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(56) Documents Cited:
WO 2016/073500 A1 **WO 2015/069896 A2**
US 20140165569 A1 **US 20140100294 A1**
US 20120226080 A1 **US 20070161716 A1**

(58) Field of Search:
INT CL **C01B, C07C**
Other: **WPI, EPODOC**

(54) Title of the Invention: **Integrated system and method for producing methanol product**
Abstract Title: **Integrated system and method for producing methanol**

(57) Integrated system (**100**, Fig. 1) for producing methanol comprising: a gas feed for supplying a methane rich feed gas; and apparatus for converting the methane rich feed gas to methanol. The apparatus comprises an autothermal reformer **206** configured to partially oxidise the methane rich feed gas to maintain the autothermal reformer at a working temperature. The autothermal reformer further comprises electrical heating to maintain the working temperature. Preferably, the electrical energy for the electrical heating is derived from a renewable energy source. The system may comprise an organic waste material digestor (**110**, Fig. 1) for providing biogas as the methane rich feed gas. The methane rich feed gas may also be natural gas. The system may comprise gas purifying and separating apparatus **204** for removing sulphur components and for separating carbon dioxide. The system may comprise electrolysis apparatus **208** for electrolysing water to provide oxygen and hydrogen feed gases. The system may comprise an agitation tank, bubbler, or continuous flow for adding an additive to the produced methanol in order to constitute a liquid fuel. Also claimed is a method for producing methanol using the integrated system.

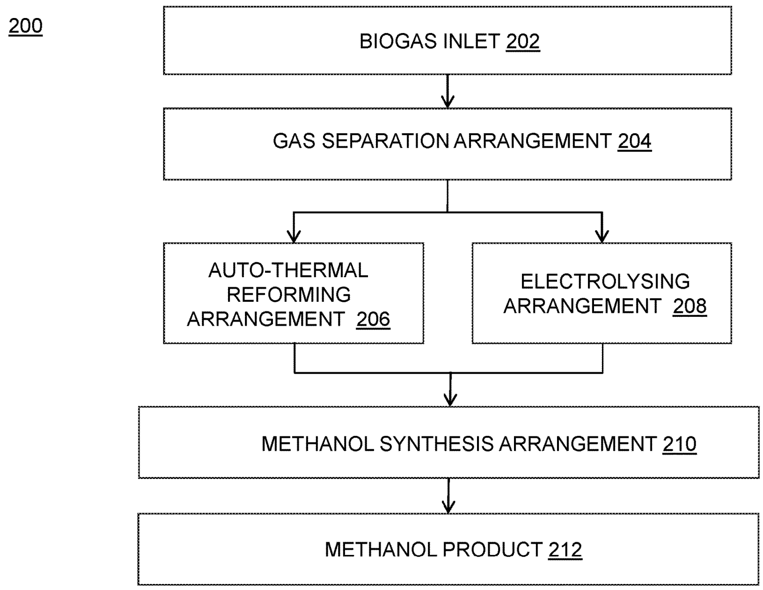

FIG. 2

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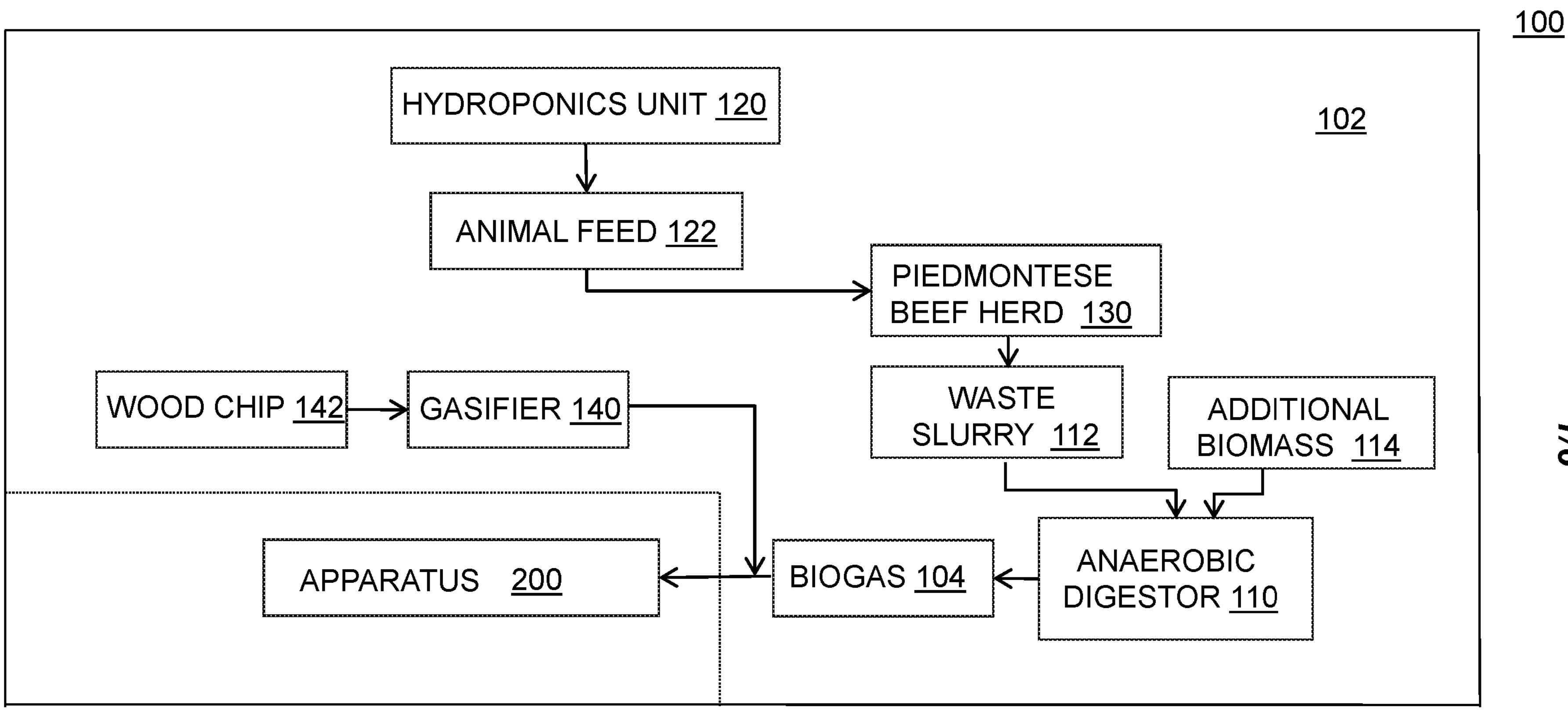
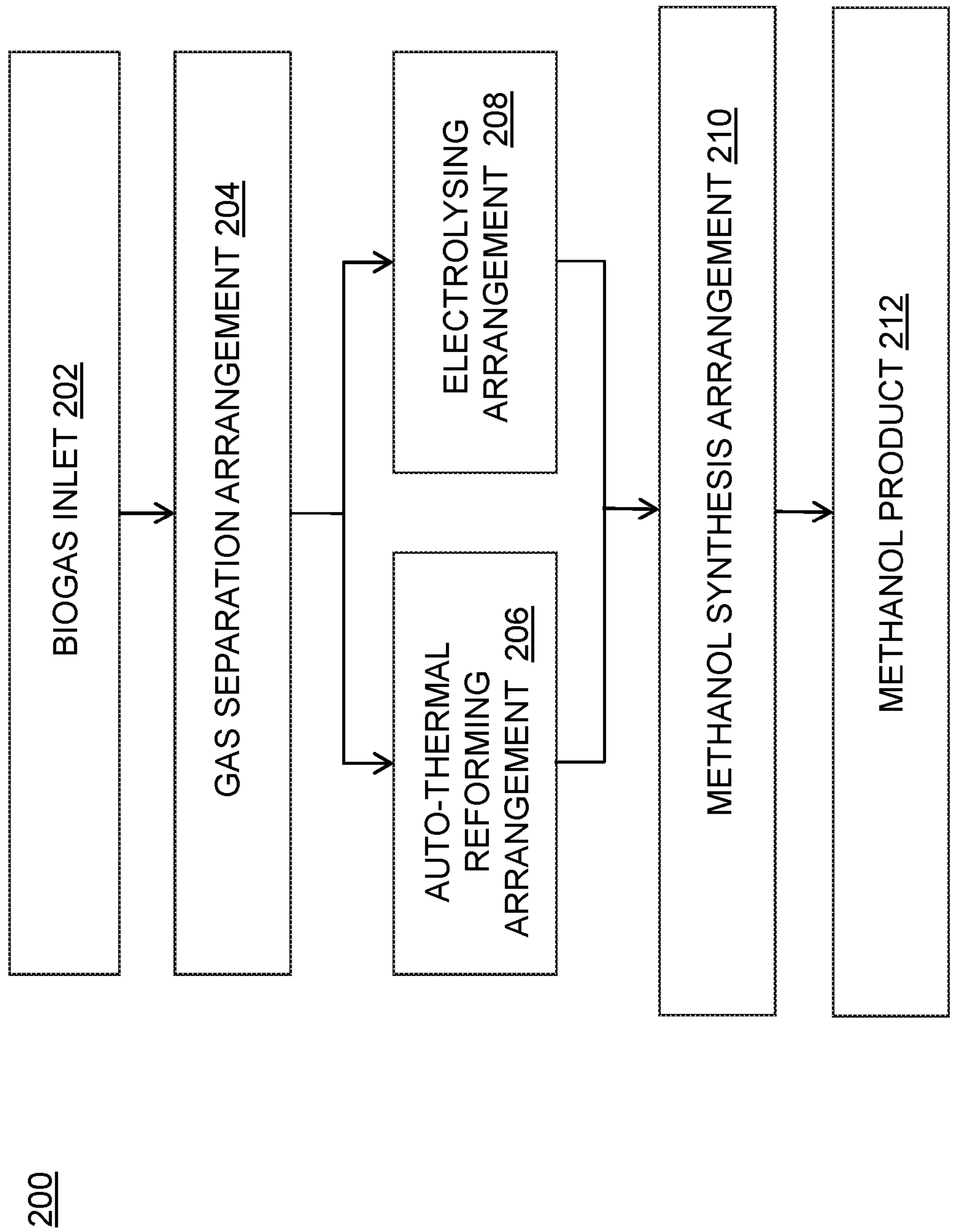

100
102
HYDROPONICS UNIT 120
ANIMAL FEED 122
PIEDMONTESE BEEF HERD 130
WASTE SLURRY 112
ADDITIONAL BIOMASS 114
WOOD CHIP 142
GASIFIER 140
ANAEROBIC DIGESTOR 110
BIOGAS 104
APPARATUS 200

FIG. 1



200
BIOGAS INLET 202
GAS SEPARATION ARRANGEMENT 204
AUTO-THERMAL REFORMING ARRANGEMENT 206
ELECTROLYSING ARRANGEMENT 208
METHANOL SYNTHESIS ARRANGEMENT 210
METHANOL PRODUCT 212

FIG. 2

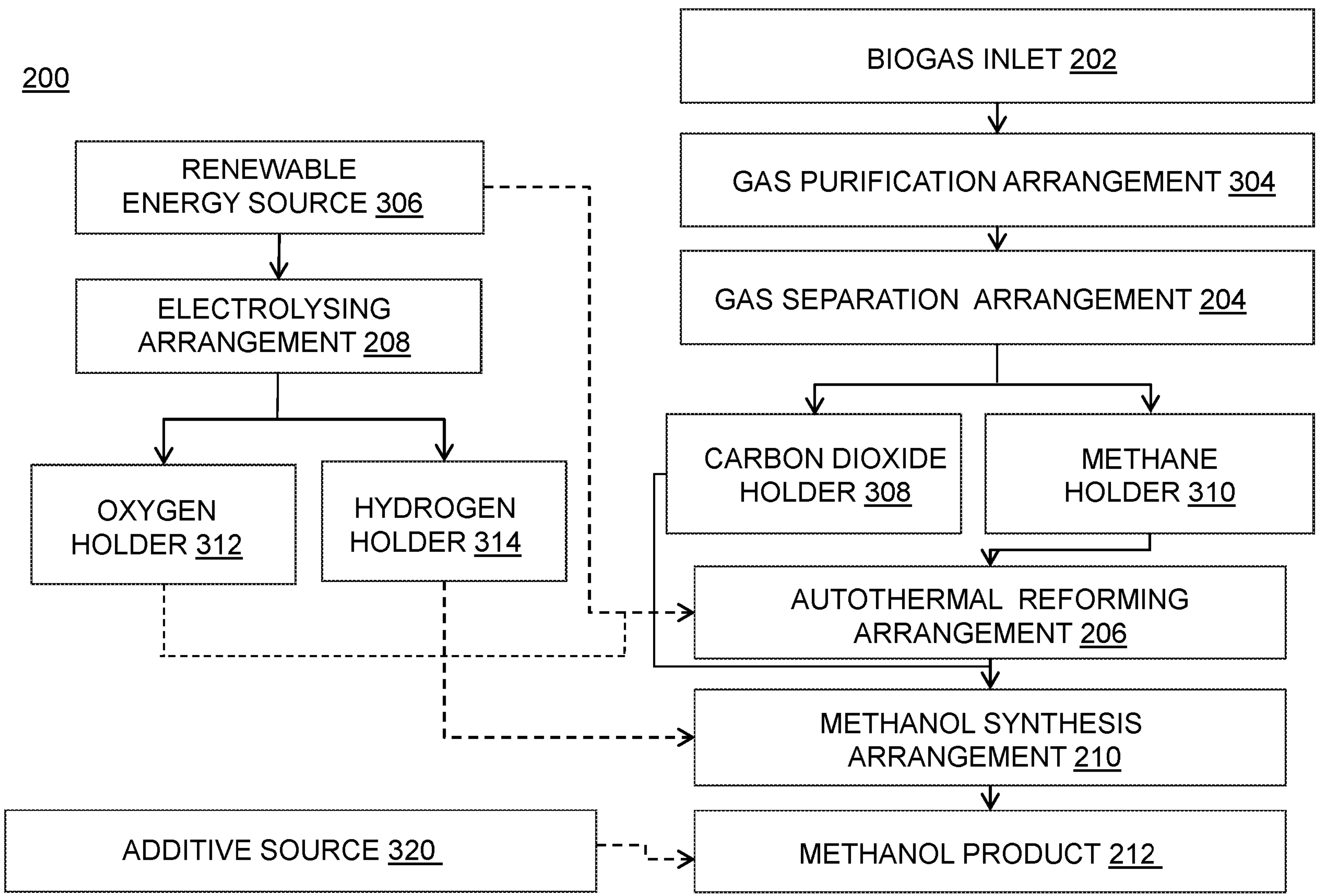

200
RENEWABLE ENERGY SOURCE 306
ELECTROLYSING ARRANGEMENT 208
OXYGEN HOLDER 312
HYDROGEN HOLDER 314
ADDITIVE SOURCE 320
BIOGAS INLET 202
GAS PURIFICATION ARRANGEMENT 304
GAS SEPARATION ARRANGEMENT 204
CARBON DIOXIDE HOLDER 308
METHANE HOLDER 310
AUTOTHERMAL REFORMING ARRANGEMENT 206
METHANOL SYNTHESIS ARRANGEMENT 210
METHANOL PRODUCT 212

FIG. 3

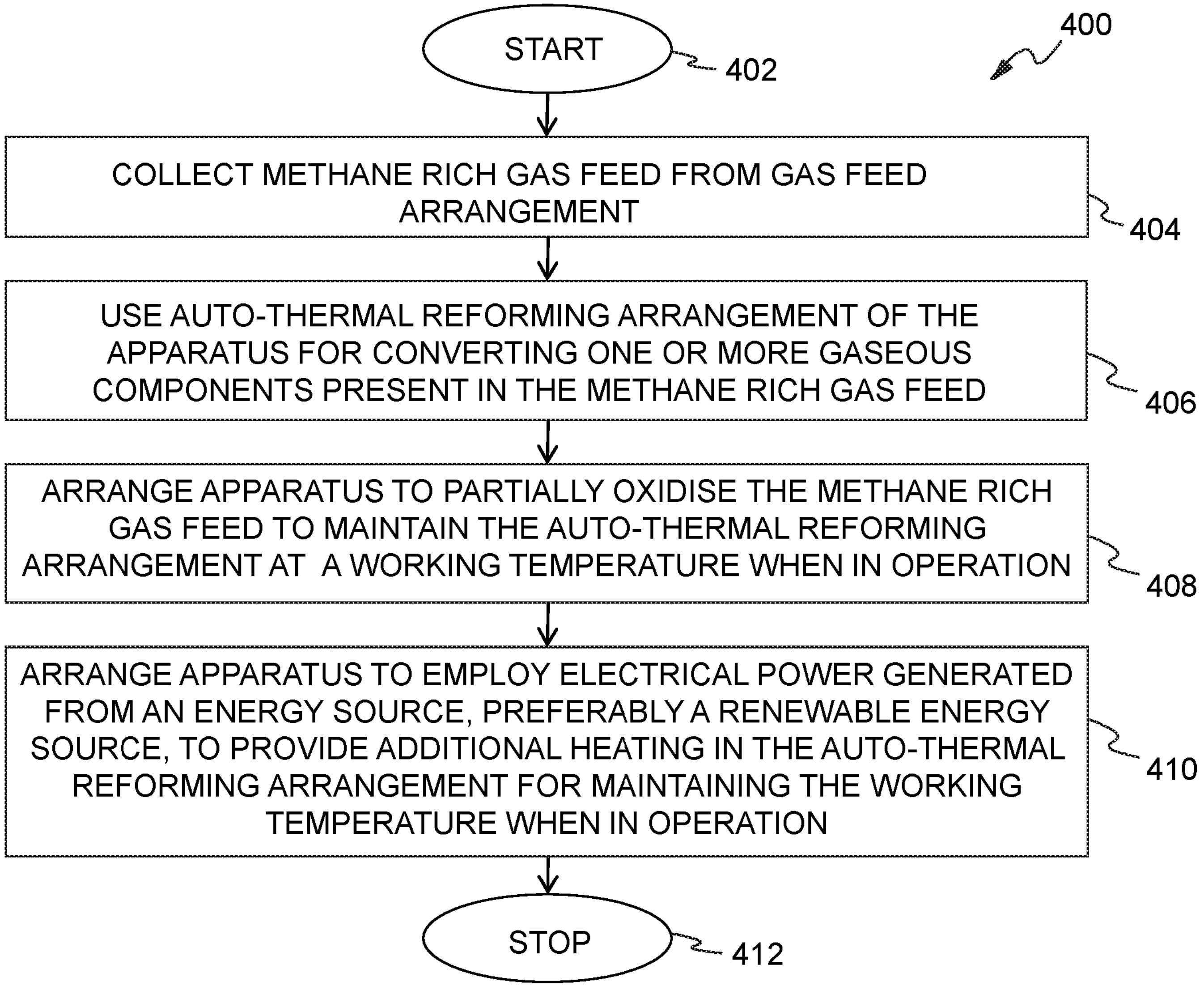

400
START
402
COLLECT METHANE RICH GAS FEED FROM GAS FEED ARRANGEMENT
404
USE AUTO-THERMAL REFORMING ARRANGEMENT OF THE APPARATUS FOR CONVERTING ONE OR MORE GASEOUS COMPONENTS PRESENT IN THE METHANE RICH GAS FEED
406
ARRANGE APPARATUS TO PARTIALLY OXIDISE THE METHANE RICH GAS FEED TO MAINTAIN THE AUTO-THERMAL REFORMING ARRANGEMENT AT A WORKING TEMPERATURE WHEN IN OPERATION
408
ARRANGE APPARATUS TO EMPLOY ELECTRICAL POWER GENERATED FROM AN ENERGY SOURCE, PREFERABLY A RENEWABLE ENERGY SOURCE, TO PROVIDE ADDITIONAL HEATING IN THE AUTO-THERMAL REFORMING ARRANGEMENT FOR MAINTAINING THE WORKING TEMPERATURE WHEN IN OPERATION
410
STOP
412

FIG. 4

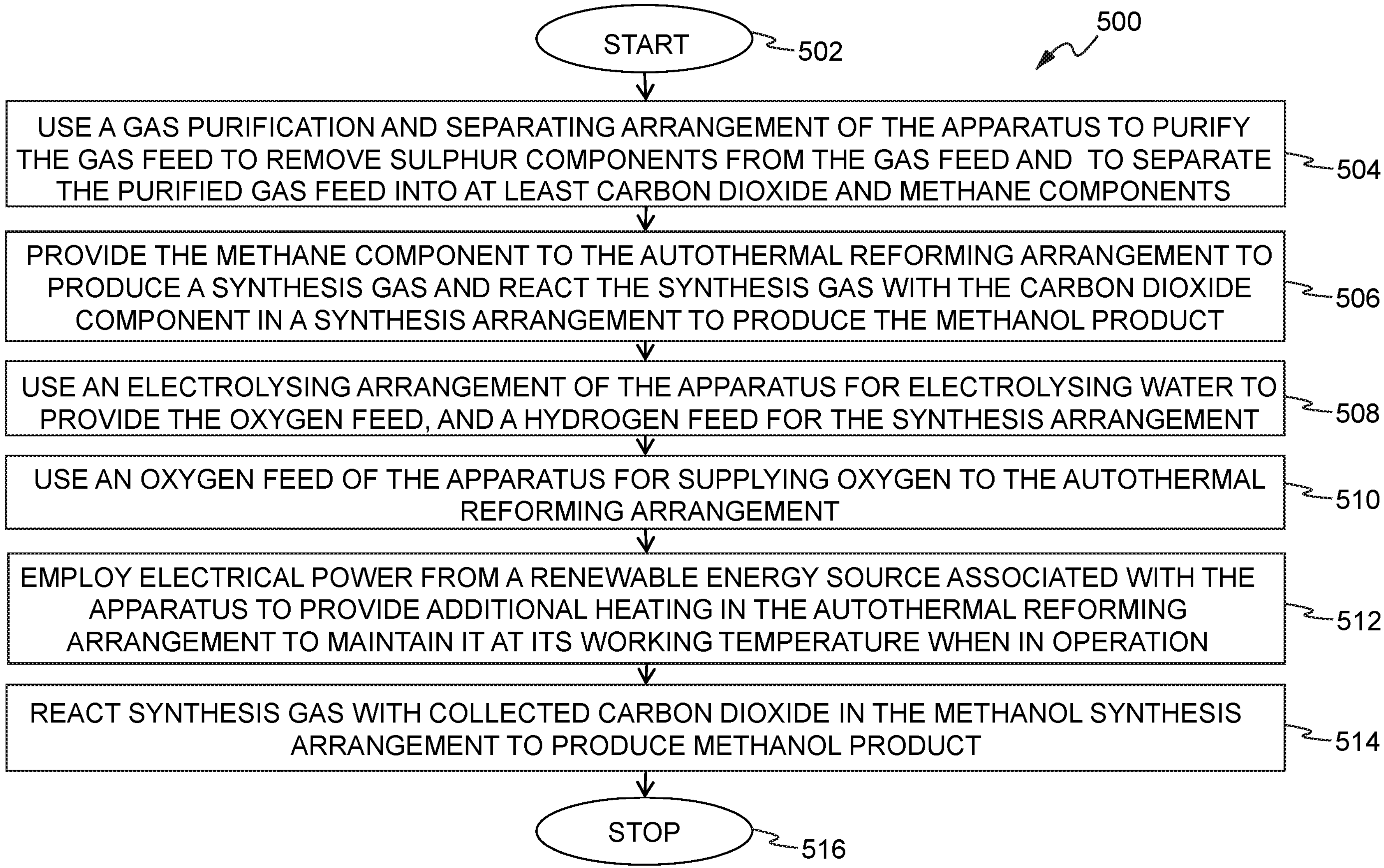

500
START
502
USE A GAS PURIFICATION AND SEPARATING ARRANGEMENT OF THE APPARATUS TO PURIFY THE GAS FEED TO REMOVE SULPHUR COMPONENTS FROM THE GAS FEED AND TO SEPARATE THE PURIFIED GAS FEED INTO AT LEAST CARBON DIOXIDE AND METHANE COMPONENTS
504
PROVIDE THE METHANE COMPONENT TO THE AUTOTHERMAL REFORMING ARRANGEMENT TO PRODUCE A SYNTHESIS GAS AND REACT THE SYNTHESIS GAS WITH THE CARBON DIOXIDE COMPONENT IN A SYNTHESIS ARRANGEMENT TO PRODUCE THE METHANOL PRODUCT
506
USE AN ELECTROLYSING ARRANGEMENT OF THE APPARATUS FOR ELECTROLYSING WATER TO PROVIDE THE OXYGEN FEED, AND A HYDROGEN FEED FOR THE SYNTHESIS ARRANGEMENT
508
USE AN OXYGEN FEED OF THE APPARATUS FOR SUPPLYING OXYGEN TO THE AUTOTHERMAL REFORMING ARRANGEMENT
510
EMPLOY ELECTRICAL POWER FROM A RENEWABLE ENERGY SOURCE ASSOCIATED WITH THE APPARATUS TO PROVIDE ADDITIONAL HEATING IN THE AUTOTHERMAL REFORMING ARRANGEMENT TO MAINTAIN IT AT ITS WORKING TEMPERATURE WHEN IN OPERATION
512
REACT SYNTHESIS GAS WITH COLLECTED CARBON DIOXIDE IN THE METHANOL SYNTHESIS ARRANGEMENT TO PRODUCE METHANOL PRODUCT
514
STOP
516

FIG. 5

Component	Formula	Concentration (% by vol.)
Methane	CH_4	55-70
Carbon Dioxide	CO_2	30-45
Nitrogen	N_2	0-5
Oxygen	O_2	<1
Hydrocarbons	C_nH_{2n+2}	<1
Hydrogen Sulphide	H_2S	0-0.5
Ammonia	NH_3	0-0.05
Water (vapour)	H_2O	1-5
Siloxanes	$C_nH_{2n+1}SiO$	0-50mg/m^3

FIG. 6

The following terms are registered trade marks and should be read as such wherever they occur in this document:

Avocet

INTEGRATED SYSTEM AND METHOD FOR PRODUCING METHANOL PRODUCT

Technical Field

The present disclosure relates to producing methanol and similar substances. In particular, the present disclosure relates to an integrated system and a method for producing methanol product from a methane rich gas, such as biogas and natural gas.

Background

Biogas refers to a gaseous fuel produced by the biological breakdown of organic matter in the absence of oxygen. It is produced by the anaerobic digestion or fermentation of biodegradable materials such as biomass, manure, sewage, municipal waste, green waste, plant material and crops. Biogas primarily comprises methane and carbon dioxide, and its production is well known in the prior art. Further, a prudent use of biogas can be seen in the generation of methanol.

Methanol, also known as wood alcohol, is a versatile compound which is used in industrial and house-hold products. Traditionally, methanol was produced as a by product of the destructive distillation of wood. Nowadays, methanol is mainly produced using hydrocarbons and, in particular, methane as a raw material. In contemporary methanol production, a feedstock material is utilized to produce a synthesis gas. Accordingly, the synthesis gas is processed to convert it into methanol. Example of the feedstock material which is rich in methane includes, but may not be limited to, natural gas and biogas.

Most of known methods to produce methanol utilise natural gas and/or bio-mass as a feedstock material. These feedstock materials often contain sulphur and other noxious compounds that need to be removed. To remove sulphur compounds, Co/Mo hydrodesulphurisation, followed by a ZnO treatment, can be performed. Other techniques are also available, including absorption onto activated materials such as activated carbon, and a well-known Claus Process for sulphur removal and the like. The methods to produce synthesis gas employ moderate-pressure steam, in a steam reforming reaction, at temperatures approximately in a range of 750ºC to 900ºC. Thereafter, the synthesis gas is converted into methanol. Moreover, surplus hydrogen from such processes which use methane as the principal feed gas is removed from the synthesis loop and can be exported as a separate product or used elsewhere within a given chemical complex. However, the known methods do not always make use of all the by-products produced in the synthesis of methanol. In addition, the steam reforming step of known methods utilizes combustion of some of the methane gas to satisfy thermodynamic demands of the steam reforming reaction and to produce associated required high temperatures, so that a forward reaction becomes thermodynamically favourable. Consequently, burning a significant proportion of the methane results in a substantial loss of the feedstock material.

In other prior arts, the methanol may be produced from renewable energy sources. Processes are employed which use biomass and water as main feedstock materials. Alternatively, auto-thermal reforming of natural gas or biogas can be used. However, these processes do not make use of all the by-products generated in the production of synthesis of gas. Moreover, the feedstock material is not efficiently utilized. Furthermore, a yield of methanol produced from these methods is relatively low.

The synthesis gas for catalytic methanol production is produced by a selection from gasification of biomass, CO_2 captured from post-combustion and an electrolysis of water for obtaining the hydrogen. The process of electrolysis requires energy, i.e. to produce hydrogen, which may be provided by renewable energy sources. However, presently, renewable energy contributes only about 5% of the commercial hydrogen production primarily via water electrolysis, while other 95% hydrogen is mainly derived from fossil fuels[1]. Renewable hydrogen production is not popular yet because the cost is still high and the poor availability of large scale electrolysis units. Photovoltaic water electrolysis may become more competitive as the cost continues to decrease with the technology advancement; but, the considerable use of small bandgap semiconducting materials may cause serious life cycle environmental impacts. However, photocatalytic water-splitting using TiO_2 for hydrogen production offers a promising

[1]Ni M, Leung MKH, Sumathy K, Leung DYC. Water electrolysis—a bridge between renewable resources and hydrogen. Proceedings of the International Hydrogen Energy forum, vol. 1, 25–28 May 2004, Beijing, PRC. p. 475–480

way for clean, low-cost and environmentally friendly production of hydrogen by solar energy.[2]

Generally, biogas to liquid fuel converters needs large amounts of equipment and investment capital. These converters require very large amounts of bio-gas at a site to justify construction, transportation and operation of large scale methanol production. The Lurgi process for low-pressure crude methanol production from bio-gas is one example of a very large scale operation.

Similarly, methane to liquid fuels processes such as the Fischer-Tropsch process have seen commercial use. However, these processes can be difficult to control and often suffer from catalyst deactivation. These processes are also only economical at very large volumes which require large initial capital investments. Therefore, none of the existing technologies provides scalable, inexpensive and reliable processes for forming hydrocarbon fuels, nor can they be deployed economically at tunable volume biogas sources. Thus, a new process, which may be an integrated system to digest waste and to utilize the biogas generated from the waste into methanol may be desirous.

In view of the aforementioned problems associated with known approaches, there is a need for a system and method that makes efficient use of feedstock material and renewable solar or wind energy source. In addition, the system and the method should make use of available alternatives for satisfying endothermic demands of the reaction. Moreover, the system and method should be able to achieve the maximum possible yield of the required products including, but may not be limited to, synthesis gas and methanol. Furthermore, the system and method should make use of renewable or agricultural by-products without producing unwanted by-products using clean, low-cost and environmentally friendly production of hydrogen from renewable energy.

Summary

The present disclosure seeks to provide an integrated system for producing a methanol product.

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[2]Ni, Meng, et al. "A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production." *Renewable and Sustainable Energy Reviews* 11.3 (2007): 401-425.

Moreover, the present disclosure seeks to provide an improved method for producing a methanol product using an integrated system having a gas feed arrangement and an apparatus for converting a gas feed from the gas feed arrangement into the methanol product.

According to a first aspect of this disclosure, an integrated system is provided for producing a methanol product. The system comprise a gas feed arrangement for providing a methane rich gas feed. The system also comprises an apparatus for converting the methane rich gas feed into the methanol product. The apparatus comprises an auto-thermal reforming arrangement for converting one or more gaseous components present in the methane rich gas feed. The auto-thermal reforming arrangement is configured to partially oxidise the methane rich gas feed to maintain the auto-thermal reforming arrangement at a working temperature when in operation. The auto-thermal reforming arrangement also employs electrical power generated from an energy source, preferably a renewable energy source, to provide additional heating in the auto-thermal reforming arrangement for maintaining the working temperature when in operation, particularly at the exit of the converter.

In one embodiment of the present disclosure, the gas feed arrangement comprises an organic waste material digestion arrangement for providing biogas as the methane rich gas feed. Alternatively, the gas feed arrangement comprises a natural gas source for providing natural gas, such as by 'anaerobic digestion' (AD) which produces a methane-rich gas produced by fermentation of biomass.

In an embodiment of the present disclosure, the apparatus includes a gas purification and separating arrangement for purifying the methane rich gas feed to remove sulphur components therein and for separating the purified gas feed into at least carbon dioxide and methane component, wherein the methane component is provided to the auto-thermal reforming arrangement for producing a synthesis gas, and the apparatus is operable to react the synthesis gas with the carbon dioxide component in a synthesis arrangement to produce the methanol product.

In an embodiment of the present disclosure, the apparatus includes an oxygen feed to an auto-thermal reforming arrangement. In addition, the apparatus includes an electrolysing arrangement for electrolysing water to provide an oxygen feed and to provide additional hydrogen feed for the synthesis arrangement.

In one embodiment of the present disclosure, the renewable energy source comprises at least one of solar energy, wind energy, geothermal energy, hydroelectricity and tidal energy.

In an embodiment of the present disclosure, the apparatus further comprises one of an agitation tank, a gas bubbling tank and a continuous flow for adding an additive to the methanol product to constitute a liquid fuel. For example, the additive comprises at least one of polyethylene glycol dinitrate, ammonium nitrate, urea, Avocet™ or any combination thereof.

According to a second aspect, there is provided a method for producing methanol product using integrated system having a gas feed arrangement and an apparatus for converting a gas feed from the gas feed arrangement into the methanol product. The method comprises collecting a methane rich gas feed from the gas feed arrangement. Thereafter, using an auto-thermal reforming arrangement of the apparatus for converting one or more gaseous components present in the methane rich gas feed. Further, arranging for the apparatus to partially oxidise the methane rich gas feed to maintain the auto-thermal reforming arrangement at a working temperature when in operation. Moreover, arranging for the apparatus to employ electrical power generated from an energy source, preferably a renewable energy source, to provide additional heating in the auto-thermal reforming arrangement for maintaining the working temperature when in operation.

In an embodiment of the present disclosure, the method further comprises using a gas purification and separating arrangement of the apparatus for purifying the methane rich gas feed to remove sulphur components therein, and for separating the purified gas feed into at least carbon dioxide and methane components; and providing the methane component to the auto-thermal reforming arrangement for producing a synthesis gas, and reacting the synthesis gas with the carbon dioxide component in a synthesis arrangement to produce the methanol product.

In an embodiment of the present disclosure, the method further comprises using an oxygen feed of the apparatus for supplying oxygen to the auto-thermal reforming arrangement. For example, the method comprises using an electrolysing arrangement of the apparatus for electrolysing water to provide the oxygen feed, and a hydrogen feed for the synthesis arrangement.

In one embodiment of the present disclosure, the method further comprises adding an additive to the methanol product to constitute a liquid fuel. For example, the additive comprises at least one of polyethylene glycol dinitrate, ammonium nitrate, urea, Avocet or any combination thereof.

In an embodiment of the present disclosure, the methane rich gas feed is one of a biogas derived from anaerobic digestion of slurry, partial ovidation of biomass such as wood chips, or any similar source.

In one embodiment of the present disclosure, the renewable energy source comprises at least one of solar energy, wind energy, geothermal energy, hydroelectricity and tidal energy.

In typical auto-thermal reforming utilizing a reactor, highest temperatures in the reactor are close to an inlet of the reactor and lowest temperatures are encountered at an outlet of the reactor. This is disadvantageous because an equilibrium constant for the steam reforming reaction becomes more favourable at the higher temperatures than at the lower temperatures. Thus, some of the methane feedstock is not converted to synthesis gas in a typical known reactor. In an embodiment of the present disclosure, the apparatus is operable to employ supplementary electrical power generated from a renewable energy source to provide additional heating in the auto-thermal reforming arrangement to maintain the exit gas at its optimum working temperature during production of methanol. For example, the partial oxidation of the methane rich gas feed may maintain a required high temperature at an inlet of the auto-thermal reforming arrangement, and the heating provided by the electrical power may maintain a required high temperature at an outlet of the auto-thermal reforming arrangement.

The invention is of advantage in that the capital costs used in the operation stated in the disclosure are very low in comparison to other processes using conventional steam reforming. In the present disclosure, biogas is beneficially used as a feedstock material. The biogas can easily be generated from biomass. In addition, other inputs, such as hydrogen and oxygen, for improving the conversion of biogas into methanol are generated using renewable energy sources. Moreover, an auto-thermal reforming is done to convert methane gas to synthesis gas. The auto-thermal reforming uses oxygen, steam and carbon dioxide as inputs to react with methane over a catalyst. Furthermore, the addition of supplementary heat to an exit part of the auto-thermal reforming arrangement results in a reduction of the amount of methane that remains unconverted to synthesis gas.

In particular, the advantage of the integrated system for generation of biogas and methanol is the optimal use of the feedstock material in the farm situation. Methane rich gas from wood chips, hydroponics, and farm waste is channelled into the apparatus to generate methanol. Costs due to location and logistics are minimized. Further, in the apparatus to generate methanol, the temperature of the auto-thermal reforming arrangement is stabilised for optimal methanol production by minimising the temperature difference between the inlet and outlet. In a conventional system the methanol production gradually decreases due to a decrease in temperature within the length of the auto-thermal reforming arrangement from the inlet to the outlet. Usually electricity is used to prevent such a fall in temperature, but prohibitive costs make it a non-viable solution. In this invention the use of renewable energy provideenergy, supplementary to that released during the autothermal reforming stage to maintain temperature uniformity and a steady generation of methanol thus making it a far more efficient system.

It will be appreciated that features of the invention are susceptible to being combined in various combinations without departing from the scope of the invention as defined by the appended claims.

Description of the diagrams

Embodiments of the present invention will now be described, by way of example only, with reference to the following diagrams wherein:

FIG. 1 is an illustration of various functional components of an integrated system for producing methanol product, in accordance with various embodiments of the present disclosure;

FIG. 2 is an illustration of various functional components of an apparatus of the integrated system of FIG. 1, in accordance with various embodiments of the present disclosure;

FIG. 3 is an illustration of a detailed view of the apparatus for converting a methane rich gas feed into a methanol product, in accordance with various embodiments of the present disclosure;

FIG. 4 is an illustration of a method for using the integrated system for producing methanol product, in accordance with an embodiment of the present disclosure;

FIG. 5 is an illustration of a detailed flowchart for using an apparatus of the integrated system for converting the methane rich gas feed into the methanol product, in accordance with another embodiment of the present disclosure; and

FIG. 6 is an illustration of a typical composition of a methane rich gas, such as biogas.

In the accompanying diagrams, an underlined number is employed to represent an item over which the underlined number is positioned or an item to which the underlined number is adjacent. A non-underlined number relates to an item identified by a line linking the non-underlined number to the item. When a number is non-underlined and accompanied by an associated arrow, the non-underlined number is used to identify a general item at which the arrow is pointing.

Description of example embodiments

FIG. 1 is an illustration of various functional components of an integrated system **100** for producing methanol product, in accordance with various embodiments of the present disclosure. The integrated system **100** includes a gas feed arrangement **102** for providing a methane rich gas feed, such as biogas **104**. The integrated system **100** also includes an apparatus **200** for converting the gas feed from the gas feed arrangement **102** into the methanol product. The gas feed arrangement **102** produces the biogas **104** by anaerobic digestion in a digestor **110** of waste slurry **112** and additional biomass **114**. For example, the waste slurry **112** may derive material from a hydroponics unit **120** providing animal feed **122**. In the present embodiment, the hydroponics unit **120** is the production system used to grow cattle feed (i.e. animal feed **122**, for example on which a piedmontese beef herd **130** feeds to produce biomass. In one embodiment, the gas feed arrangement **102** also includes a gasifier **140** for cleaning methane rich gas generated from wood chips **142**, and is further connected to the main biogas gas **104** feed to the apparatus **200**.

The biogas **104** generated from the anaerobic digestor **110** (as well as the methane rich gas provided by the gasifier **140**) is fed into the apparatus **202** which has an auto-thermal reforming arrangement for converting one or more gaseous components present in the gas feed into methanol product. In the present embodiment, the gas feed arrangement **102** is an organic waste material digestion arrangement for providing biogas **104** as the methane rich gas feed. For example, the organic waste material digestion arrangement may include a digester unit (such as digestor **110**) and a technical unit (not shown) for the control of digestion parameters and composition adjustment for the production of biogas.

In another embodiment, the apparatus **200** is arranged to operate another gas feed arrangement, such as a natural gas source that providing natural gas as the methane rich gas feed. For example, the natural gas can be AD gas.

FIG. 2 is an illustration of an overview of different functional arrangements of an apparatus **200** for producing methanol from biogas included in a gas feed, in accordance with various embodiments of the present disclosure. The apparatus **200** is optionally an industrial plant set-up having different arrangements for performing different processes. The apparatus **200** includes a biogas inlet **202** (to be operatively coupled with the gas feed arrangement **102**, for example the biogas **104** holder of FIG. 1). The apparatus **200** also includes a gas separation arrangement **204**, an auto-thermal reforming arrangement **206**, an electrolysing arrangement **208** and a methanol synthesis arrangement **210**. The biogas inlet **202** receives biogas (i.e. methane rich gas feed) from the gas feed arrangement **102**, and the gas separation arrangement **204** separates contents of methane rich gas feed and extracts carbon-dioxide and methane. A typical composition of biogas (shown in a table **600** of **FIG. 6**) includes a gaseous mixture of methane, carbon dioxide (CO_2), nitrogen, oxygen, hydrocarbons, hydrogen sulphide, ammonia, water vapour, siloxanes, and the like. Accordingly, the auto-thermal reforming arrangement **206** utilizes the methane including similar light hydrocarbons from the biogas to produce synthesis gas. In addition, the electrolysing arrangement **208** electrolyses water to produce hydrogen and oxygen used for producing methanol. Furthermore, the methanol synthesis arrangement **210** utilizes hydrogen, carbon dioxide and synthesis gas to produce methanol product **212**, described in detail with reference to **FIG. 3**.

It will be appreciated that the apparatus **200** shown in **FIG. 1** uses biogas as a feedstock material; however, it will also be appreciated that natural gas (such as AD gas) or methane from any appropriate source may be used as a feedstock material in the absence of biogas. In addition, the auto-thermal reforming arrangement **206** may be fully or partially replaced with the steam reforming arrangement. Moreover, the electrolysing arrangement **208** may be replaced by externally-provided oxygen and hydrogen cylinders.

FIG. 3 is an illustration of a detailed view of different functional arrangements of the apparatus **200** for converting a gas feed into the methanol product **212,** in accordance with various embodiments of the present disclosure. The apparatus **200** includes a gas purification arrangement **304,** a carbon-dioxide holder **308**, a methane holder **310,** an oxygen holder **312** and a hydrogen holder **314** apart from the biogas inlet **202**, the gas separation arrangement **204,** the auto-thermal reforming arrangement **206**, the methanol synthesis arrangement **210** and the electrolysing arrangement **208**, also shown in **FIG. 2.**

As aforementioned, the apparatus **200** may be an industrial plant set-up having different arrangements for performing different processes. For example, the biogas inlet **202** may be provided by the gas feed arrangement **102**, shown in FIG. 1, responsible for generating biogas from biomass. The gas purification arrangement **304** purifies the generated biogas to remove sulphur compounds therefrom. In an embodiment of the present disclosure, the sulphur components may be removed using conventional ZnO technology or some other known technology or processes. After the purification, the gas separation arrangement **204** separates methane and carbon-dioxide from the gas feed. The carbon-dioxide holder **308** collects the separated carbon-dioxide and the methane holder **310** collects separated methane. Accordingly, the auto-thermal reforming arrangement **206** converts methane to synthesis gas. In an embodiment, the auto-thermal reforming arrangement **206** utilizes energy from different energy sources which include, but may not be limited to, a renewable energy source **306**. The renewable energy source **306** includes at least one of solar energy, wind energy, geothermal energy and tidal energy.

The electrolysing arrangement **208** simultaneously electrolyses water to produce oxygen and hydrogen. The oxygen holder **312** and the hydrogen holder **314** collect oxygen and hydrogen respectively. Part or all of the collected oxygen is supplied to the inlet of the auto-thermal reforming arrangement **206** to react with methane to generate sufficient heat, so that, in the presence of added steam, the methane is converted over the reforming catalyst to produce synthesis gas. The synthesis gas, rich in hydrogen, reacts with collected carbon dioxide in the methanol synthesis arrangement **210** to produce the methanol product **212**. In an embodiment, hydrogen may be fed to the methanol synthesis arrangement **210** to react with any additional carbon dioxide obtained from the separation stage and hence increase an overall yield of methanol product **212** from a given quantity of biogas.

In an example, methanol synthesis gas is characterised by the stoichiometric ratio (H_2 – CO_2) / (CO + CO_2), often referred to as the module M. A module of 2 defines a stoichiometric synthesis gas for formation of methanol. Further, the process is based on known chemistry but the methane is separated and purified (and steam reformed (known) using autothermal reformers to produce synthesis gas. The reactions of the synthesis process are:

$CH_4 + H_2O \Rightarrow CH_3OH + H_2$... (1)

$CH_4 + H_2O \Rightarrow CO + 3H_2$ .... (2)

$CH_4 + 2H_2O \Rightarrow + CO_2 + 4H_2$...(3)

Reaction (2) of catalytic methane steam reforming is strongly endothermic so that steam reforming for production of methanol requires an external heat supply. In this invention the reaction can be run much closer to stoichiometric ratios, allowing more carbon content from the methane rich gas (AD gas or biogas) to produce Methanol, thus obtaining more methanol for the same amount of methane input. The composition of the synthesis gas is too rich in Hydrogen for stoichiometric methanol synthesis so by adding in some of the separated CO_2 the stoichiometric ratios of methanol are balanced.

It will be appreciated that both the auto-thermal reforming reaction and the steam reforming reaction require the addition of steam as a key reactive component in the reaction; however, the auto-thermal reforming reaction retains the methane as a carbon source and does not burn it externally. Hence, the oxidation products from the methane are not lost to atmosphere.

It will be further appreciated that the apparatus **200** shown in **FIG. 2** removes sulphur compounds from the gas feed by the gas purification arrangement **304**; however, it will be appreciated that the removal of sulphur can be done by ZnO technology or some other conventional techniques. In addition, the auto-thermal reforming arrangement **206** may be fully or partially replaced by conventional steam reforming.

Moreover, the heat required for various processes may be generated by various sources including burning of methane, electrical induction and the like. Furthermore, carbon dioxide may be utilized to make use of the excess hydrogen generated during the production of synthesis gas **212**. Furthermore, oxygen and carbon dioxide used in the processes may be supplied externally.

In one embodiment, the apparatus **200** further includes an additive source **320**. In an example, the additive source **320** includes one of an agitation tank, a gas bubbling tank and a continuous flow for adding an additive to the methanol product to constitute a liquid fuel. For example, the additive includes at least one of polyethylene glycol dinitrate, ammonium nitrate, urea, Avocet (Avocet is a registred trade mark in the United Kingdom) or any combination thereof. The additive source **320** provides additive, which may be mixed with the methanol product **212** to constitute the liquid fuel, for example a diesel replacement.

Although the composition of Avocet is proprietary, and may have varied over time, the composition of the original Avocet additive includes following components as provided below:

PEG (PolyEthyleneGlycol) dinitrate	- 80%
Methanol	- 18%
Lubricity additive	- 1.5%
Antioxidant	- 0.1%

FIG. 4 is an illustration of a method **400** for using an integrated system (such as the integrated system **100** of FIG. 1) for producing methanol product, in accordance with an embodiment of the present disclosure. As mentioned above, the integrated system includes a gas feed arrangement (such as gas feed arrangement **102**) and an apparatus (such as the apparatus **200**) for converting a gas feed from the gas feed arrangement into the methanol product. At a step **402**, the flowchart **400** initiates. At a step **404**, as aforementioned, a methane rich gas feed is collected from the gas feed arrangement. At a step **406**, an auto-thermal reforming arrangement of the apparatus is used for converting one or more gaseous components present in the methane rich gas feed. At a step **408**, the apparatus is arranged to partially oxidise the methane rich gas feed to maintain the auto-thermal reforming arrangement at a working temperature when in operation. At a step **410**, the apparatus is arranged to employ electrical power generated from an energy source, preferably a renewable energy source, to provide additional heating in the auto-thermal reforming arrangement for maintaining the working temperature when in operation. The flowchart **400** terminates at a step **412**.

FIG. 5 is an illustration of a detailed flowchart **500** for using an apparatus (such as the apparatus **200** of FIG. 3) of the integrated system for converting the methane rich gas feed into the methanol product, in accordance with another embodiment of the present disclosure. The flowchart **500** initiates at a step **502**. At a step **504**, a gas purification arrangement **304** purifies the gas feed (i.e. methane rich gas feed provide by the gas feed arrangement **102**) to remove sulphur components from the gas feed. In addition, the gas separating arrangement **204** of the apparatus **200** separates the purified gas feed into carbon dioxide and methane components. Following the step **504**, at a step

506, the methane component is fed to the auto-thermal reforming arrangement **206** to produce a synthesis gas. Moreover, the hydrogen-rich synthesis gas reacts with the carbon dioxide component in the methane synthesis arrangement **210** to produce the methanol product **212**. Following the step **506**, at a step **508**, the electrolysing arrangement **208** electrolyses water to provide the oxygen feed and the hydrogen feed for the methane synthesis arrangement **210**. Following the step **508**, at a step **510**, the oxygen feed supplies oxygen to the auto-thermal reforming arrangement **206**. Following the step **510**, at a step **512**, electrical power from a renewable energy source provides additional heating in the auto-thermal reforming arrangement **210** to maintain the required working exit temperature during the operation to minimise the methane loss due to lower conversion to synthesis gas. The renewable energy sources used to provide heating and operating the electrolysing arrangement **208** include, but may not be limited to, solar and wind generators. Simultaneously, the electrolysing arrangement **208** electrolyses water to produce oxygen and hydrogen. The oxygen holder **312** and the hydrogen holder **314** collect oxygen and hydrogen respectively. The collected oxygen is supplied to the auto-thermal reforming arrangement **206** to react with methane in the presence of catalyst to form synthesis gas. At a step **514**, the synthesis gas reacts with collected carbon dioxide in the methanol synthesis arrangement **210** to produce methanol product **212**. At a step **516**, the flowchart **500** terminates.

In one embodiment, the flowchart **500** may include addition of an additive to the methanol product to constitute a liquid fuel, for example using the additive source **320**. For example, the additives may include at least one of polyethylene glycol dinitrate, ammonium nitrate, urea, Avocet™ or any combination thereof. Specifically, the additive may be mixed with the methanol product to constitute the liquid fuel, for example, a diesel replacement.

The different functional arrangements of the integrated system **100** explained in conjunction of description of **FIGS. 1-3** for converting gas feed into the methanol product **212** provide many benefits over known apparatus and methods for methanol production. The integrated system **100** employs integration into a single process concept, whereby simply using biogas, water and a source of electricity, a liquid fuel is produced that makes use of all of by-products of an agricultural facility, for example a farm, without a disadvantage of simultaneously forming unwanted by-products.

In addition, steam reforming, is a highly endothermic reaction. However, in the case of auto-thermal reforming, for example by using auto-thermal reforming arrangement **206** of the apparatus **200**, all the heat is generated at an inlet of a catalytic converter and gas flowing through the catalytic converter gradually cools down as it proceeds through a catalyst bed of the catalytic converter. Thus, an exit temperature of the catalytic converter is significantly lower than the inlet temperature. The conversion of methane to synthesis gas is strongly favoured by high temperatures, thus the equilibrium conversion of methane to synthesis gas gradually falls as the temperature falls. As a result, the conversion to synthesis gas is lower in an auto-thermal reforming arrangement **206** than would be the case in a conventional steam reformer. Moreover, the capital cost benefit associated with the auto-thermal reforming arrangement **206** is eroded by the lower conversion to product. However, owing to the surplus electrical energy, the temperature at the outlet of the auto-thermal reforming arrangement **206** is maintained by a form of electrical heating to achieve efficient use of some of the energy that might otherwise not be used. In addition, the exit temperature of the gaseous products is increased to achieve a maximum possible yield of synthesis gas, and therefore methanol, from the resources at disposal for use by the apparatus **200**.

In addition, the apparatus **200** of the present disclosure focuses at a reforming stage employed in the methanol production. Conventional steam reforming uses externally fired reaction tubes. In this instance, some of the methane feed is simply burnt to heat the reaction tubes to sufficiently high reaction temperatures, and to provide sufficient energy to satisfy the thermodynamic demands of the endothermic steam reforming reaction occurring within the reaction tubes. Virtually all contemporary known methanol production plants employ high-temperature reaction tubes for implementing steam reforming. In an agrarian farm location, a huge amount of gas is often not available. The burning of methane potentially results in an unacceptable loss of feedstock material. Hence, at least, the reaction tubes can be optionally heated electrically using infrared or induction heating. However, pursuant to the present disclosure, a more advantageous implementation utilizes “auto-thermal reforming”.

In addition, auto-thermal reforming used in the apparatus **200** is advantageous on account of being susceptible to being implemented at a lower capital expenditure in comparison to known conventional reforming. In auto-thermal reforming, oxygen and steam are added to a methane feed to generate a gas mixture. The gas mixture is then passed over a catalyst heated to a suitable temperature. Some of the methane is burned internally in a spatial proximity of the catalyst to produce carbon monoxide (CO) and the heat thereby generated is sufficient to sustain the steam reforming reaction at the catalyst. Sufficient oxygen is provided to allow for an exit temperature in an order of 775°C, for example in a range of 750°C to 800°C. Beneficially, such a reforming reaction is implemented in an equilibrium state, and a product generated from such an auto-thermal reforming process is identical to the product obtained by employing a conventional known steam reforming process. The use of oxygen, rather that air, is essential and a suitable supply is provided when implementing apparatus pursuant to the present disclosure.

Moreover, the production of methanol from synthesis gas derived from methane via steam reforming always results in an excess of hydrogen in a reactor loop of associated apparatus. In a conventional chemical works, such an excess of hydrogen is normally exported to another process that requires hydrogen, such as an ammonia plant and so forth. In a rural agrarian situation, for example a farm location, such other processes such as ammonia production would not be implemented, thereby raising an issue of employing the excess hydrogen in an economically beneficial manner. However, in many rural situations, a source of carbon dioxide is often available, for example arising from biogas generation. Some of the carbon dioxide is advantageously blended back into the methanol synthesis loop employed, to make best use of the excess hydrogen. In many situations, excess of hydrogen is likely to be insufficient to be able to use all of the carbon dioxide. Thus, a significant quantity of additional hydrogen must beneficially be generated separately, if optimal use of all of the available carbon dioxide is to be achieved. Such additional hydrogen is optionally beneficially obtained by electrolysis; such electrolysis has an additional advantage in providing oxygen for use in the auto-thermal reformer.

Modifications to embodiments of the invention described in the foregoing are possible without departing from the scope of the invention as defined by the accompanying claims. Expressions such as “including”, “comprising”, “incorporating”, “consisting of”, “have”, “is” used to describe and claim the present invention are intended to be construed in a non-exclusive manner, namely allowing for items, components or elements not explicitly described also to be present. Reference to the singular is also to be construed to relate to the plural. Numerals included within parentheses in the accompanying claims are intended to assist understanding of the claims and should not be construed in any way to limit subject matter claimed by these claims.

CLAIMS

1. An integrated system for producing a methanol product, the system comprising
- a gas feed arrangement for providing a methane rich gas feed; and
- an apparatus for converting the methane rich gas feed into the methanol product, characterized in that the apparatus comprises an auto-thermal reforming arrangement for converting one or more gaseous components present in the methane rich gas feed, wherein the auto-thermal reforming arrangement configured to partially oxidise the methane rich gas feed to maintain the auto-thermal reforming arrangement at a working temperature when in operation, and wherein the auto-thermal reforming arrangement employs electrical power generated from an energy source, preferably a renewable energy source, to provide additional heating in the auto-thermal reforming arrangement for maintaining the working temperature when in operation.

2. An integrated system as claimed in claim 1, characterized in that the gas feed arrangement comprises an organic waste material digestion arrangement for providing biogas as the methane rich gas feed.

3. An integrated system as claimed in claim 1, characterized in that the gas feed arrangement comprises a natural gas source for providing natural gas as the methane rich gas feed.

4. An integrated system as claimed in claim 1, characterized in that the apparatus comprises a gas purification and separating arrangement for purifying the methane rich gas feed to remove sulphur components therefrom, and for separating the purified gas feed into at least carbon dioxide and methane component, wherein the methane component is provided to the auto-thermal reforming arrangement for producing a synthesis gas, and the apparatus is operable to react the synthesis gas with the carbon dioxide component in a synthesis arrangement to produce the methanol product.

5. An integrated system as claimed in claim 1, characterized in that the apparatus comprises an oxygen feed to the auto-thermal reforming arrangement.

6. An integrated system as claimed in claim 5, characterized in that the apparatus comprises an electrolysing arrangement for electrolysing water to provide the oxygen feed, and hydrogen feed for the synthesis arrangement.

7. An integrated system as claimed in claim 1, characterized in that the renewable energy source comprises at least one of solar energy, wind energy, geothermal energy, hydroelectricity and tidal energy.

8. An integrated system as claimed in claim 1, characterized in that the apparatus further comprises one of an agitation tank, a gas bubbling tank and a continuous flow for adding an additive to the methanol product to constitute a liquid fuel.

9. An integrated system as claimed in claim 8, characterized in that the additive comprises at least one of polyethylene glycol dinitrate, ammonium nitrate, urea, Avocet or any combination thereof.

10. A method for producing a methanol product using an integrated system having a gas feed arrangement and an apparatus for converting a gas feed from the gas feed arrangement into the methanol product, characterized in that the method comprising:
- collecting a methane rich gas feed from the gas feed arrangement;
- using an auto-thermal reforming arrangement of the apparatus for converting one or more gaseous components present in the methane rich gas feed;
- arranging for the apparatus to partially oxidise the methane rich gas feed to maintain the auto-thermal reforming arrangement at a working temperature when in operation; and
- arranging for the apparatus to employ electrical power generated from an energy source, preferably a renewable energy source, to provide additional heating in the auto-thermal reforming arrangement for maintaining the working temperature when in operation.

11. A method as claimed in claim 10, characterized in that the method further comprises:
    - using a gas purification and separating arrangement of the apparatus for purifying the methane rich gas feed to remove sulphur components therefrom, and for separating the purified gas feed into at least carbon dioxide and methane components; and
    - providing the methane component to the auto-thermal reforming arrangement for producing a synthesis gas, and reacting the synthesis gas with the carbon dioxide component in a synthesis arrangement to produce the methanol product.

12. A method as claimed in claim 10, characterized in that the method comprises using an oxygen feed of the apparatus for supplying oxygen to the auto-thermal reforming arrangement.

13. A method as claimed in claim 12, characterized in that the method comprises using an electrolysing arrangement of the apparatus for electrolysing water to provide the oxygen feed, and a hydrogen feed for the synthesis arrangement.

14. A method as claimed in claim 10, characterized in that the method further comprises adding an additive to the methanol product to constitute a liquid fuel.

15. A method as claimed in claim 14, characterized in that the additive comprises at least one of polyethylene glycol dinitrate, ammonium nitrate, urea, Avocet™ or any combination thereof.

16. A method as claimed in claim 11, characterized in that the methane rich gas feed is one of a biogas and a natural gas.

17. A method as claimed in claim 11, characterized in that the renewable energy source comprises at least one of solar energy, wind energy, geothermal energy and tidal energy.

Intellectual Property Office

Application No:	GB1522326.6	**Examiner:**	Dr Richard Wood
Claims searched:	1-17	**Date of search:**	7 October 2016

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X,E	1-7, 10-13, 16, 17	WO 2016/073500 A1 (ZTEK) - see especially Figs. 1, 3, 9, 11; p. 23 lines 1-25.
Y	1-5, 7-12, 14-16, 17	US 2012/226080 A1 (MEYER-PITTROFF) - see especially Fig. 3; paras. [0049], [0070]-[0072].
Y	1-5, 7-12, 14-16, 17	US 2014/165569 A1 (HSU) - see especially Figs. 1, 3; para. [0038].
Y	1-5, 7-12, 14-16, 17	US 2014/100294 A1 (COHN et al.) - see especially paras. [0032] - [0035].
Y	1-5, 7-12, 14-16, 17	US 2007/161716 A1 (XIE et al.) - see especially para. [0034].
Y	1-5, 7-12, 14-16, 17	WO 2015/069896 A2 (WATT FUEL CELL CORP) - see especially para. [0080].

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

C01B; C07C

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC

Intellectual Property Office

International Classification:

Subclass	**Subgroup**	**Valid From**
C07C	0029/151	01/01/2006
C01B	0003/38	01/01/2006