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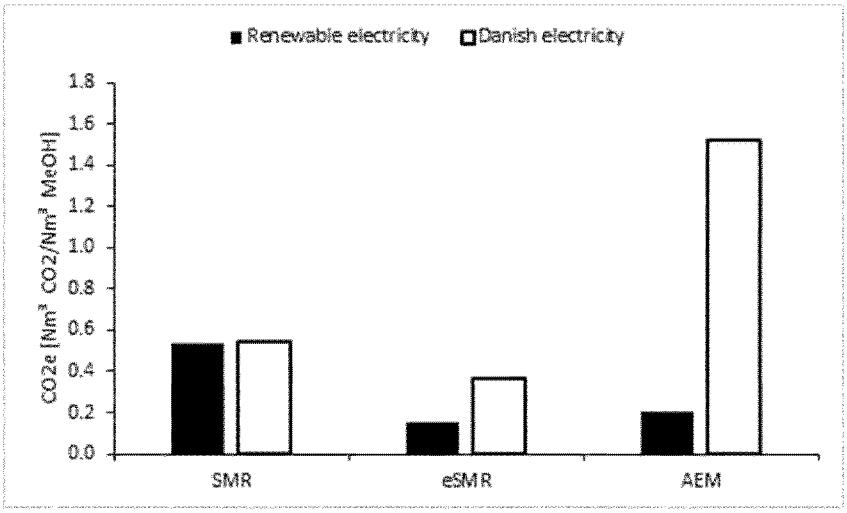

Fig. 3

(57) Abstract: The invention relates to a method for upgrading biogas to methanol, comprising the steps of:- providing a reformer feed stream comprising biogas, - optionally, purifying the reformer feed stream in a gas purification unit, - optionally, prereforming the reformer feed stream together with a steam feedstock in a prereforming unit, - carrying out steam methane reforming in a reforming reactor heated by means of an electrical power source, providing the synthesis gas to a methanol synthesis unit to provide a product comprising methanol and an off-gas. Then invention also relates to a system for upgrading biogas to methanol.

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Biogas upgrading to methanol

FIELD OF THE INVENTION

Embodiments of the invention generally relate to a method and a system for upgrading biogas to methanol.

BACKGROUND

Biogas is a renewable energy source that can be used for heating, electricity, and many other operations. Biogas can be cleaned and upgraded to natural gas standards, when it becomes bio-methane. Biogas is considered to be a renewable resource because its production-and-use cycle is continuous, and it generates no net carbon dioxide. When the organic material has grown, it is converted and used. It then regrows in a continually repeating cycle. From a carbon perspective, as much carbon dioxide is absorbed from the atmosphere in the growth of the primary bio-resource as is released, when the material is ultimately converted to energy. Biogas is a mixture of gases produced by the breakdown of organic matter in the absence of oxygen. Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. Biogas is primarily methane (CH_4) and carbon dioxide (CO_2) and may have small amounts of hydrogen sulfide (H_2S), moisture, siloxanes, and possibly other components. Up to 30% or even 40% of the biogas may be carbon dioxide. Typically, this carbon dioxide is removed from the biogas and vented in order to provide a methane rich gas for further processing or to provide it to a natural gas network.

Biogas is indicated as an essential platform to realize circular industrial economy, where it allows for integrating waste streams back into industry. Such an approach will allow moving away from the “Take, Make, Dispose” society established in the 20th century and into the “Make, Use, Return” society, which will be needed for achieving a truly sustainable future. This thought is gaining increased focus within Europe and

large biogas plants are already installed. Within Denmark alone, a large capacity is already installed and is expected to increase to a capacity of 17 PJ/a by 2020, but the overall potential could be as high as 60 PJ/a for Denmark. Today, biogas plants are typically coupled to the natural gas grid, because this is the most feasible utilization. However, the nature of the biogas with roughly 40% CO_2 and 60% CH_4 does not allow for its direct mixing into the natural gas network, why CO_2 must be removed from the gas, and this requires a gas separation plant.

It is an object of the invention to provide a method and system where the carbon dioxide of the biogas is also utilized to manufacture a product. It is an object of the invention to provide a method and system for converting biogas to methanol. It is a further object of the invention to provide a sustainable method and system for converting biogas to methanol.

SUMMARY OF THE INVENTION

The invention relates to sustainable production of methanol from biogas by applying the electrically heated steam methane reformer (eSMR) technology that will allow for a practical zero-emission chemical plant with complete or substantially complete carbon utilization.

Embodiments of the invention generally relate to a method and system for upgrading biogas to methanol.

A first aspect of the invention relates to a method for upgrading biogas to methanol, comprising the steps of:

a) providing a reformer feed stream comprising biogas,

b1) optionally, purifying the reformer feed stream in a gas purification unit,

b2) optionally, prereforming the reformer feed stream together with a steam feedstock in a prereforming unit,

c) carrying out steam methane reforming of said reformer feed stream in a reforming reactor with a comprising a pressure shell housing a structured catalyst arranged to catalyze steam reforming of the reformer feed stream, where the structured catalyst comprises a macroscopic structure of an electrically conductive material, where the macroscopic structure supports a ceramic coating, where the ceramic coating supports a catalytically active material.

The steam methane reforming comprises the following steps:

- c1) supplying the reformer feed stream to the reforming reactor,
- c2) allowing the reformer feed stream to undergo steam reforming reaction over the structured catalyst and outletting a synthesis gas from the reforming reactor, and
- c3) supplying electrical power via electrical conductors connecting an electrical power supply placed outside the pressure shell to the structured catalyst, allowing an electrical current to run through the electrically conductive material of the macroscopic structure, thereby heating at least part of the structured catalyst to a temperature of at least 500°C,

d) providing at least part of the synthesis gas of step c2) to a methanol synthesis unit to provide a product comprising methanol and an off-gas.

The traditional methanol production involves steam reforming of hydrocarbons followed by a methanol synthesis unit; this provides for a major associated CO_2 emission. It should be noted that step d) of providing at least part of the synthesis gas to the methanol synthesis unit also covers the case, where water is removed from the synthesis gas prior to leading the synthesis gas, in this case a dry or drier synthesis gas, to the methanol synthesis unit. The synthesis gas obtained in step c) may e.g. be cooled to a temperature below the dew point of the gas and be separated to a liquid phase comprising water and a gas phase comprising the dry synthesis gas, upstream the methanol synthesis unit.

Moreover, CO_2 is typically removed from the biogas, viz. from the reformer feed stream, in a gas separation unit prior to feeding the remaining gas, together with steam, into a steam methane reformer. The byproduct of CO_2 is typically emitted into the atmosphere, or, when possible, collected and sold as a chemical. Instead of building a separation plant to remove/upgrade the CO_2 of the biogas, the inherent mixture of CO_2 and CH_4 makes it a good feedstock for methanol production by eSMR ("eSMR-MeOH"), where essentially all carbon atoms can be converted into methanol. Such a plant in combination with the biogas plant may easily be more attractive, because by producing methanol over methane a substantially higher valorization of the end product is achieved.

Moreover, this traditional methanol production gives little opportunity for energy storage and no debottlenecking of the energy fluctuations associated with renewable electricity. As the highly endothermic steam reforming reaction is facilitated in fired reformers using large furnaces operating at temperatures in the vicinity of 1000°C, the process economy is heavily favored by economy of scale to enable high process efficiency and integrated waste heat management. Such plants are therefore difficult to scale down economically due to the integrated design and high upfront capital investment. Consequently, the typical methanol plants exceed production capacities of 2000 MT/day.

An alternative route to methanol production is electrolysis of water for hydrogen production mixed with CO_2 for methanol production. This concept is proven and large-scale operation has already been performed with a capacity of 11 MT/day in Iceland, using alkaline electrolysis for hydrogen production. However, such plants are limited to locations with high availability of electricity, low electricity prices, and/or readily available high-grade CO_2. Especially CO_2 is a sparse resource and is typically financially unattractive to utilize. Overall, the process economy of the electrolysis-driven frontend to a methanol plant remains very expensive compared with the classical steam reforming approach, because CO_2-separation/purification combined with water electrolysis and

subsequent compression has a very high net energy use, overall giving methanol production prices 4–6 higher than equivalent fossil fuels. The use of only CO_2 and hydrogen as make-up gas to the methanol synthesis also requires more catalyst inventory and reactor size, etc. due to the low reactivity of the gas. The application of co-electrolysis by solid oxide electrolysis cells (SOEC) could produce a more efficient and smaller methanol synthesis, but this approach is currently only at laboratory scale. In addition, electrolysis in general also has a high upfront capital investment presently, which only makes the process economy more challenged.

By the term "methanol synthesis unit" is understood one or several reactors configured to convert synthesis gas into methanol. Such reactors can for example be a boiling water reactor, an adiabatic reactor, a condensing methanol reactor or a gas-cooled reactor. Moreover, these reactors could be many parallel reactor shells and sequential reactor shells with intermediate heat exchange and/or product condensation. It is understood that the methanol synthesis unit also contains equipment for recycling and pressurizing feed to the methanol reactor(s). The term "reformer feed stream" is meant to cover both the reformer feed stream comprising the biogas as well as a purified reformer feed stream, a prereformed reformer feed stream and a reformer feed stream with added hydrocarbon gas and/or with added steam and/or with added hydrogen and/or with added off-gas from the methanol synthesis unit. All constituents of the reformer feed stream are pressurized, either separately or jointly, upstream the reforming reactor. Typically, steam is pressurized separately, whilst the other constituents of the reformer feed stream may be pressurized jointly. The pressure(s) of the constituents of the reformer feed stream is/are chosen so that the pressure within the reforming reactor lies between 5 to 100 bar, preferably between 20 and 40 bar, or preferably between 70 and 90 bar.

In an embodiment, the electrical power supplied has been generated at least in part by means of renewable energy sources. Full utilization of methanol as an energy vector

cannot be realized unless a more optimal production route is introduced. For this purpose, the method and plant of the invention uses renewable electricity to increase the energy value of biogas in the reformer feed stream into methanol. The electrically heated steam methane reformer (eSMR) is a very compact reforming reactor, resulting in a lower capital investment than classical steam reforming equipment. The feedstock to the eSMR can in principle come from any methane-containing source such as biogas or natural gas, but because heating is facilitated by electricity, it will be an improvement over the existing fired reformer by saving the direct CO_2 emissions. In addition, an excellent synergy exists with a biogas feedstock that will allow for practically full conversion of all carbon in the biogas to methanol.

The term “biogas” in connection with the present invention means a gas with the following composition:

Compound	Formula	%
Methane	CH_4	50–75
Carbon dioxide	CO_2	25–50
Nitrogen	N_2	0–10
Hydrogen	H_2	0–1
Oxygen	O_2	0-1

In an embodiment, the reformer feed stream has a first H/C ratio and a second hydrocarbon feed gas with a second H/C ratio is mixed with the reformer feed stream upstream the reforming reactor, wherein the second H/C ratio is larger than the first H/C ratio. Examples of a second hydrocarbon feed could be natural gas or shale gas. Here, the H/C ratio of a gas is the ratio between hydrogen atoms and carbon atoms in the gas, both in hydrocarbons and other gas components.

In an embodiment, wherein an electrolysis unit is used to generate a hydrogen rich stream from a water feedstock and where the hydrogen rich stream is added to the synthesis gas to balance the module M of the synthesis gas to be in the range of 1.5 to 2.5. The module M of a synthesis gas is $M = \frac{H_2 - CO_2}{CO + CO_2}$. Preferably, the module M of the synthesis gas is balanced to be in the range of 1.95 to 2.1. The hydrogen rich stream is advantageously added between step a) and d), in particular between step b1) and step c) and in particular between step c) and step d).

In an embodiment, the electrolysis unit is a solid oxide electrolysis cell unit and the water feedstock is in the form of steam produced from other processes of the method. Steam is e.g. generated in the methanol synthesis unit, steam produced in the methanol synthesis unit or a waste heat boiler downstream the eSMR within the system for upgrading biogas to methanol.

In an embodiment, a membrane unit or a pressure swing adsorption (PSA) unit is included in the methanol synthesis unit to extract at least part of the hydrogen from the off-gas and return the at least part of the hydrogen to the synthesis gas to balance the module M of the synthesis gas to be in the range of 1.5 to 2.5. Preferably, the module M of the synthesis gas is balanced to be in the range of 1.95 to 2.1. Again, the module M is defined as: $M = \frac{H_2 - CO_2}{CO + CO_2}$.

In an embodiment, a combination of steam superheating and steam generation is integrated in the waste heat recovery of the hot synthesis gas from the reforming reactor, and the superheated steam is used as steam feedstock in step c) of the method for upgrading biogas to methanol.

In an embodiment, the pressure of the gas inside the reforming reactor is between 20 and 100 bar, preferably between 50 and 90 bar.

In an embodiment, the temperature of the gas exiting the reforming reactor is between 900 and 1150°C.

In an embodiment, the space velocity evaluated as flow of gas relative to the geometric surface area of the structured catalyst is between 0.6 and 60 $Nm^3/m^2/h$ and/or the flow of gas relative to the occupied volume of the structured catalyst is between 700 $Nm^3/m^3/h$ and 70000 $Nm^3/m^3/h$. Preferably, the flow of gas relative to the occupied volume of the structured catalyst is between 7000 $Nm^3/m^3/h$ and 10000 $Nm^3/m^3/h$.

In an embodiment, the plot area of the reforming reactor is between 0.4 m^2 and 4 m^2. Preferably, the plot area is between 0.5 and 1 m^2. Here the term "plot area" is meant to be equivalent to "ground area", viz. the area of land that the reforming reactor will take up when installed.

In an embodiment, the production of methanol is regulated according to availability of renewable energy.

In an embodiment, the method further comprises the step of upgrading the raw methanol to fuel grade methanol.

In an embodiment, the methanol is upgraded to chemical grade methanol.

In an embodiment, the method further comprises the step of using at least part of the methanol of step d) to a system for producing transportation fuel. In particular, the methanol is used as feedstock in a system for methanol to gasoline synthesis.

In an embodiment, between 80% and 100% of the carbon in the biogas of the reformer feed stream is converted into MeOH.

In an embodiment, the biogas of the reformer feed stream amounts to 500 Nm^3/h to 8000 Nm^3/h.

In an embodiment, a separation unit is used to remove part of the CO_2 of the biogas of the reformer feed stream subsequent to step a) and preceding step d). If a prereforming unit is present, the removal of CO_2 preferably takes place upstream the prereforming unit, viz. before step b2). If a purification unit is present, the removal of CO_2 preferably takes place upstream the purification unit, viz. before step b1). The separation unit is e.g. a membrane unit.

Advantageously, a system for upgrading biogas to methanol comprises both a membrane unit for removing part of the CO_2 in the biogas of the reformer feed stream upstream the reforming reactor as well as an SOEC. Thus, the system can shuffle between using the membrane unit in periods with low electricity availability and the SOEC in periods with higher electricity availability. In this way, it is rendered possible to regulate the module down by reducing CO_2 addition to the process, while bypassing the membrane in periods with high electricity availability and instead producing extra hydrogen to balance the module by SOEC.

When a reformer feed stream with more than 25% CO_2 is used as feedstock to the method of the invention, it is advantageous to remove some of the CO_2 in order to reach a reformer feed stream with about 25% CO_2 and about 75% CH_4 due to the overall reaction scheme for methanol production below:

$0.75CH_4 + 0.25CO_2 + 0.5H_2O \rightarrow CO + 2H_2 \rightarrow CH_3OH$.

In an embodiment of the invention, a part of the off-gas produced in step d) is recycled to a biogas production facility for producing the biogas to be upgraded in the method of the invention. As said off-gas typically has a high content of hydrogen, this hydrogen can be used in a biogas production facility, i.e. a fermentation plant, where it can react

with carbon oxides to produce methane. Effectively, this means that in a process constellation where an amount of hydrogen rich off-gas is recycled to the biogas production facility, the produced biogas will have higher CH_4/CO_2 ratio than a biogas produced in a biogas production facility with no recycling of said hydrogen-rich off-gas.

Another aspect of the invention, relates to a system for upgrading biogas to methanol, comprising:

- an optional gas purification unit,
- an optional prereforming unit,
- a reforming reactor with a comprising a pressure shell housing a structured catalyst arranged to catalyse steam reforming of a feed gas comprising hydrocarbons, the structured catalyst comprising a macroscopic structure of an electrically conductive material, the macroscopic structure supporting a ceramic coating, where the ceramic coating supports a catalytically active material; wherein the reforming reactor moreover an electrical power supply placed outside the pressure shell and electrical conductors connecting the electrical power supply to the structured catalyst, allowing an electrical current to run through the electrically conductive material of the macroscopic structure to thereby heat at least part of the structured catalyst to a temperature of at least 500°C,
- a methanol synthesis unit arranged to receive a synthesis gas from the reforming reactor and produce a product comprising methanol and an off-gas.

The structured catalyst of the reforming reactor of the system is configured for steam reforming. This reaction takes place according to the following reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$
$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$$
$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$$

The structured catalyst is composed a metallic structure, a ceramic phase, and an active phase. The metallic structure may be FeCrAlloy, Alnico, or similar alloys. The ce-

ramic phase may be Al_2O_3, $MgAl_2O_3$, $CaAl_2O_3$, ZrO_2, or a combination thereof. The catalytically active material may be Ni, Ru, Rh, Ir, or a combination thereof.

In an embodiment, catalyst pellets are loaded on top of, around, inside, or below the structured catalyst of the reforming reactor. The catalyst material for the reaction may be Ni/Al_2O_3, $Ni/MgAl_2O_3$, $Ni/CaAl_2O_3$, $Ru/MgAl_2O_3$, or $Rh/MgAl_2O_3$. The catalytically active material may be Ni, Ru, Rh, Ir, or a combination thereof. This can improve the overall gas conversion inside the reforming reactor.

In an embodiment, the macroscopic structure(s) has/have a plurality of parallel channels, a plurality of non-parallel channels and/or a plurality of labyrinthic channels. The channels have walls defining the channels. Several different forms and shapes of the macroscopic structure can be used as long as the surface area of the structured catalyst exposed to the gas is as large as possible. In a preferred embodiment, the macroscopic structure has parallel channels, since such parallel channels render a structured catalyst with a very small pressure drop. In a preferred embodiment, parallel longitudinal channels are skewed in the longitudinal direction of the macroscopic structure. In this way, molecules of the gas flowing through the macroscopic structure will mostly tend to hit a wall inside the channels instead of just flowing straight through a channel without necessarily getting into contact with a wall. The dimension of the channels should be appropriate in order to provide a macroscopic structure with a sufficient resistivity. For example, the channels could be quadratic (as seen in cross section perpendicular to the channels) and have a side length of the squares of between 1 and 3 mm; however, channels having a maximum extent in the cross section of up to about 4 cm are conceivable. Moreover, the thickness of the walls should be small enough to provide a relatively large electrical resistance and large enough to provide sufficient mechanical strength. The walls may e.g. have a thickness of between 0.2 and 2 mm, such as about 0.5 mm, and the ceramic coating supported by the walls has a thickness of between 10 µm and 500 µm, such as between 50 µm and 200 µm, such as 100 µm. In

another embodiment, the macroscopic structure of the structured catalyst is cross-corrugated. In general, when the macroscopic structure has parallel channels, the pressure drop from the inlet to the outlet of the reforming reactor system may be reduced considerably compared to a reactor where the catalyst material is in the form of pellets such as a standard SMR.

In an embodiment, the macroscopic structure(s) is/are extruded and sintered structures. Alternatively, the macroscopic structure(s) is/are 3D printed structure(s). A 3D printed structure can be provided with or without subsequent sintering. Extruding or 3D printing a macroscopic structure, and optional subsequent sintering thereof results in a uniformly and coherently shaped macroscopic structure, which can afterwards be coated with the ceramic coating.

Preferably, the macroscopic structure has been manufactured by 3D printing or extrusion of a mixture of powdered metallic particles and a binder to an extruded structure and subsequent sintering of the extruded structure, thereby providing a material with a high geometric surface area per volume. Preferably, the 3D printed extruded structure is sintered in a reducing atmosphere to provide the macroscopic structure. Alternatively, the macroscopic structure is 3D printed a metal additive manufacturing melting process, viz. a 3D printing processes, which do not require subsequent sintering, such as powder bed fusion or direct energy deposition processes. Examples of such powder bed fusion or direct energy deposition processes are laser beam, electron beam or plasma 3D printing processes. As another alternative, the macroscopic structure may have been manufactured as a 3D metal structure by means of a binder-based metal additive manufacturing process, and subsequent sintered in a non-oxidizing atmosphere at a first temperature T_1, where $T_1 > 1000^{\circ}C$, in order to provide the macroscopic structure.

A ceramic coating, which may contain the catalytically active material, is provided onto the macroscopic structure before a second sintering in an oxidizing atmosphere, in order to form chemical bonds between the ceramic coating and the macroscopic structure. Alternatively, the catalytically active material may be impregnated onto the ceramic coating after the second sintering. When chemical bonds are formed between the ceramic coating and the macroscopic structure, an especially high heat conductivity between the electrically heated macroscopic structure and the catalytically active material supported by the ceramic coating is possible, offering close and nearly direct contact between the heat source and the catalytically active material of the structured catalyst. Due to close proximity between the heat source and the catalytically active material, the heat transfer is effective, so that the structured catalyst can be very efficiently heated. A compact reforming reactor system in terms of gas processing per reforming reactor system volume is thus possible, and therefore the reforming reactor system housing the structured catalyst may be compact. The reforming reactor system of the invention does not need a furnace and this reduces the overall reactor size considerably. Moreover, it is an advantage that the amount of synthesis gas produced in a single pressure shell is increased considerably compared to known tubular steam reformers. In a standard tubular steam reformer, the amount of synthesis gas produced in a single tube of the tubular steam reformer is up to 500 Nm^3/h. In comparison, the reactor system of the invention is arranged to produce up to or more than 2000 Nm^3/h, e.g. even up to or more than 10000 Nm^3/h, within a single pressure shell. This can be done without the presence of O_2 in the feed gas and with less than 10% methane in the synthesis gas produced. When a single pressure shell houses catalyst for producing up to 10000 Nm^3/h synthesis gas, it is no longer necessary to provide a plurality of pressure shells or means for distributing feed gas to a plurality of such separate pressure shells.

As used herein, the terms “3D print” and “3D printing” is meant to denote a metal additive manufacturing process. Such metal additive manufacturing processes cover 3D printing processes in which material is joined to a structure under computer control to

create a three-dimensional object, where the structure is to be solidified, e.g. by sintering, to provide the macroscopic structure. Moreover, such metal additive manufacturing processes cover 3D printing processes, which do not require subsequent sintering, such as powder bed fusion or direct energy deposition processes. Examples of such powder bed fusion or direct energy deposition processes are laser beam, electron beam or plasma 3D printing processes.

Preferably, the catalytically active material is particles having a size from 5 nm to 250 nm. The ceramic coating may for example be an oxide comprising Al, Zr, Mg, Ce and/or Ca. Exemplary coatings are calcium aluminate or a magnesium aluminum spinel. Such a ceramic coating may comprise further elements, such as La, Y, Ti, K or combinations thereof. Preferably, the conductors are made of different materials than the macroscopic structure. The conductors may for example be of iron, nickel, aluminum, copper, silver or an alloy thereof. The ceramic coating is an electrically insulating material and will typically have a thickness in the range of around 100 µm, e.g. about 10-500 µm.

The macroscopic structure is advantageously a coherent or consistently intra-connected material in order to achieve electrical conductivity throughout the macroscopic structure, and thereby achieve thermal conductivity throughout the structured catalyst and in particular providing heating of the a catalytically active material supported by the macroscopic structure. By using coherent or consistently intra-connected material, it is possible to ensure uniform distribution of current within the macroscopic structure and thus uniform distribution of heat within the structured catalyst. Throughout this text, the term “coherent” is meant to be synonymous to cohesive and thus refer to a material that is consistently intra-connected or consistently coupled. The effect of the structured catalyst being a coherent or consistently intra-connected material is that a control over the connectivity within the material of the structured catalyst and thus the conductivity of the macroscopic structure is obtained. It is to be noted that even if further modifications of the macroscopic structure are carried out, such as provision of

slits within parts of the macroscopic structure or the implementation of insulating material within the macroscopic structure, the macroscopic structure is still denoted a coherent or consistently intra-connected material.

In an embodiment, the structured catalyst has electrically insulating parts arranged to increase the current path between the conductors to a length larger than the largest dimension of the structured catalyst. The provision of a current path between the conductors larger than the largest dimension of the structured catalyst may be by provision of electrically insulating parts positioned between the conductors and preventing the current running through some part of the structured catalyst. Such electrically insulating parts are arranged to increase the current path and thus increase the resistance through the structured catalyst. In an embodiment, the at least one electrically insulating part has a length arranged to ensure that the minimum current path between the conductors is larger than the largest dimension of the macroscopic structure.

Non-limiting examples of such insulating parts are cuts, slits, or holes in the structure. Optionally, a solid insulating material such as ceramics in cuts or slits in the structure can be used. In a case where the solid insulating material is a porous ceramic material, the catalytically active material may advantageously be incorporated in the pores, by e.g. impregnation. A solid insulating material within a cut or slit assists in keeping the parts of the structured catalyst on the sides of the cut or slit from each other. As used herein, the term “largest dimension of the structured catalyst” is meant to denote the largest inner dimension of the geometrical form taken up by the structured catalyst. If the structured catalyst is box-formed, the largest dimension would be the diagonal from one corner to the farthest corner, also denoted the space diagonal.

It should be noted that even though the current through the structured catalyst may be arranged to twist or wind its way through the structured catalyst due to the electrically insulating parts arranged to increase the current path, the gas passing through

the reforming reactor system is inlet at one end of the reforming reactor system, passes through the structured catalyst once before being outlet from the reforming reactor system. Inert material is advantageously present in relevant gaps between the structured catalyst and the rest of the reforming reactor system to ensure that the gas within the reforming reactor system passes through the structured catalyst and the catalytically active material supported thereby.

In an embodiment, the length of the gas passage through the structured catalyst is less than the length of the passage of current from one conductor through the structured catalyst and to the next conductor. The ratio of the length of the gas passage to the length of the current passage may be less than 0.6, or 0.3, 0.1, or even down to 0.002.

In an embodiment, the structured catalyst has electrically insulating parts arranged to make the current path through the structured catalyst a zigzag path. Here, the terms "zigzag path" and "zigzag route" is meant to denote a path that has corners at variable angles tracing a path from one conductor to another. A zigzag path is for example a path going upwards, turning, and subsequently going downwards. A zigzag path may have many turns, going upwards and subsequently downwards many times through the structured catalyst, even though one turn is enough to make the path a zigzag path.

The following is a detailed description of embodiments of the invention depicted in the accompanying drawings. The embodiments are examples and are in such detail as to clearly communicate the invention. However, the amount of detail offered is not intended to limit the anticipated variations of embodiments; but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the present invention as defined by the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing of a system for biogas upgrading to methanol production;

Figures 2a-2c shows comparative cases for methanol plants based on a fired reformer versus an electric reformer versus alkaline electrolysis;

Figure 3 shows CO_2 equivalent emissions (CO_2e) associated with production of MeOH as the combined contribution from: Plant emissions + Emissions from electricity generation; and

Figure 4 is a graph of technologies with lowest operating expenses as a function of natural gas price and electricity price.

DETAILED DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing of a system 100 for biogas upgrading to methanol production. The system is a methanol plant comprising an electrically heated steam methane reformer (eSMR) 10.

The system 100 for biogas upgrading to methanol comprises a reforming section 10 and a methanol section 60. The reforming section 10 comprises a preheating section 20, a purification unit 30, e.g. a desulfurization unit, a prereformer 40 and an eSMR 50. The methanol section comprises a first separator 85, a compressor unit 70, a methanol synthesis unit 80, a second separator 90 as well as heat exchangers. The first and second separators 65 and 90 may e.g. be flash separators.

A reformer feed stream 1 comprising biogas is preheated in the preheating section 20 and becomes a preheated reformer feed stream 2, which is led to the purification unit 30. A purified preheated reformer feed stream 3 is sent from the purification unit 30 to the preheating section 20 for further heating. Moreover, steam 4 is added to the purified preheated reformer feed stream, resulting in feed gas 5 sent to a prereformer 40. Prereformed gas 6 exits the prereformer 40 and is heated in the preheating section 20, resulting in gas 7. In the embodiment of figure 1, hydrogen 14 is added to the gas 7, resulting in a feed gas 8 sent to the eSMR 50. The feed gas 8 undergoes steam methane

reforming in the eSMR 50, resulting in a reformed gas 9 which is led from the eSMR 50 and from the reforming section 10 to the methanol section 60.

In the methanol section 60, the reformed gas 9 heats water 12 to steam 13 in a heat exchanger. In a first separator 85 water is separated from the synthesis gas 9 to provide a dry synthesis gas 11, which is sent to a compressor 70 arranged to compress the dry synthesis gas before it is mixed with recycle gas from a second separator 90 enters the methanol synthesis unit 80. Most of the produced methanol from the methanol synthesis unit 80 is condensed and separated in the second separator 90 and exits the methanol section as methanol 25. The gaseous component from the second separator 90 is split into a first part that is recycled to the methanol synthesis unit 80 and a second part that is recycled as an off-gas 17 to be used as fuel 18 to the preheating section 20 of the reforming section 10 and/or recycled as feed 16 to the eSMR 50. An additional compressor is typically used for recycling the first part of the gaseous component from the second separator 95 to the methanol synthesis unit 80. Water 12 is heated to steam within heat exchangers of the system 100 and in the given embodiment inside the cooling side of the methanol synthesis unit 80.

To achieve full carbon utilization, synergy can be obtained if an SOEC-based water electrolysis unit 110 is used. The SOEC unit 110 can utilize some of the steam production available from waste-heat management in the reforming and methanol sections, e.g. stream 13 and convert the steam to i.a. H_2. The H_2 can be used as a hydrogen source in the feed gas to the reforming reactor. It should be noted that a relatively small SOEC unit is needed to achieve this. Alternatively, any other appropriate hydrogen source may be utilized.

In the case, where a second hydrocarbon feed gas is added to or mixed with the reformer feed stream upstream the reforming reactor, the second hydrocarbon feed gas is typically added to the reformer feed stream upstream the prereforming unit and the purification unit. In figure 1, this would correspond to adding the second hydrocarbon

feed gas to the preheated reformer feed stream 2. The second hydrocarbon feed gas may be a stream of natural gas having a higher H/C ratio than the H/C ratio of the reformer feed stream of stream 1.

In the case, where a separation unit is used to remove part of the CO_2 in the biogas upstream the reforming unit, this separation units is advantageously upstream the preheating unit 20. When a major part of the reformer feed stream is biogas, by removing part of the CO_2 in the reformer feed stream, it is possible to achieve a reformer feed stream with about 25% CO_2, which is preferable for the downstream methanol production.

A system 100 according to the invention, comprising an electrically heated steam methane reformer and a methanol synthesis unit is also abbreviated eSMR-MeOH. Such an eSMR-MeOH system resembles a plant used in classical industrial process (SMR-MeOH) to a large extent, but deviates on some essential aspects. Firstly, use of the eSMR 10 removes the requirement for the intensive firing in the fired steam reformer of a classical SMR-MeOH system and thereby leaves only a small CO_2 emission from the eSMR-MeOH layout associated with purge gas handling. Secondly, the use of biogas rather than natural gas as the reformer feed stream or as the main part thereof removes the requirement for oxygen addition to the synthesis gas as the natural high CO_2 content of biogas allows for the module adjustment inherently, as described below:

From an overall plant stoichiometry where methane (as natural gas) is used as feedstock, the reaction scheme can be expressed as:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \rightarrow CH_3OH$$

Alternatively, if a CO_2 feedstock is available, this can be used as oxygen source, giving an overall plant stoichiometry of:

$$0.75CH_4 + 0.25CO_2 + 0.5H_2O \rightarrow CO + 2H_2 \rightarrow CH_3OH.$$

Higher temperatures can be reached in an eSMR compared with a fired reformer, which gives a better conversion of methane in this layout; in the end, this provides for less off-gas handling. It should be noted, that the CO_2 content in biogas can vary, and therefore, an addition of hydrogen to the synthesis gas can be advantageous to increase the carbon utilization of the process. To achieve full carbon utilization, an excellent synergy can be obtained if SOEC based water electrolysis unit 110 is used, which can utilize some of the steam production available from waste-heat management in the reforming section 10 and the methanol section 60. This is illustrated as the parallel hydrogen source 14 in Figure 1. Notice that a relatively small SOEC unit 110 is needed to achieve this, and the process can also run without it. The same methanol synthesis technology as in the classical approach can be used and the methanol reactor will in this layout have a CO/CO_2 ratio corresponding to that of a typical methanol plant and therefore have a similar activity and stability. To some extent, at least part of the off-gas from the methanol synthesis unit can be recycled to the reforming section as feedstock to increase the carbon efficiency and recover unconverted methane. In the same way, it is also possible to recover at least part of the off-gas from a potential methanol distillation and return this as feedstock, if this is compressed to operating pressure. At least to some extent, preheating can be done by the excess steam, because high preheating. Electrically heated reforming can e.g. use a monolithic-type catalyst heated directly by Joule heating to supply the heat for the reaction. In its essence, the eSMR 10 is envisioned as a pressure shell having a centrally placed catalytic monolith, which is connected to an externally placed power supply by a conductor threaded through a dielectric fitting in the shell. The shell of the eSMR is refractory lined to confine the high-temperature zone to the center of the eSMR.

From a reforming reactor point of view, the eSMR has several advantages over a conventional fired reformer. One of the most apparent is the ability to make a significantly more compact reactor design when using electrically heated technology, as the reforming reactor no longer is confined to a system of high external heat transfer area. A

size reduction of two orders of magnitudes is conceivable. This translates into a significantly lower capital investment of this technology. The combined preheating and reforming section of an eSMR (including power supply) configuration was estimated to have a significant lower capital investment. As the synthesis gas preparation section of a methanol plant accounts for more than 60% of the capital investment in a classical fired reformer based methanol plant, a drastic saving on the reformer equipment will translate into a significant reduction in the cost of a methanol plant based on eSMR.

Figures 2a-2c show comparative cases for methanol plants based on a fired reformer (figure 2a) versus an electric reformer (figure 2b) versus alkaline electrolysis (figure 2c). A major advantage of the eSMR of figure 2b is that it does not require burning hydrocarbons to provide the heat for the reaction, and consequently direct CO_2 emissions of this technology is significantly decreased. This is exemplified in Figures 2a-2c, showing how the consumables and CO_2 emissions can be markedly changed when using the eSMR-MeOH technology compared with both the fired reformer approach and electrolysis. The consumption figures of the fired reformer layout (figure 2a) and the eSMR-MeOH layout (figure 2b) are both based on Haldor Topsoe developed flowsheets for chemical-grade methanol production (i.e., including product distillation), while electrolysis layout (figure 2c) is an overall best-case stoichiometric analysis coupled with published consumption figures for alkaline electrolysis (AEL) based H_2 production and CO_2 purification. It should be noticed that the consumables are, from a chemical standpoint, divided in substantially pure CH_4 and CO_2 to not disadvantage the SMR-MeOH layout by requiring firing with biogas, which would have increased the CO_2 emissions from this plant considerably. In the given case, 30% reduction in methane consumption and 80% reduction in CO_2 emissions are achieved by the eSMR-MeOH compared to the fired reformer (SMR-MeOH). It is emphasized that process improvement may be considered for all presented cases, and should therefore not be considered limiting. When no units are given, the presented figures represent relative molar flow of components in figure 2a-2c.

The overview of the consumables of Figures 2a-2c illustrates a markedly lower electricity use for methanol production when using eSMR-MeOH over electrolysis. By use of SOEC instead of AEL in the electrolysis layout, the electricity use could potentially decrease to 11–13 kWh/Nm³ MeOH (depending on availability of steam), which would be an improvement for this technology, but still markedly higher than eSMR-MeOH. Notice that the concept development still can be done on the electrolysis approach to improve the performance of this technology, but this is all at research stage and only established electrolysis technology, as AEL, combined with classical methanol synthesis technology can be considered ready for industrial application presently, why this is also the focus of the comparison.

Energy consumption of methanol production by AEL ("AEL-MeOH") is calculated as: $E_{total} = E_{AEL} + E_{CO_2} + E_{compress} - E_{steam}$. Here, E_{AEL} is energy use of alkaline electrolysis with an energy efficiency of 71%. E_{CO_2} is the energy use of CO_2 purification estimated as 2.6 MJ/Nm³ CO_2 when using flue gas as feedstock. $E_{compress}$ is the compression power calculated at an efficiency of 75%, without including energy for cooling water, to be 0.7 kWh/Nm³ methanol. E_{steam} is the potential energy recovery from steam production calculated as 75% recovery of the exothermic energy removed in the methanol synthesis estimated to be 0.7 kWh/Nm³ methanol. The calculation does not include any considerations on byproduct formation in the methanol synthesis unit or their integration in the plant layout.

Figure 3 shows CO_2 equivalent emissions (CO_2e) associated with production of methanol for SMR, eSMR and AEM, respectively. For each of these production technologies, the black box represent overall equivalent emissions (CO_2e) if the methanol was produced by renewable energy and the white box represent overall equivalent emissions (CO_2e) if the methanol was produced with electricity from the Danish electricity network in 2019. When calculating the overall CO_2 emissions from a chemical plant, the electricity consumption must be evaluated as well, as this could potentially also have a

large CO_2 emission footprint. The exact emissions will be dependent on the source of the electricity. Looking at the associated equivalent CO_2 emissions (CO_2e) when electricity is provided either by fully sustainable resources or as an example the Danish energy grid in 2019, in which more than 60% of the annual electricity use is covered by sustainable sources as solar cells, wind power, and biomass. The actual CO_2e for production of methanol by the eSMR-MeOH technology was on this basis calculated as shown in Figure 3 and benchmarked against the conventional fired technologies and AEL-MeOH. Irrespective of the source of electricity, eSMR-MeOH will markedly better the CO_2 footprint of the methanol product over the conventional approach, viz. SMR-MeOH. While, based on the energy grid in Denmark in 2019, the electrolysis approach will not have a positive effect on the CO_2e. Only when the electricity is fully renewable, the electrolysis approach will have an CO_2e comparable to the eSMR-MeOH route, but AEL-MeOH will still be 35% higher

Figure 4 is an overview of technologies with lowest operating expenses as a function of natural gas price and electricity price.

To make sustainable technology attractive, it must be cost-competitive compared to the established production routes. Figure 4 shows an overview of which technology gives the lowest operating expenses as a function of gas and electricity price. It should be noted, that the overview only shows operating expenses. If expenses to plant depreciation are included in the production costs, the size of the area indicated “eSMR-MeOH” would markedly increase into the areas denoted “AEL-MeOH” and “SMR-MeOH”, because the eSMR-MeOH technology has a significantly lower capital investment compared with the two other technologies. From this overview it can be seen that the fired technology (SMR-MeOH) has been the cheapest production route for the last century because it is favored by the low gas prices. However, the decreasing electricity prices opens for an incentive toward the electrically driven technologies. An eSMR driven frontend is proposed as a next step for a cost-competitive route for methanol production. To exemplify the opportunity, competitive cases can be found when

comparing with natural gas prices of ca. 6–8 $/MMBTU in Europe. The operating expenses of the eSMR-MeOH technology will be further favored in cases with CO_2 taxation, which will increase the operating expenses of the fired reformer approach significantly. This is indicated by the dashed line in Figure 4, with a representative CO_2 tax of the Nordic countries today. It is emphasized that Figure 4 is only indicative, as the development within the eSMR-MeOH layout is still in a relatively early phase. It is foreseen that development within eSMR-MeOH will improve the consumption figures further, and thereby the operating expenses.

While the invention has been illustrated by a description of various embodiments and while these embodiments have been described in considerable detail, it is not the intention of the applicant to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications will readily appear to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details, representative methods, and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of applicant's general inventive concept.

EXAMPLE 1

Example 1 relates to an embodiment of the invention where a biogas is converted into methanol, cf. Fig. 1 for reference. A feed gas (1) is mixed with a recycle gas from a methanol loop to provide hydrogen for the subsequent desulfurization (30) and prereforming (40) steps. Using an electrically heated reformer (50), the gas is converted with steam (4) into a synthesis gas. This is cooled and separated into a condensate and dry synthesis gas (11), where the dry synthesis gas is compressed and fed to a methanol loop using a boiling water type methanol reactor (80). The compressed make-up synthesis gas is mixed with recycled gas (95) in the loop and sent to the methanol reactor (80) to produce methanol. By cooling and condensing this methanol is separated to produce the final product (25). Most of the off-gasses from this separation are recycled

(95) directly to the methanol reactor, another fraction (16) is recycled to the feed, while the last fraction is exported as a fuel rich off-gas.

Overall, this embodiment of the process allows for converting 95.4% of the carbon feedstock (CO_2 + CH_4) into methanol.

Example 1	Feed (1)	Off-gas recycle	Inlet de-sulfuriza-tion (2)	Inlet pre-reformer (5)	Inlet re-former (8)	Outlet re-former
T [°C]	179	40	380	27	26.3	1050
P [barg]	30	85.5	29.5	293	343	25.3
Components [Nm^3/h]						
CH_3OH	0	3	3	3	0	0
CH_4	1863	71	1933	1933	1997	113
CO	0	27	27	100	1	2208
CO_2	627	24	651	580	617	294
H_2	0	322	322	240	93	5421
N_2	5	13	18	18	18	18
O_2	5	0	5	1	0	0
H_2O	0	0	0	2898	2926	1365

Example 1 continued	Outlet flash sepa-rator (11)	Outlet make-up-gas com-pressor	After re-cycle mix-ing and inlet MeOH re-actor	Outlet MeOH re-actor	Outlet re-cycle compres-sor	MeOH Product (25)
T [°C]	40	123	220	260	46	40
P [barg]	23.9	90	90	87	90	90

Components [Nm^3/h]						
CH_3OH	0	0	92	2468	92	2376
CH_4	113	113	2659	2659	2547	92
CO	2208	2203	3169	1005	966	39
CO_2	293	293	1177	966	885	81
H_2	5420	5409	17081	12116	11670	446
N_2	18	18	471	471	453	18
O_2	0	0	0	0	0	0
H_2O	24	14	17	229	3	226

Example 1 continued	Off-gas re-cycle	Off-gas
T [°C]	40	40
P [barg]	85.5	85.5
Components [Nm^3/h]		
CH_3OH	3	0
CH_4	71	21
CO	27	8
CO_2	24	8
H_2	322	103
N_2	13	3
O_2	0	0
H_2O	0	0

CLAIMS:

1. A method for upgrading biogas to methanol, comprising the steps of:

a) providing a reformer feed stream comprising said biogas,

b1) - optionally, purifying said reformer feed stream in a gas purification unit,

b2) - optionally, prereforming said reformer feed stream together with a steam feedstock in a prereforming unit,

c) carrying out steam methane reforming of said reformer feed stream in a reforming reactor comprising a pressure shell housing a structured catalyst arranged to catalyse steam reforming of said reformer feed stream, said structured catalyst comprising a macroscopic structure of an electrically conductive material, said macroscopic structure supporting a ceramic coating, where said ceramic coating supports a catalytically active material; said steam methane reforming comprising the following steps:

- c1) supplying said reformer feed stream to the reforming reactor,
- c2) allowing the reformer feed stream to undergo steam reforming reaction over the structured catalyst and outletting a synthesis gas from the reforming reactor, and
- c3) supplying electrical power via electrical conductors connecting an electrical power supply placed outside said pressure shell to said structured catalyst, allowing an electrical current to run through the electrically conductive material of said macroscopic structure, thereby heating at least part of the structured catalyst to a temperature of at least 500°C, and

d) providing at least part of the synthesis gas of step c2) to a methanol synthesis unit to provide a product comprising methanol and an off-gas.

2. The method according to claim 1, wherein the electrical power supplied has been generated by means of renewable energy sources.

3. The method according to claim 1 to 2, wherein the reformer feed stream has a first H/C ratio and where a second hydrocarbon feed gas with second H/C ratio is mixed

with the reformer feed stream upstream the reforming reactor, wherein the second H/C ratio is larger than the first H/C ratio

4. The method according to any of the claims 1 to 3, wherein an electrolysis unit is used to generate a hydrogen rich stream from a water feedstock and where said hydrogen rich stream is added to the synthesis gas to balance the module of said synthesis gas to be in the range of 1.5 to 2.5.

5. The method according to claim 4, wherein said electrolysis unit is a solid oxide electrolysis cell unit and said water feedstock is in the form of steam produced from other processes of the method.

6. The method according to any of the claims 1 to 5, wherein a membrane or PSA unit is included in the methanol synthesis unit to extract at least part of the hydrogen from said off-gas and return said at least part of the hydrogen from said off-gas to the synthesis gas to balance the module of said synthesis gas to be in the range of 1.5 to 2.5.

7. The method according to any of the claims 1 to 6, wherein a combination of steam superheating and steam generation is integrated in waste heat recovery of said synthesis gas from said reforming reactor, and wherein the superheated steam is used as steam feedstock in step c) of the method for upgrading biogas to methanol.

8. The method according to any of the claims 1 to 7, wherein the pressure of the gas inside said reforming reactor is between 20 and 100 bar, preferably between 50 and 90 bar.

9. The method according to any of the claims 1 to 8, wherein the temperature of the gas exiting said reforming reactor is between 900 and 1150°C.

10. The method according to any of the claims 1 to 9, wherein the space velocity evaluated as flow of gas relative to the geometric surface area of the structured catalyst is between 0.6 and 60 $Nm^3/m^2/h$ and/or wherein the flow of gas relative to the occupied volume of the structured catalyst is between 700 $Nm^3/m^3/h$ and 70000 $Nm^3/m^3/h$.

11. The method according to any of the claims 1 to 10, wherein the plot area of said reforming reactor is between 0.4 m^2 and 4 m^2.

12. The method according to any of the claims 1 to 11, wherein the production of methanol is regulated according to availability of renewable energy.

13. The method according to any of the claims 1 to 12, wherein the method further comprises the step of upgrading the methanol to fuel grade methanol.

14. The method according to any of the claims 1 to 12, wherein the method further comprises the step of upgrading the methanol to chemical grade methanol.

15. The method according to any of the claims 1 to 14, wherein the method further comprises the step of using at least part of the methanol of step d) to a system for producing transportation fuel.

16. The method according to any of the claims 1 to 13, wherein at least part of the off-gas is recycled to upstream said reforming reactor.

17. The method according to any of the claims 1 to 16, wherein between 80% and 100% of the carbon of the biogas in said reformer feed stream is converted into methanol.

18. The method according to any of the claims 1 to 17, wherein the biogas of said reformer feed stream amounts to 500 Nm^3/h to 8000 Nm^3/h.

19. The method according to any of the claims 1 to 18, wherein a separation unit is used to remove part of the CO_2 of the reformer feed stream subsequent to step a) and preceding step c).

20. The method according to any of claims 1-19, wherein part of the off-gas produced in step d) is recycled to a biogas production facility for producing the biogas to be upgraded.

21. A system for upgrading biogas to methanol, comprising:
- an optional gas purification unit,
- an optional prereforming unit,
- a reforming reactor comprising a pressure shell housing a structured catalyst arranged to catalyse steam reforming of a bio gas, said structured catalyst comprising a macroscopic structure of an electrically conductive material, said macroscopic structure supporting a ceramic coating, where said ceramic coating supports a catalytically active material; wherein said reforming reactor moreover comprises an electrical power supply placed outside said pressure shell and electrical conductors connecting said electrical power supply to said structured catalyst, allowing an electrical current to run through the electrically conductive material of said macroscopic structure to thereby heat at least part of the structured catalyst to a temperature of at least 500°C,
- a methanol synthesis unit arranged to receive a synthesis gas from said reforming reactor and produce a product comprising methanol and an off-gas.

22. The system according to claim 21, wherein catalyst pellets are loaded on top of, around, inside, or below the structured catalyst of the reforming reactor.

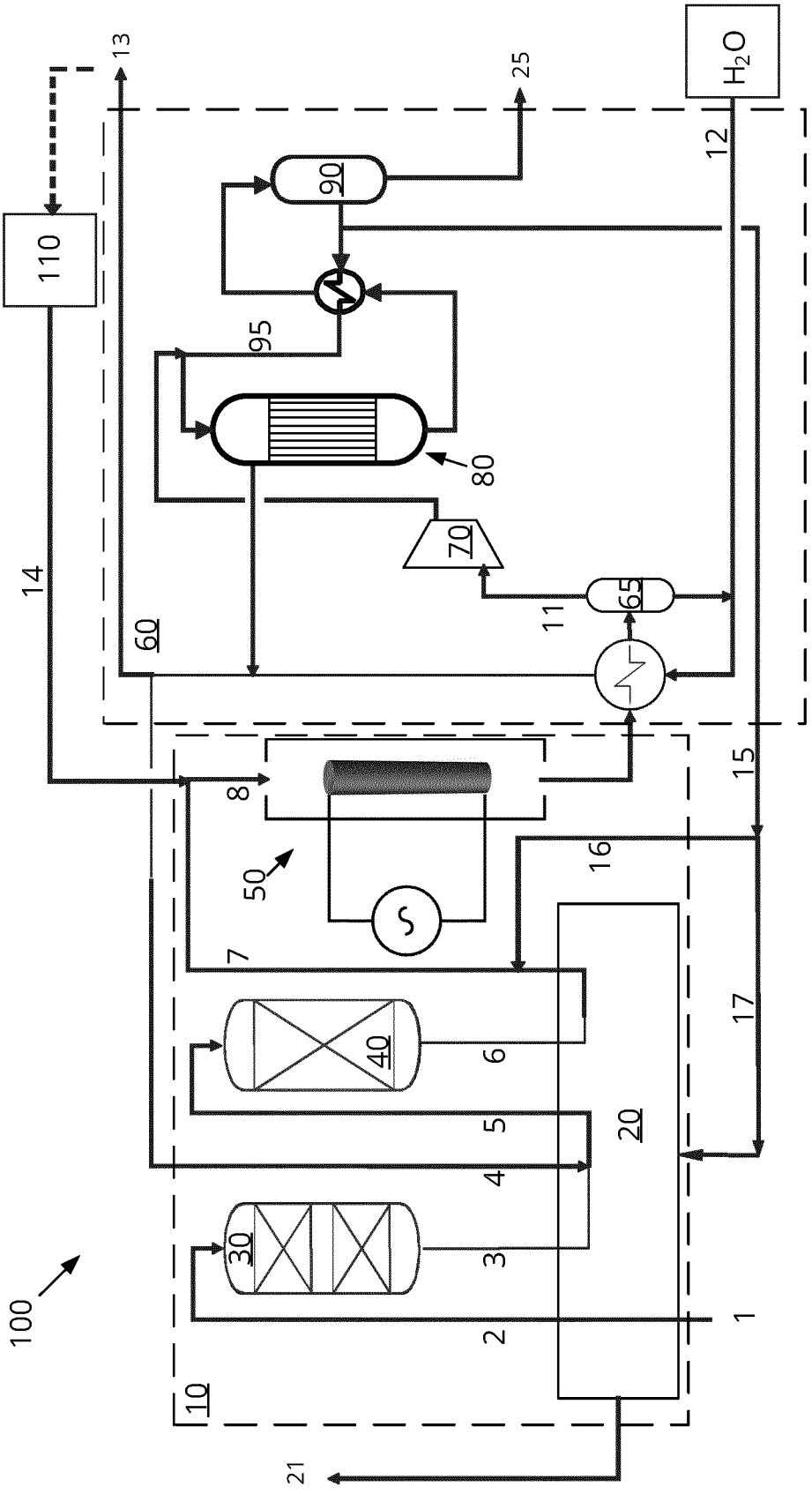
H2O
13
25
12
90
110
95
80
70
14
60
11
65
15
8
50
16
7
40
6
17
5
20
4
30
3
100
1
2
10
21

Fig. 1

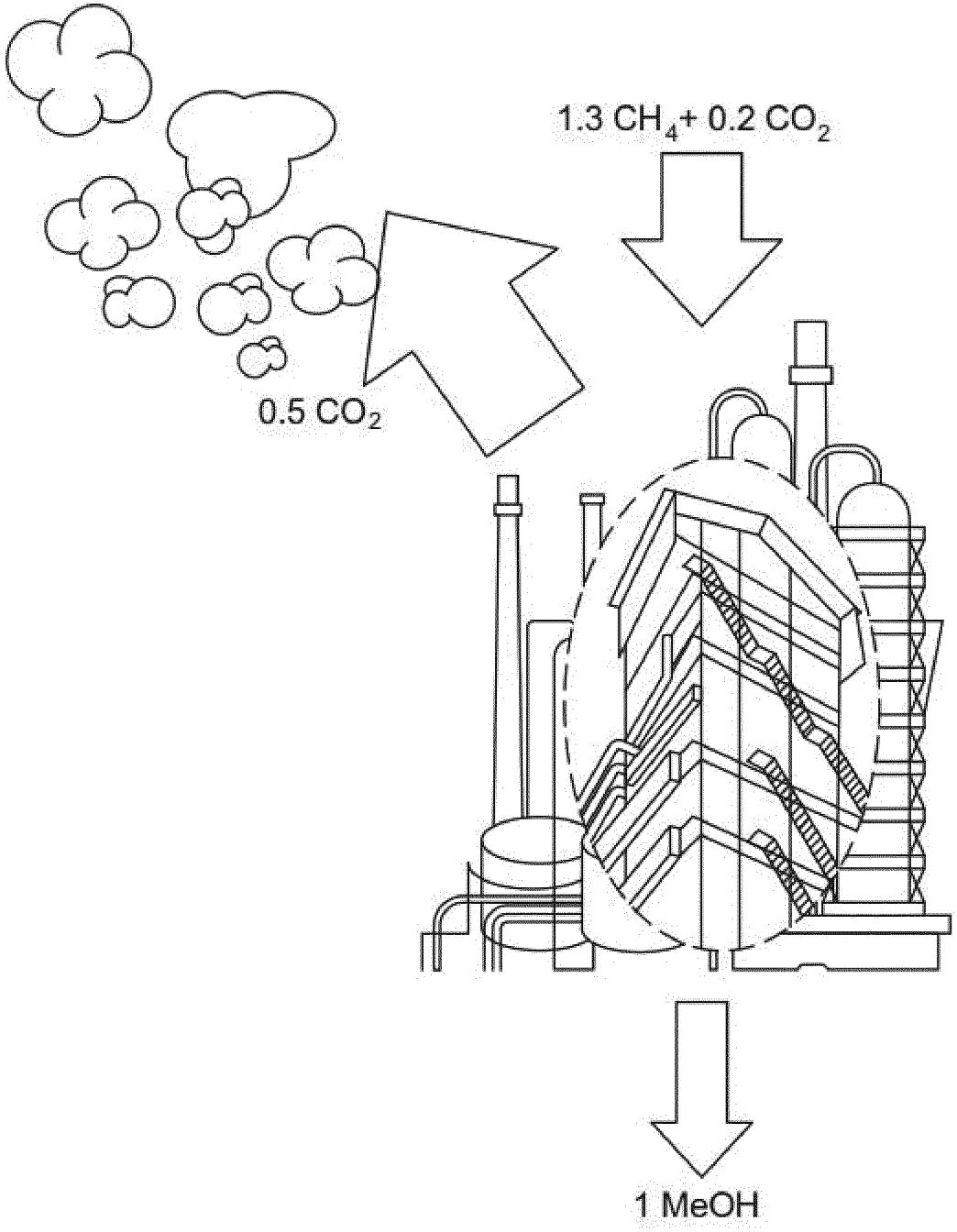

Fig. 2a

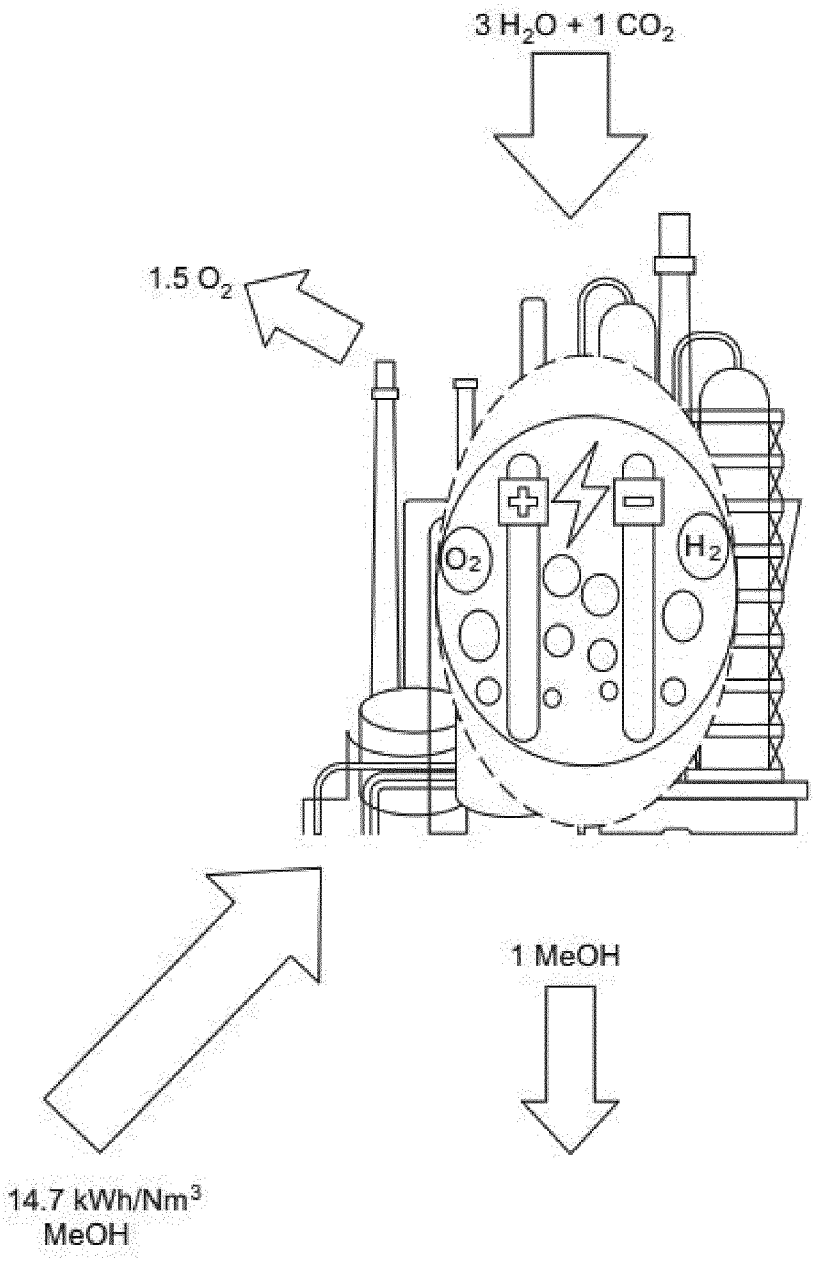

Fig. 2b

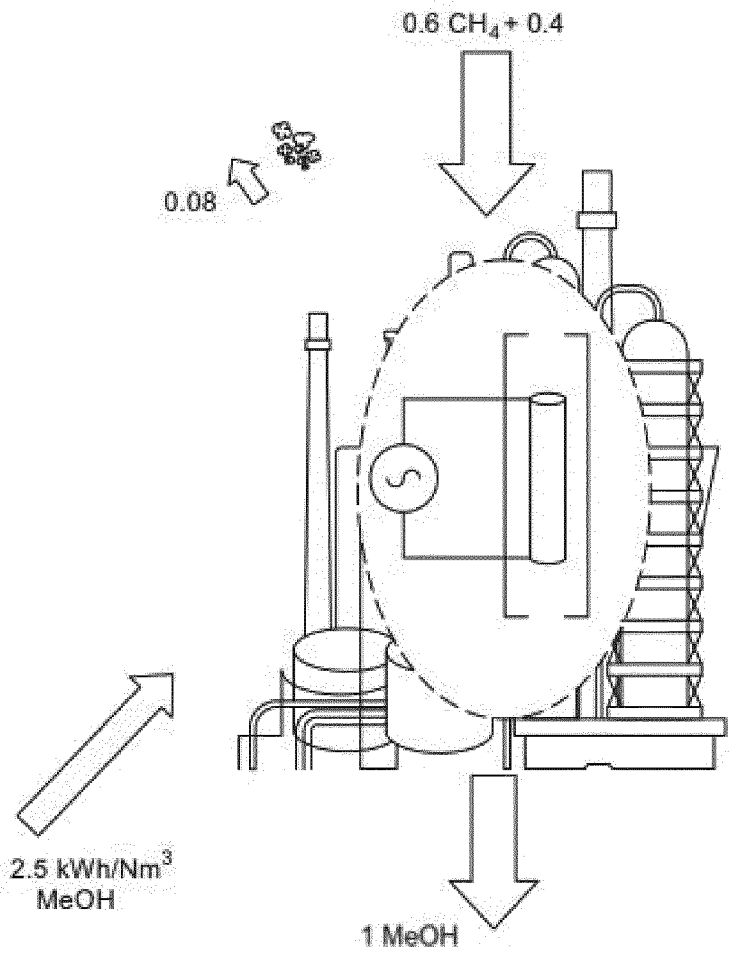

Fig. 2c

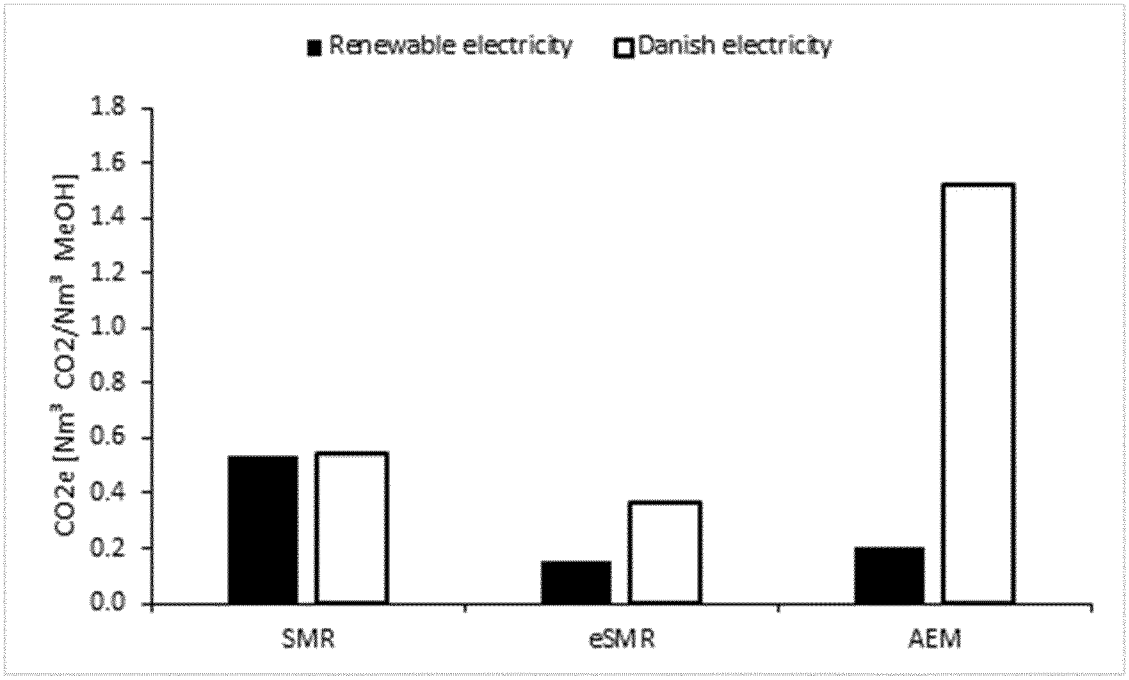
Renewable electricity
Danish electricity
CO2e [Nm³ CO2/Nm³ MeOH]
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
SMR
eSMR
AEM

Fig. 3

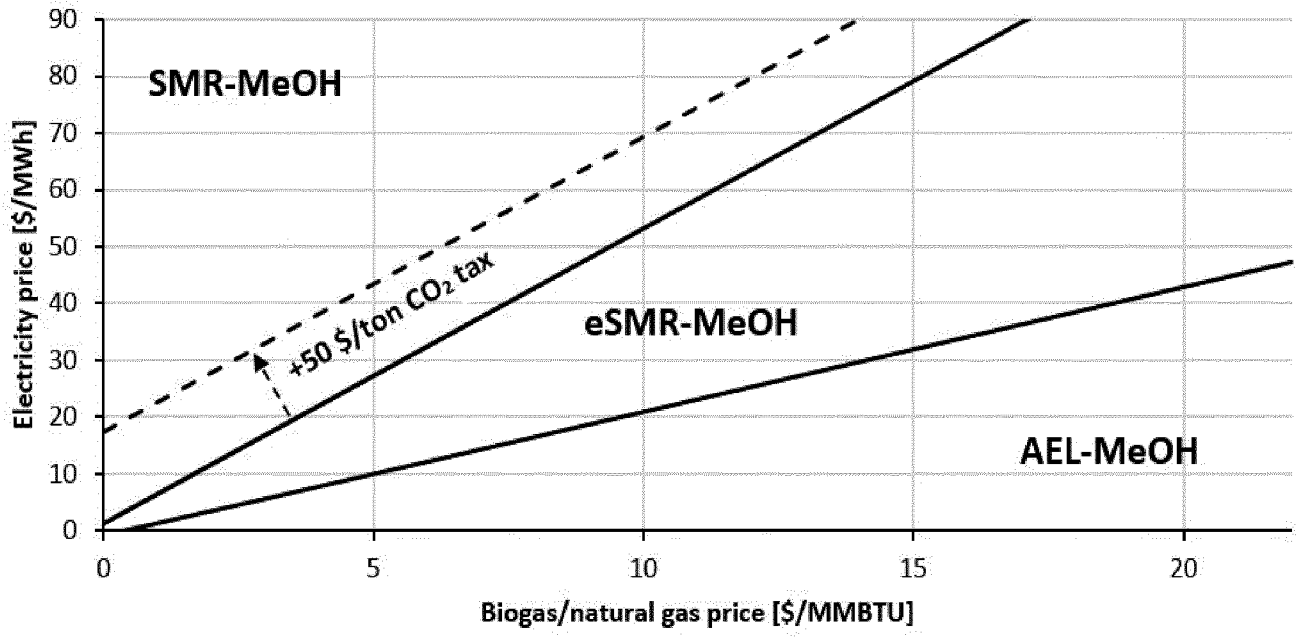
Electricity price [$/MWh]
90
80
70
60
50
40
30
20
10
0
SMR-MeOH
+50 $/ton CO2 tax
eSMR-MeOH
AEL-MeOH
0
5
10
15
20
Biogas/natural gas price [$/MMBTU]

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/065475

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38 C01B3/40 C07C29/151 C25B1/04 B01J8/00
ADD.

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)
C01B C07C C25B B01J

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2016/060537 A1 (HSU MICHAEL S [US]) 3 March 2016 (2016-03-03) abstract paragraphs [0040], [0048], [0062] - [0065], [0085], [0086], [0091] claims 1-6 figures 4,9,10	1-22
Y	WO 2019/110268 A1 (TOPSOE HALDOR AS [DK]) 13 June 2019 (2019-06-13) abstract claims 1,2 page 22, lines 7-27	1-22

-/--

[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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	Date of mailing of the international search report
17 July 2020	28/07/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Alvarez Rodriguez, C

2

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2018/115596 A1 (AVEFORI OY [FI]) 28 June 2018 (2018-06-28) abstract claims 1-10 figure 1	8,9

Y	GB 2 545 474 A (AVOCET INFINITE PLC [GB]) 21 June 2017 (2017-06-21) abstract	4,19

Y	US 2018/258019 A1 (ROESCH ALEXANDER [US] ET AL) 13 September 2018 (2018-09-13) abstract figure 2 claims 1-20	6,16

Y	DE 10 2013 226126 A1 (TECH UNIVERSITÄT BERGAKADEMIE FREIBERG [DE]) 18 June 2015 (2015-06-18) abstract claims 10,11	22

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2020/065475

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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