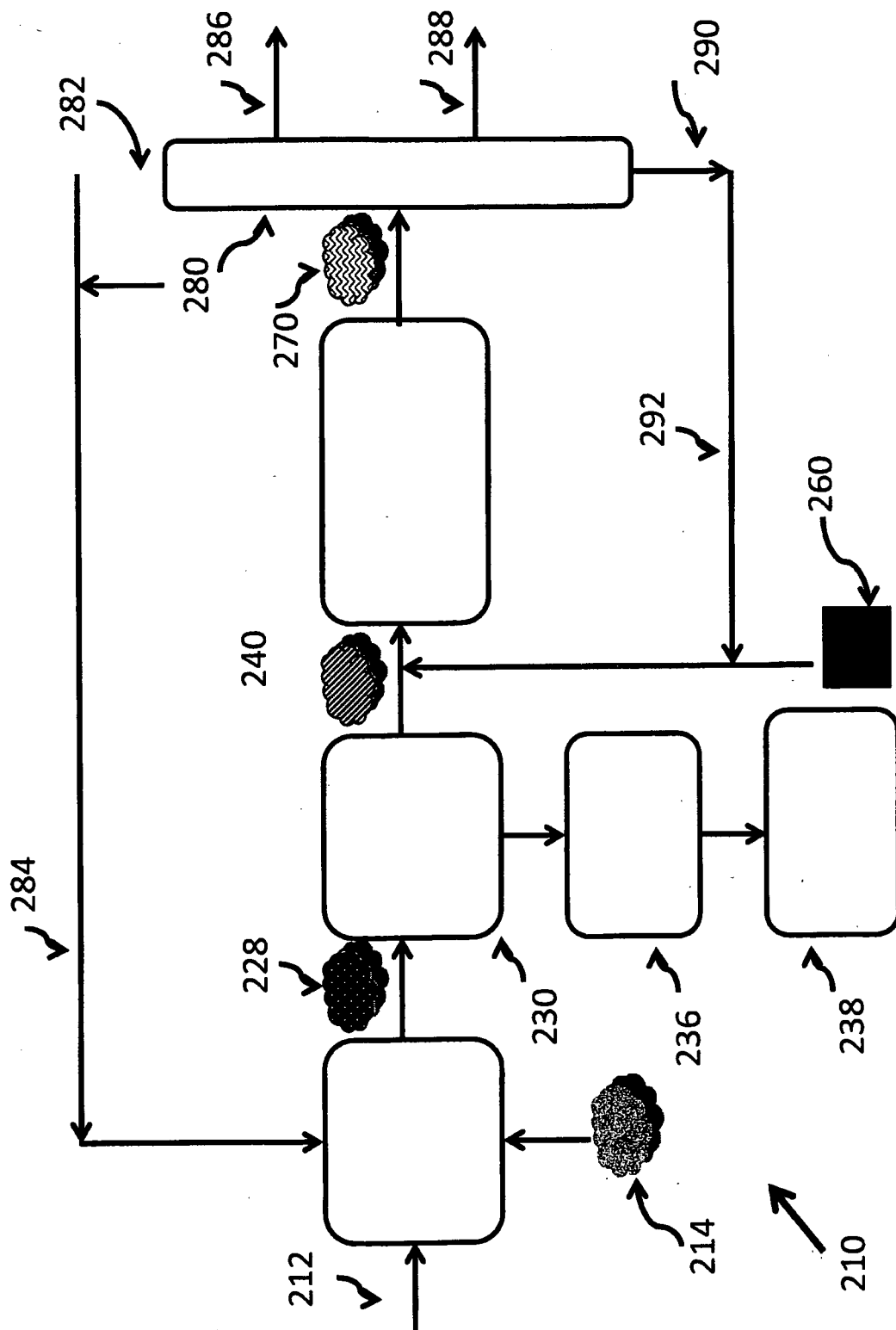
wherein the hydroprocessing reactor is configured to receive excess hydrogen produced by the methanol reactor and the steam reformer is configured to receive a separated C₁ to C₄ hydrocarbon product produced by the hydroprocessing reactor.



Prior art

Figure 1

INTERNATIONAL SEARCH REPORT



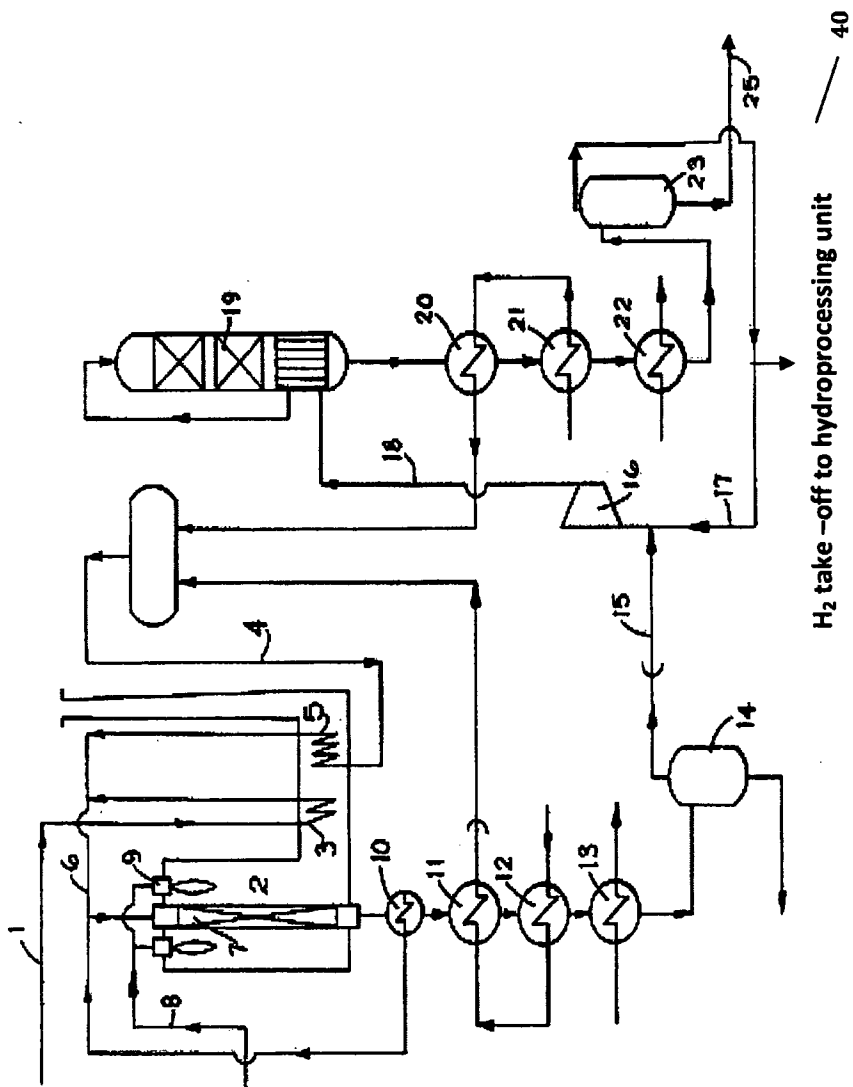


Figure 3

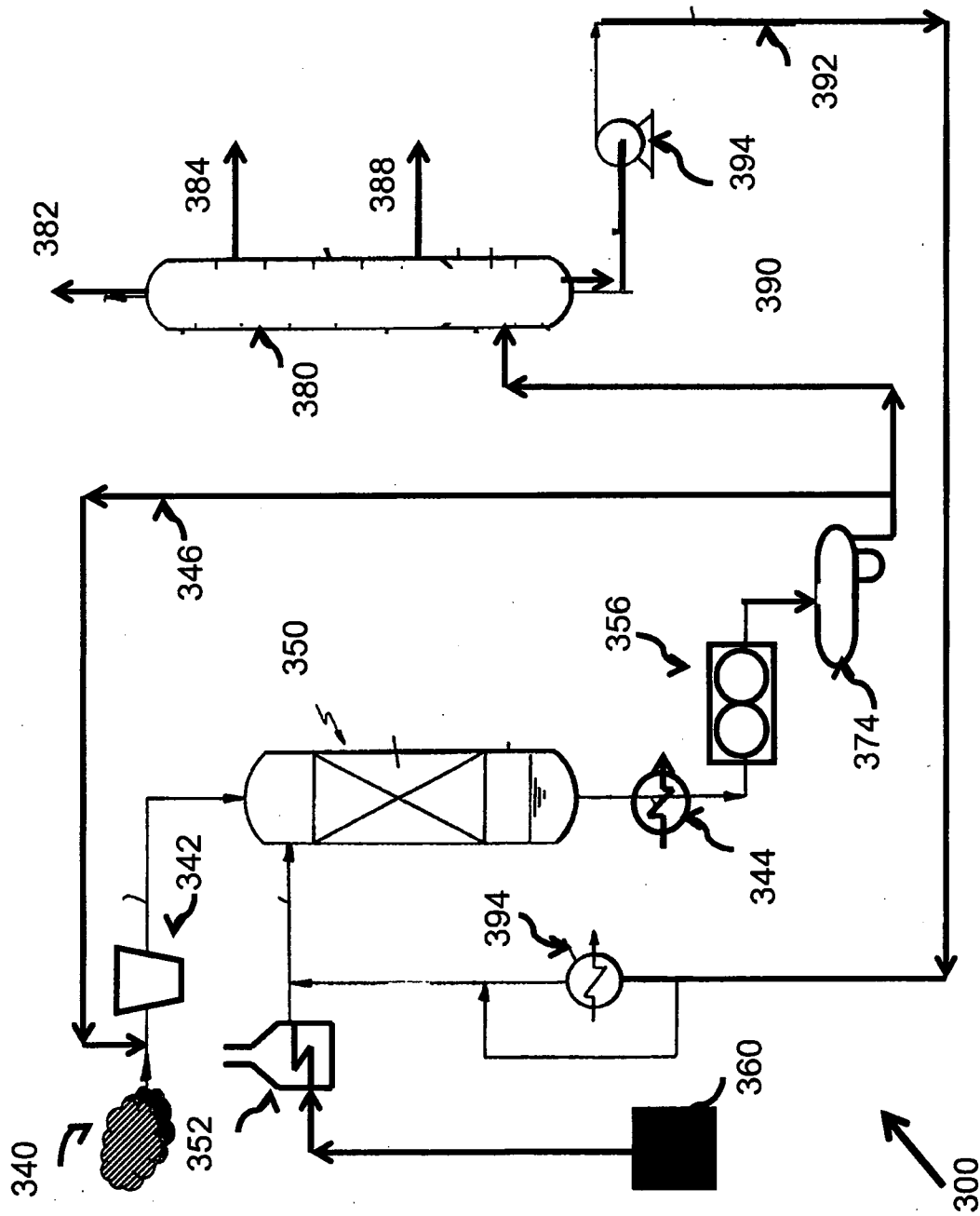


Figure 4

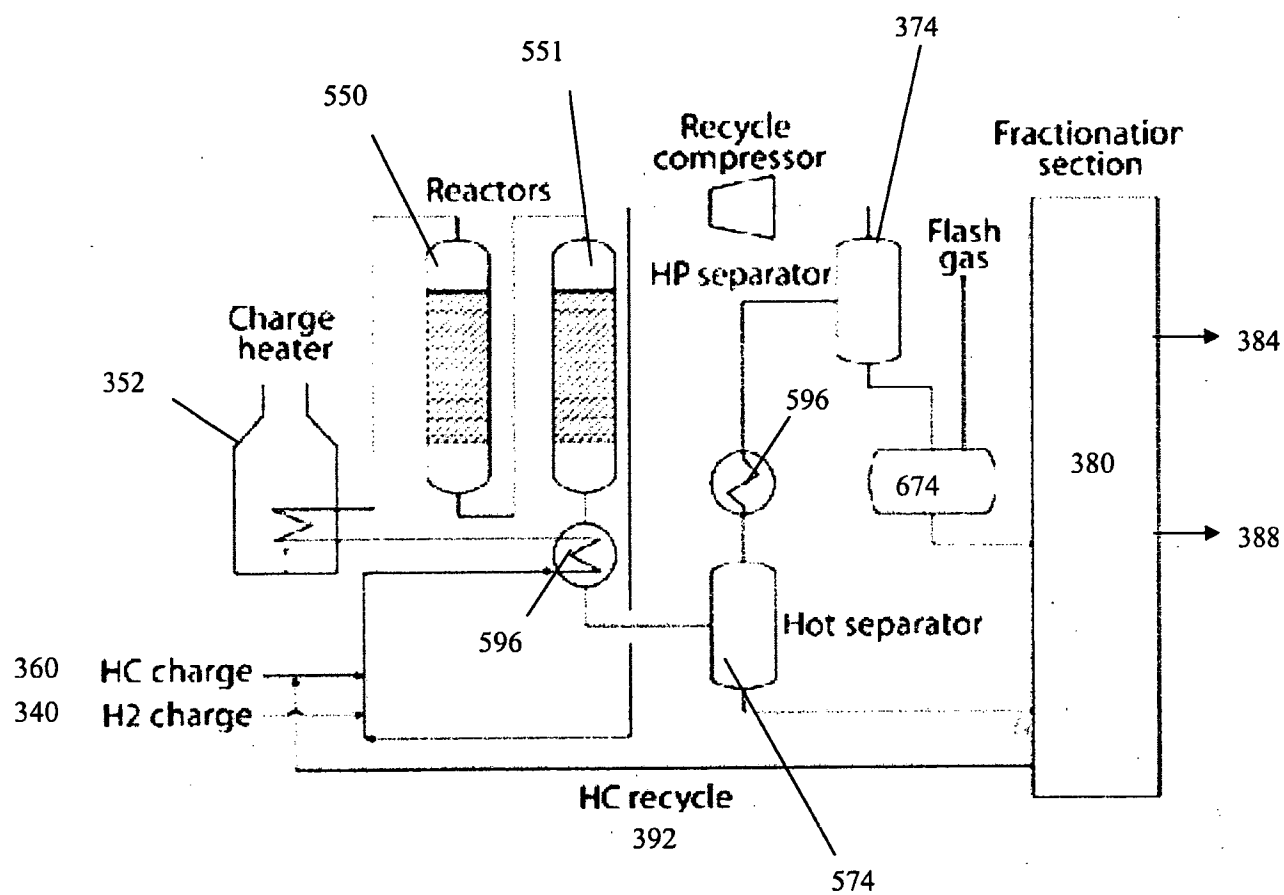


Figure 5

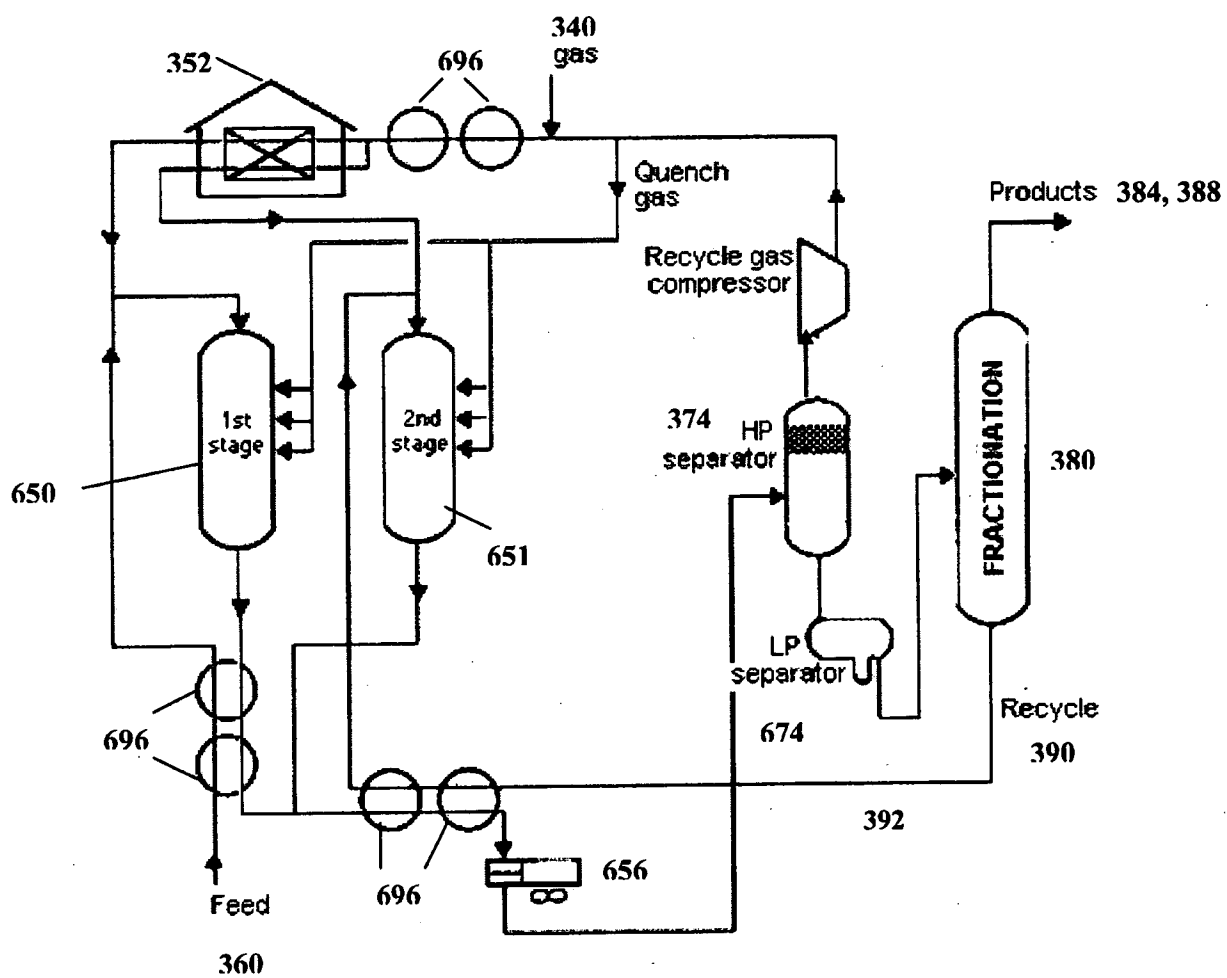


Figure 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2010/000105

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. <i>C10G 45/00</i> (2006.01) <i>C07C 29/15</i> (2006.01) <i>C10G 49/00</i> (2006.01) <i>C01B 3/00</i> (2006.01) <i>C10G 47/00</i> (2006.01)		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPODOC & WPI: IPC & EC (C10G, C07C, C07B, C10J, C10K, C01B3) & KEYWORDS (hydroprocessing, hydrogen, steam reform, methanol, integration)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2002/026677 A2 (EXXONMOBIL CHEMICAL PATENTS INC.) 4 April 2002 Claims 1, 2 and page 11 lines 18-page 22 line 2	1-11, 13-15, 18-21, 26-36 and 40
Y	As above	12, 16-17, 22-25, 37-39
X	US 4413153 A (GARWOOD et al.) 1 November 1983 Figure 1, column 3 lines 37-41, column 7 lines 20-67, column 9 lines 46-47, claim 7	1, 3, 7, 9-11, 19-20, 26, 28, 30-31 and 34
Y	As above	12, 16-17, 22-25, 37-39
X	GB 2092172 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ BV) 11 August 1982 Abstract, experiments 3, 5-7, page 2 lines 47-55	26 and 27
☒ Further documents are listed in the continuation of Box C ☒ See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 13 August 2010		Date of mailing of the international search report 24 AUG 2010
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. +61 2 6283 7999		Authorized officer THANH-TAM CHAU AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No: +61 3 9935 9627

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2010/000105

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/0150820 A1 (GUO) 14 July 2005 Claim 11, figures 1 and 3, paragraphs [0033], [0041], [0062]-[0063]	1-3, 26-28, 30-32
X	WO 2009/059936 A2 (UPM-KYMMENE OYJ) 14 May 2009 Figure 1, abstract, example 1	1-40
Y	US 2006/0207166 A1 (HERSKOWITZ et al.) 21 September 2006 Paragraphs [0022], [0028], [0029], [0036], [0031]-[0034]	12, 16-17, 22-25, 37-39
A	US 2009/0084666 A1 (AGRAWAL et al.) 2 April 2009 Abstract, figures 3 and 7	
A	US 6486219 B1 (JANDA et al.) 26 November 2002 Whole document	
A	WO 2000/048969 A1 (SHELL INTERNATIONALE RESEARCH MATTSCHAPPIJ) 24 August 2000 Abstract, all claims	
A	US 6147126 A (DEGEORGE et al.) 14 November 2000 Figures 1, 2; column 9 lines 23-27	
A	US 4076612 A (HOLLAWAY) 28 February 1978 Figure 1 and whole document	1, 3, 26, 28, 30-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/NZ2010/000105

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	0226677	AU	88901/01	CA	2422844	CN	1561320
		CN	101028997	EP	1328497	MX	PA03002744
		NO	20031381	US	6444712		
US	4413153	AU	17894/83	NO	833840	NZ	205218
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		CA	1260019	DE	3148745	FR	2496094
		IN	155483	JP	57131728	NL	8006751
		NZ	199221	ZA	8108539		
US	2005150820	AU	2006305606	EP	1966349	RU	2008119995
		US	2006106119	WO	2007045966		
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WO	2009059936	CA	2693401	CA	2696860	CA	2696867
		CA	2704999	CA	2705064	CA	2705066
		EP	2179009	EP	2185670	EP	2190950
		FI	20075557	FI	20075794	WO	2009013232
		WO	2009013233	WO	2009013392	WO	2009059819
		WO	2009059920				
US	2006207166	AU	2006226062	CA	2601708	EP	1866266
		KR	20080012831	MX	2007011534	WO	2006100584
US	2009084666	NONE					
US	6486219	AU	85344/01	WO	0226676		
WO	0048969	AU	31538/00	CA	2362687	CN	1343187
		DZ	2966	EP	1153004	GC	0000088
		ID	29612	NO	20013949	US	6479557
US	6147126	AU	24962/99	BR	9907761	CA	2314332
		EP	1054850	NO	20003944	WO	9940048
		ZA	9900736				
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							