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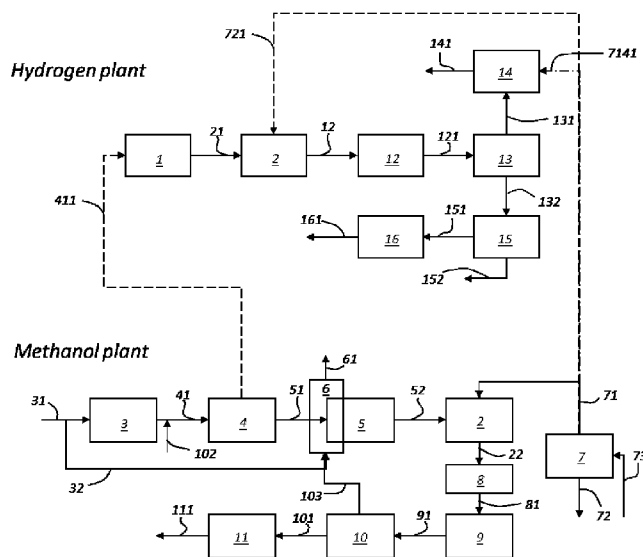


Figure 4

(57) **Abstract:** Disclosed herein is a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; wherein the method is performed in a hydrogen production plant that is integrated with one or more further processing plants.



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GAS PROCESSING

Field

5 The present disclosure relates to the production of hydrogen. More particularly, embodiments generate hydrogen by performing a gas-heated reforming process and an autothermal reforming process, with heat generated by the autothermal reforming process supplied to the gas-heated reforming process. Advantageously, the production of hydrogen is more efficient than known techniques. The hydrogen production process can also be integrated into other processes, such as methanol synthesis processes.

Background

15 The greenhouse effect and the climate on earth are generally believed to be closely connected to human made emissions of carbon dioxide, CO₂. These emissions are primarily formed by combustion of coal and hydrocarbons, i.e. by generation of heat, electric power as well as use in internal combustion engines in vehicles. A desirable goal is to reduce the emission of CO₂ to the atmosphere. It is known art to reduce the emission of CO₂ from combustion of natural gas, e.g. by gas reforming and shift technology for preparation of a mixture consisting of hydrogen and carbon dioxide. These components are then separated, where after hydrogen is used for energy generation, heat or in different types of transportation, and carbon dioxide is deposited after compression to desired pressure. The deposition can be made on the bottom of the sea or in geological reservoirs, often called aquifers. The reservoirs can also contain hydrocarbons.

25 Hydrogen in the transport sector as fuel for fuel cells is gaining increased attention, and fueling stations for transportation vehicles are being deployed in several areas of the world, notably in the USA, Europe and Japan. Practically all of these fueling stations are based on hydrogen made by splitting water through electrolysis and compressing hydrogen to typically 700 bar. Liquid hydrogen is being considered for heavier transport like ships and trains. A problem with electrolysis is that it is expensive and also requires a substantial supply of electrical power. Electrolysis has been calculated as being at least twice as expensive as producing hydrogen by reforming natural gas. These calculations include separation and liquefaction of coproduced CO₂ and payment of tariffs for deposition of CO₂ in underground reservoirs. Another issue with water electrolysis is the calculation of its contribution to the greenhouse gas effect as required electricity may have been produced from hydrocarbons with significant emission of CO₂ to the atmosphere. Producing hydrogen from natural gas with CO₂ storage is therefore significantly advantageous over hydrogen production by electrolysis.

There are a number of factors that have prevented or postponed production of hydrogen for the transport sector from natural gas. One is that the location of the hydrogen production site should be at an appropriate distance from CO₂ storage facilities. Due to cost of scale, CO₂ storage in off-shore underground reservoirs will have to be supplied by CO₂ from a number of CO₂ emitting facilities. There is also the matter of scale of the hydrogen production. As the demand for hydrogen presently is limited, hydrogen production facilities need to be small compared to what is regarded as world scale processing units. For example, a world scale methanol plant produces, say, 5000-10.000 metric tons/day. Comparing with a more moderately sized plant of 2500 tons/day, this corresponds to a hydrogen production of 400 metric tons/day. The hydrogen demand for one ferry or small cruise ship typically is in the range 1-5 metric tons/day of hydrogen, a hydrogen truck (Nikolai One) has reported a consumption of 4.6 kg per 100 km, and a small passenger train (Alstom Cordura) is designed for 94 kg hydrogen in one tank reaching 600 km.

There is a general need to improve known technology for hydrogen production from natural gas.

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Statements of invention

According to a first aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; wherein the method is performed in a hydrogen production plant that is integrated with one or more further processing plants.

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Preferably, the method further comprises: optionally saturating the received feed gas with at least water; and pre-reforming the gas to generate a pre-reformed gas; wherein the reforming processes are performed on the pre-reformed gas.

30 Preferably, the method further comprises adding a hydrogen rich stream to the received feed gas before the feed gas is input to the pre-reforming process.

Preferably, the method further comprises: performing a water-gas-shift on the gas output from the reforming processes; and separating hydrogen from the shifted gas.

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Preferably, the method further comprises compressing and, optionally, liquifying the separated hydrogen.

Preferably, the method further comprises separating carbon dioxide from the shifted gas.

Preferably, the method further comprises compressing and, optionally, liquifying the separated carbon dioxide.

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Preferably, the method further comprises removing sulfur from the received feed gas prior to saturating the received feed gas with water.

Preferably, ZnO is used to remove sulfur from the feed gas.

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Preferably, the feed gas is natural gas.

Preferably, the feed gas is a hydrocarbon rich gaseous stream from, or within, an oil refinery and/or a petrochemical plant.

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Preferably, the one or more further processing plants include any of a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.

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Preferably, the method is performed in a hydrogen production plant that is integrated with a methanol synthesis plant; and one or both of saturating the received feed gas with water and pre-reforming the gas is performed by the methanol synthesis plant; and the method comprises supplying at least part of the feed gas that is saturated with water, and/or at least part of the pre-reformed gas, from the methanol synthesis plant to the hydrogen plant.

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Preferably, the hydrogen rich stream that is added to the feed gas is generated by a synthesis loop in a methanol synthesis plant.

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Preferably, the method further comprises supplying at least part of any product that is generated in the hydrogen production plant to at least one of the one or more of the further processing plants that the hydrogen production plant is integrated with such that the supplied product can be used by the at least one of the one or more of the further processing plants; and/or supplying at least part of any product that is generated in at least one of the one or more of the further processing plants that the hydrogen production plant is integrated with to the hydrogen production plant such that the supplied product can be used by the hydrogen production plant.

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Preferably, the temperature of gas output from the autothermal reforming process is in the range 900-1100 °C, and preferably between 1000 and 1050 °C.

Preferably, the temperature of gas output from the gas-heated reformer is in the range 400-800 °C, and preferably 450-700 °C, and further preferably 500-600 °C.

5 Preferably, the method further comprises providing the autothermal reforming process with: oxygen from an air separation unit such as a cryogenic air separation unit; oxygen or oxygen enriched air from a membrane air separation unit; and/or oxygen from a pressure or vacuum swing adsorption unit.

10 Preferably, the autothermal reforming process is supplied with oxygen from an auxiliary air separation unit that is part of a methanol synthesis plant or a nitrogen production plant.

Preferably, the water-gas-shift is performed in both a high-temperature-shift reactor and a low-temperature shift reactor.

15

Preferably, the water-gas-shift is performed in a single reactor.

Preferably, hydrogen is separated by one or more of a PSA unit, a membrane that is optionally a Pd-membrane and/or a membrane in which the permeate side of the membrane is flushed by steam.

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Preferably, carbon dioxide is separated by cryogenic processes and/or a solvent that is optionally methanol.

25 Preferably, hydrogen and/or carbon dioxide is liquified using the excess cooling capacity of an auxiliary processing plant, wherein optionally the auxiliary processing plant is an air-separation plant and the excess cooling capacity is in the form of cold oxygen and/or nitrogen.

30 Preferably, the further processing plant is a methanol synthesis plant and all, or part of, the separated hydrogen is used to adjust the stoichiometric number of the methanol synthesis plant so that the stoichiometric number is 2.0 or slightly above 2.

35 Preferably, in use, all, or part of, the separated hydrogen is used to reduce carbon dioxide emission from an auxiliary processing plant, optionally the hydrogen being added to burners of a fired heater and, optionally, the burners are part of a steam reformer.

Preferably, the process of separating hydrogen from the shifted gas comprises generating a rest gas; and the method further comprises using at least part of the rest gas.

Preferably, at least part of the rest gas is used as a fuel for one or more of: pre-heating one or more of the feed gas, the gas input to a pre-treatment process, the gas input to a pre-reforming process and the gas input to the gas-heated reforming process; generating steam for use in a pre-reforming process and/or for adding to the gas stream input to a water gas shift reactor; and powering a gas turbine.

Preferably, at least part of the rest gas is fed into the autothermal reforming process and/or the gas-heated reforming process.

Preferably, the hydrogen production plant is integrated with a methanol synthesis plant; and the product $G \cdot H$ is at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2; wherein: G is the natural gas consumption in the hydrogen plant relative to the methanol plant; and H is the fraction of hydrogen produced by the hydrogen production plant that is directed to the methanol synthesis plant for consumption in burners therein.

According to a second aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; the method further comprising saturating the received feed gas with water; and pre-reforming the gas to generate pre-reformed gas; wherein the reforming processes are performed on the pre-reformed gas.

According to a third aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; the method further comprising: performing a water-gas-shift on the gas output from the reforming processes; and separating hydrogen from the shifted gas; wherein the process of separating hydrogen from the shifted gas comprises generating a rest gas; and the method further comprises using at least part of the rest gas.

According to a fourth aspect of the invention, there is provided a hydrogen production plant arranged to perform the method of the second aspect or the third aspect.

According to a fifth aspect of the invention, there is provided a hydrogen production plant and one or more further processing plants arranged to perform the method of the first aspect.

Preferably, the one or more further processing plants include any of a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.

List of Figures

Figure 1 shows a reforming process according to an embodiment;

Figure 2 shows a configuration of a methanol synthesis plant;

Figure 3 shows a configuration of a hydrogen production plant according to an embodiment;

Figure 4 shows a configuration of an integrated methanol and hydrogen plants according to an embodiment;

Figure 5 shows a configuration of an integrated methanol and hydrogen plants according to an embodiment; and

Figure 6 is a graph that shows the effect of the relative sizes of the methanol and hydrogen plants in integrated methanol and hydrogen plants according to embodiments.

Description of Embodiments

Embodiments provide a new method for producing hydrogen. Embodiments further include the integration of the method for producing hydrogen according to embodiments into other processes, in particular methanol synthesis processes. Advantageously, the integrated processes provide improved performance over individual processes.

Syngas is gas containing mainly H_2 and CO , with some CO_2 and unconverted CH_4 , possibly some higher hydrocarbons and inert gases, and H_2O . Production and perspectives on syngas production has been described by J. R. Rostrup-Nielsen in *Catalysis Today*, volume 18, pages 305-324, 1993, and in volume 71, pages 243-247, 2002. There are several types of reformers for production of synthesis gas comprising steam reforming, autothermal reforming and partial oxidation. There are methods for producing synthesis gas by a combination of steam reforming and autothermal reforming. Combined reforming comprises steam reforming and autothermal reforming, normally in

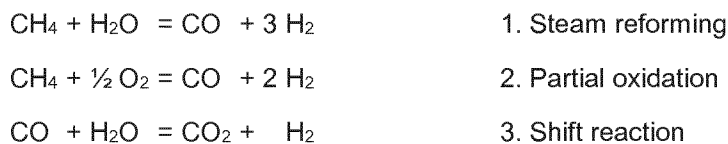
series. Gas heated reforming (GHR) utilizes hot gas, e.g. off-gas from autothermal reforming, to provide heat for reforming of a feed gas. GHR is described in a paper by K. J. Elkins et al. entitled "The ICI Gas-Heated Reformer (GHR) System" presented at the Nitrogen '91 International Conference, Copenhagen, June 1992.

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In a preferred embodiment, cleaning and pre-treatment of natural gas is performed so that the gas feed mainly comprises methane after these processes. Such cleaning may comprise sulfur removal, e.g. in a ZnO absorber. Pre-treatment may comprise pre-reforming whereby higher hydrocarbons, such as ethane, are converted by steam to methane and CO₂. The reforming takes place at a pressure within the interval 10 to 200 bar. It is preferred to use a shift reactor when carrying out embodiments. Steam can be supplied to the shift reactor, but it can also be operated without supply of steam. At the outlet of the shift reactor a content on carbon basis of CO up to 2 % by volume, preferably 5% by volume, and methane with 2% by volume, preferably 5% by volume, is preferred.

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15 The following chemical reactions take place by production of synthesis gas and hydrogen by reforming of natural gas:



The heat of reaction for the strongly endothermic steam reforming can be provided either by external heating, as in a steam reformer, or by combination with the partial oxidation in an autothermal reformer. In a steam reformer (SR) natural gas (methane) is converted in a tube reactor at high temperature and relatively low pressure. A steam reformer comprises many reactor tubes, e.g. 200-250 tubes with typical lengths of 12-13 meters, inside diameter of about 10 cm and an outside diameter of about 12 cm. This is a space demanding unit with a length of 30-50 meters, width of 10-12 meters and a height of 15-20 meters. Conventional steam reformers are operated in the pressure range from 15 to 30 bar. The outlet temperature of the gas from a conventional steam reformer lies in the temperature area of 950 °C. The energy which is used to carry out the endothermic reactions is supplied by external firing/heating (top-, side-, bottom- or terrace-fired). The ratio between steam and carbon is from 2.5 to 3.5, and the ratio between hydrogen and carbon monoxide in the product stream is from 2.7 to 3.0. A typical synthesis gas produced from a steam reformer contains approximately 3% by volume of methane.

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30 Alternatively, the reforming of natural gas (equation 1 and 2 above) can take place in an autothermal reformer (ATR). In an ATR natural gas (methane) is fed together with oxygen or air

into a combustion chamber. The energy which is required to operate the endothermic steam reforming reactions is provided by the exothermic reactions between hydrocarbons and/or hydrogen and oxygen. The temperature in the combustion chamber can reach more than 2000 °C. After the combustion chamber the reactions are driven to equilibrium over a catalyst bed before the synthesis gas is leaving the reactor at approximately 1000-1050 °C. The size of such a unit could be a height of 10-15 meters and a diameter of 5-6 meters. Typical ratio of steam:carbon is from 0.6 to 1.4. The ratio between hydrogen and carbon monoxide in the exit gas is lower than 2. Typical methane slip, i.e. amount of unconverted methane, is 1-2% by volume in the product stream. The ATR can be operated at higher pressure than the SR. A further option for reforming natural gas is a partial oxidation reactor (POX) which also is an autothermal reformer except that the unit does not comprise a catalyst bed. The exit temperature for a POX is somewhat higher than for a typical ATR. Reforming of natural gas can also be made by combined reforming (CR) which is a combination of a steam reformer (SR) and an autothermal reformer (ATR). A combination of SR and ATR makes it possible to adjust the composition out of the reformer unit by regulating the efforts on the two reformers. SR is in CR operated at milder conditions, i.e. lower outlet temperature, which leads to a high methane slip. The residual methane is reacted in the ATR. The ratio steam:carbon is in the area 1.8-2.4, with a ratio between hydrogen and carbon monoxide in the product gas higher than 2.

From the above, it is clear that the reformer unit has a very large footprint (SR), and that the exit gas is at a high temperature, typically 950-1100 °C. Conventionally, the exit gas is cooled down rapidly using a waste-heat-boiler (WHB) that produces steam. Rapid cooling and using tubes with boiling water are important to be able to control material corrosion by metal dusting.

Figure 1 shows a more efficient reforming process according to an embodiment in which the hot exit gas is used to reform part of the natural gas before it enters the autothermal reformer.

It is only known for a combination of ATR with oxygen and a gas-heated-reformer (GHR) to be used in this way for production of methanol. However, the present inventor has found that the same GHR and ATR combination can be used in a hydrogen production process. The hydrogen production process comprises the separation of hydrogen and carbon dioxide after the reforming processes.

According to embodiments, instead of burning fuel gas to provide the heat for the reforming reactions, the hot, autothermally reformed gas 22 is used to heat the catalyst tubes in a GHR 1. The feed gas 11 first passes through the catalyst in the GHR, then the ATR 2 by stream 21 and finally the heating side of the GHR to provide the heat for the initial reaction. Thereby the exit temperature of the syngas 12 is reduced significantly to the range 500-600 °C and needs only moderate further cooling before WGS.

After reforming of the natural gas and cooling, the gas mixture according to embodiments is shifted. The gas mixture from the reformer reactor contains mainly the gas components CO, H₂, H₂O, CO₂ and some CH₄. Between these components there is an equilibrium relation given by the stoichiometric equation:

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This reaction is called the water-gas-shift reaction (WGS), and by operating a shift reactor at certain conditions the equilibrium can be forced to the right and a gas mixture is obtained which is rich in hydrogen and carbon dioxide, and where the concentration of carbon monoxide is low. Sufficient reaction velocity is provided by use of suitable catalysts, and in processes where a high degree of reaction of CO is desirable (e.g. ammonia synthesis) two fixed bed reactors are used in series, a high temperature shift reactor and a low temperature shift reactor, respectively. Two steps are chosen because the equilibrium is favored by low temperature, whereas the reaction velocity is favored by high temperature. By selecting two reactors working in series, a smaller total reactor volume is achieved. The process is nearly pressure independent and normally the same pressure as in the reformer is used. Typical temperature out of the first reactor is 420 °C. and out of the second reactor 230 °C. Catalyst in the first step is normally based on chromium/iron, whereas the catalyst in the second step normally is a copper/zinc catalyst. In the shift unit CO and H₂O are reacted to CO₂ and H₂, and in known techniques it is often a requirement that the mentioned reaction to a highest possible degree is driven to the right, so that as little CO as possible is present in the gas mixture out of the shift unit. A low content of CO in the mentioned gas mixture again gives a high purity of the H₂-rich gas stream out of the separation unit. In known art the ratio H₂O:CO to the shift reactor is high, e.g. equal to 10:1, which gives a high conversion of CO. However, there are other process configurations where different arrangements of WGS are preferred. One such configuration is when hydrogen is separated by a palladium membrane. A Pd membrane requires a certain elevated temperature to operate efficiently. Therefore, only high-temperature WGS may be applied before the membrane. It is also possible to use low-temperature WGS after the membrane and partly recycle the shifted gas.

Gases in the mixture after the shift reactor or the shift reactors can be separated more or less completely based on the different properties of the gas molecules. The most common principles are absorption, adsorption, membranes and cryogenic distillation. CO₂ is an acid gas, and the most widely used method to separate the mentioned gas from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid, the acid gases will to a high degree be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can then be set free either by

altering the composition of the liquid or by altering pressure and temperature. For separation of CO₂, aqueous solutions of alcoholamines can be used. The absorption is taking place at a relatively low temperature and a high pressure, while stripping of the gas from the liquid is carried out at a relatively high temperature and low pressure. To liberate CO₂ from the amine phase in the stripping unit, stripping steam is usually used. If the partial pressure of CO₂ in the gas into the absorber is high, e.g. higher than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO₂ can be set free in the stripping unit at elevated pressure, e.g. 5-8 bar. Other absorption technologies rely on alternative liquid absorbents like methanol at reduced temperature.

By the use of one or more semipermeable or dense membrane unit, like using a Pd-film, it is possible to achieve that molecules of different size and different properties permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture in question membranes can be selected where H₂ permeates rapidly, whereas CO₂ permeates slowly or not at all, where after separation of the different gas components is achieved. The driving force over the membrane is difference in partial pressure, e.g. of hydrogen between the process gas and the permeate side of a Pd-membrane. As hydrogen in many cases is required at an elevated pressure, one preferred way to secure partial pressure difference is to use a sweep gas of steam at the permeate side and then condense out water afterwards, leaving hydrogen at a pressure comparable to the process gas. By combining solid membranes and liquid membranes it is also possible to achieve a rapid permeation of CO₂, while H₂ is kept back.

Another frequently used method in gas separation is pressure-swing adsorption (PSA). PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It is normally operated at near-ambient temperatures and differs significantly from cryogenic distillation techniques of gas separation. Specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed molecules. In the present mixture of gases, CO, CO₂ and CH₄ are adsorbed, letting the hydrogen pass through at process pressure. Not to overload the adsorbent, water is condensed before the PSA unit.

Embodiments include using any known technique for hydrogen and carbon dioxide separation.

In embodiments of the present invention it is desirable to deposit out-separated CO₂. Large amounts of CO₂ can be deposited according to various methods, such as deposition in very deep oceans, deposition in deep water geological reservoirs and deposition in oil reservoirs wherein the gas at the same time functions as drive agent for enhanced oil recovery. The two last mentioned storage methods are operated commercially. In these storage forms the CO₂ gas has to be brought

to high pressure and in liquid form for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO₂ gas can be separated from the H₂/CO₂ mixture at an elevated pressure, significant compression work can be avoided. However, it might be necessary to select between hydrogen and CO₂ to be
 5 collected at the high (process) pressure. Hydrogen pressure requirement varies with application, but high pressure or liquid hydrogen will be needed for storage and in transportation applications. As it is more demanding to pressurize hydrogen than CO₂, separation technologies that provide hydrogen at high pressure is sometimes preferred. This benefit can, however, be outweighed by the efficiency of a hydrogen permeable membrane.

10 Methanol is a commodity used for number of purposes, mainly as a feedstock for production of chemicals. These chemicals comprise formaldehyde, acetic acid and dimethyl ether. Another use is in the petrochemical industry for making olefins through the methanol-to-olefins route, or more selectively by methanol-to-propylene. Methanol is also used as a fuel or a fuel additive. Two widely different applications are in production of the gasoline additive MTBE (methyl-tertbutyl ether) and in
 15 manufacture of biodiesel through transesterification of triglycerides. Occasionally, methanol is used directly as a blending component in gasoline or diesel.

Methanol is for the large part produced from natural gas by first making syngas according to eqs. 1-3. Then methanol is produced over a copper based catalyst by the overall reaction



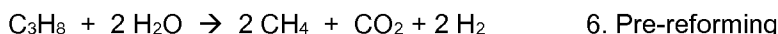
The mechanism is, however thought to be through CO₂;



CO₂ is partially formed in-situ in the reactor by the water-gas shift reaction



25 but can also be provided externally. Often the feed contains a certain amount of CO₂ that has been formed by pre-reforming natural gas containing some higher alkanes, e.g. propane;



It follows that the gas consumption in methanol synthesis is dictated by the stoichiometric number (SN):

30
$$\text{SN} = (\text{P}_{\text{H}_2} - \text{P}_{\text{CO}_2}) / (\text{P}_{\text{CO}} + \text{P}_{\text{CO}_2}) = 2$$

where P signifies partial pressure.

Figure 2 illustrates one typical configuration of a methanol synthesis plant. The natural gas 31 is pretreated in unit 3 that comprises sulfur removal followed by saturation with water. A small portion of the hydrogen rich stream 103 is added to the pretreated natural gas 41 and fed to the pre-reformer 4, ref. eq. 6. The pre-reformed gas 51 is fed to steam reformer 5 that encompasses a combustion chamber 6 to provide heat for the reaction in eq. 2, giving an exhausted gas 61 where carbon in the combined feed (32+103) has been combusted to CO₂. After partial conversion of methane, the gas 52 is fed to an autothermal reformer 2 for further conversion to the syngas 22 according to eqs. 1 and 3. Oxygen 71 from an air separation unit (7; ASU) is added to the ATR 2. The ASU separates cryogenically air 73 to oxygen and nitrogen 72, sometimes also producing noble gases like argon. Other means for air separation or producing oxygen enriched air are possible, typically using membranes. A steam reformer and an autothermal reformer in series is often called combined reforming (CR). The produced syngas (22) is cooled in a WHB 8 and in subsequent heat exchangers before the gas 81 is entering the methanol synthesis block 9. This synthesis block can contain one or several methanol synthesis reactors and means for gas mixing and recycle of syngas that is not converted to methanol. To suppress production of unwanted byproducts, the composition of the gas fed to the methanol reactor contains surplus hydrogen. The following separation block 10, which is supplied by 91, contains distillation units for separation of methanol and water. Unconverted syngas is partly used as fuel 103 for the SR and partly added before the pre-reformer 4 (102). Finally, methanol, from path 101, is stored 11 before being shipped 111 to customers.

The production of methanol and production of hydrogen have similarities in that both processes rely on reforming natural gas to a syngas mixture comprising major amounts of hydrogen and CO, with some CO₂ and residual methane and water. The present inventor has surprisingly found that these similarities call for novel ways of integration between such process units.

Examples of embodiments are provided below.

EMBODIMENT EXAMPLE 1

Production of hydrogen and CO₂ by GHR and ATR according to an embodiment of the present invention.

Figure 3 shows production of hydrogen and CO₂ by combination of ATR 2 and GHR 1 according to an embodiment.

Natural gas, NG, is fed in at 31. NG pretreatment 3 and pre-reforming 4 are performed as described in Figure 2 with units with corresponding reference signs.

The syngas production, by the ATR 2 and GHR 1, is as described in Figure 1 with units with corresponding reference signs. The heat recycle 22 is the exit gas from the ATR used to heat the GHR. Oxygen may be added to the ATR by an ASU 7, as described in Figure 2 with units with
5 corresponding reference signs. It should be understood that embodiments include any other means for producing oxygen, or air enriched in oxygen, such as by using vacuum or pressure swing adsorption, or by using a membrane.

The produced syngas 12 is shifted to increase the content of hydrogen and CO₂ in one or more
10 shift reactors 12, i.e. water gas shift reactor(s) 12, to produce the shifted gas 121. Steam may be added to the gas mixture before the gas mixture is input into the shift reactor(s) 12. The addition of steam increases the efficiency of the shift reaction. The shifted gas 121 may be subsequently cooled to remove its water content. Separation process 13 separates CO₂ 131 from the shifted gas, and the CO₂ is compressed 14 and optionally liquified. The produced CO₂ 141 may be stored at
15 site, shipped for permanent storage or directly injected into a geological formation for storage. Hydrogen 151 is separated in the process 15, e.g. by PSA, that separates the hydrogen from the gas 132 that has already been depleted of CO₂ by the process 13. The separate outputs from the process 15 are hydrogen and a rest gas. The rest gas 152 contains remnants of CO and CH₄ together with unseparated CO₂ and hydrogen. As described in more detail later, the energy in the
20 rest gas may be utilized for fuel in fired heater(s) for preheating of feed gases, or it can be recycled 153 to the GHR 1 and/or ATR 2 for maximum carbon efficiency. Finally, the produced hydrogen is compressed and optionally liquified 16 before being transported to customers.

Process simulations of the flow-sheet in Figure 3 using the program HYSYS is based on natural
25 gas with molar composition 88.8% methane, 5.6% ethane, 2.0% propane, 1.6% higher hydrocarbons, 1.5% CO₂ and 0.6% nitrogen. The gas is delivered at 48 barg and 400 °C, and after sulfur removal. Hydrogen specification is > 99.97 mol% for fuel cells, and specification for CO₂ is dry at > 95 mol%. Oxygen is supplied at 40 barg and 20 °C. The simulations show that production of 100 kNm³/hr hydrogen requires 35.7 kNm³/hr of NG and 16.7 kNm³/hr of oxygen. 622 tons of
30 CO₂ is captured each year, assuming that the PSA off-gas (152) is used for combustion and the exhaust gas CO₂ emitted to the atmosphere. This gives a CO₂ capture efficiency of 95.4%. Electric power demand at 18.5 MW for compressors is delivered as renewable energy. Energy efficiency from natural gas to hydrogen is 80.4% based on lower heating values.

35

EMBODIMENT EXAMPLE 2

The use of both an ATR 2 and a GHR 1 in order to produce hydrogen and described in embodiment example 1 is compared with known techniques for producing hydrogen in Table 1.

Reformer	NG feed (kNm ³ /hr)	Oxygen feed (kNm ³ /hr)	Captured CO ₂ (metric tons/yr)	Capture efficiency (%)	Energy efficiency (%)	Import power (MW)
GHR + ATR	35.7	16.7	622	95.4	80.4	18.5
ATR	38.4	23.0	681	96.4	74.5	14.6
SR	42.0	(air)	682	95.0	74.0	n.a.

n.a.: not available

5 **Table 1**

HYSYS simulations for production of 100 kNm³/hr hydrogen are provided in Table 1 for the techniques of embodiment example 1 as well as with known techniques.

- 10 The GHR 1 and ATR 2 combination according to an embodiment gives significantly lower consumption of natural gas, less CO₂ needs to be captured (capture efficiencies being approximately equal), and the energy efficiency is significantly improved. Compared to using only an ATR reformer, the GHR 1 and ATR 2 combination requires significantly less imported oxygen. SR has the highest NG consumption and will cost significantly more. The cost drivers in SR are the
- 15 large reformers, the operation at a lower pressure, and most importantly, very cost demanding capture of CO₂ from flue gas.

EMBODIMENT EXAMPLE 3

- 20 In the present embodiment, both an ATR 2 and a GHR 1 are used to produce hydrogen and CO₂, as already described in embodiment example 1 with reference to Figure 3. The present embodiment further improves the efficiency of the overall processes by using the rest gas 152 that remains after the hydrogen separation process 15. The rest gas may alternatively be referred to as a tail gas or recycle gas.

25

The rest gas may comprise three components. These are pre-treated natural gas 41 or pre-reformed natural gas 11 that has not been converted to syngas by the GHR and ATR processes;

- CO that has not been shifted in the shift reactor; and CO₂ and hydrogen constituents left after the respective separation processes 13 and 15. The first of these components arise mainly due to equilibrium restrictions in reforming methane to CO and hydrogen. The higher the temperature in the reforming process, the lower the amount of methane is left unconverted. The second
- 5 component of the rest gas is CO that due to equilibrium or kinetic limitations has not been shifted to CO₂. The last component of the rest gas, gas constituents left after separation, is due to inadequate separation of CO₂ and hydrogen as 100% separation seldom can be achieved; with the possible exception of when dense separation membranes are used.
- 10 The rest gas 152 and/or 153 may therefore comprise any of CH₄, CO, H₂ and CO₂ as well as possible traces of water and some inert gasses, such as nitrogen. The present embodiment comprises using the energy rich components of the rest gas. For example, the rest gas may be used as a fuel in fired heater(s) for the preheating of the feed gas at one or more of the stages that process the feed gas. The feed gas, that may be natural gas, may be heated at one or more of:
- 15 immediately prior to its input into the pre-treatment 3, immediately prior to its input into the pre-reformer 4 and immediately prior to its input into the GHR 1. The rest gas may also be used as a fuel for generating steam 102 that is added before the pre-reformer and before the WGS reactor 12.
- 20 The rest gas may also be used as a fuel for a separate gas turbine, for example to generate electricity.

The rest gas 153 may also be recycled by feeding it back to the ATR 2, shown by 153 in Figure 3, and/or to the GHR 1, to improve the carbon utilization efficiency. A purge of inert gasses may be

25 applied to the gas stream 153 so that a large amount of inert gasses do not accumulate.

The energy in the rest gas may therefore be used to advantageously increase the efficiency of the processes.

30 EMBODIMENT EXAMPLE 4

According to a particularly preferred embodiment, the production of hydrogen is integrated with the production of methanol.

35 Process integration between a methanol plant and a hydrogen plant, that is preferably smaller than the methanol plant, is shown in Figure 4. The dashed lines illustrate that, if spare capacity is available or decision to reduce methanol production capacity has been made, that pre-treated NG 411 can be imported to the hydrogen plant. The figure shows import from the pre-reformer 4, but

the input can be from any stage from the arrival of NG at the production site. Further, another dashed line 721 shows that produced oxygen in the ASU of the methanol plant is used in the ATR of the hydrogen plant. Also illustrated, by a dotted dash line 7141, is that extra cooling capacity of the ASU, in the form of oxygen or nitrogen, can be used to cool down the captured CO₂;
5 alternatively, this capacity can be used to cool down hydrogen.

Embodiments include a number of other ways in which the methanol and hydrogen plants can be integrated, such as safety systems, nitrogen blanketing, harbor facilities, maintenance etc.

10 Advantageously, by integrating a methanol plant and a hydrogen plant, the overall efficiency of both methanol and hydrogen production is improved over the individual efficiencies of separate methanol and hydrogen plants. In addition, the production of methanol is flexible and, by changing the amount of hydrogen production, the amount of methanol production can be increased or
15 decreased as may be required by both supply and demand fluctuations. Similarly, the production of hydrogen is flexible and, by changing the amount of methanol production, the amount of hydrogen production can be increased or decreased as may be required by both supply and demand fluctuations.

EMBODIMENT EXAMPLE 5

20

According to a particularly preferred embodiment, the production of hydrogen is integrated with the production of methanol. That is to say, the hydrogen generated by the hydrogen plant may also be flexibly provided to the methanol plant.

25 The techniques of embodiment example 5 may be performed either on their own or in addition to those of embodiment example 4.

It is preferable to have an additional sink of hydrogen other than the main purpose of the hydrogen plant, which would typically be transporting or containing the generated hydrogen for use
30 elsewhere. According to embodiment example 5, an additional possible use of the generated hydrogen is as fuel gas for the combustion chamber 6 in the methanol plant, as shown in Figure 5.

Figure 5 shows a dotted hydrogen supply line 1561 that connects the PSA unit 15 with the chamber 6. Preferably, compression and/or cooling of the hydrogen in unit 16, is avoided, and/or
35 reduced, and this is a further energy saving.

EMBODIMENT EXAMPLE 6

According to a particularly preferred embodiment, the techniques of the embodiment example 5 are used to reduce CO₂ emissions from a methanol plant.

5 Using the principle of the hydrogen outlet to the method plant as shown in Figure 5, and considering hydrogen production plants of different sizes, it is possible to target a certain reduction in CO₂ emission in the methanol plant. Most of this emission comes from the burners in the steam reformer and, as an acceptable approximation, it can be assumed that all CO₂ emissions comes from the SR.

10 A simple relationship between reduction in CO₂ emission from a methanol plant, size of separate hydrogen plant and fraction of hydrogen produced used in the SR burners was found to be:

$$R = k \cdot G \cdot H$$

15 R is percent reduction in overall CO₂ emission during methanol synthesis, G is the NG consumption in the hydrogen plant relative to the methanol plant, H is the fraction of produced hydrogen directed to the SR burners, and k is a parameter specific to the methanol plant at hand. For a given methanol plant employing combined reforming, the parameter k was found to be 330. Calculations using this value of k are shown in Figure 6.

20 Figure 6 shows effect of the relative sizes of the methanol and hydrogen plants. For example, to reach a CO₂ reduction of 33% the product G*H must be 0.1. If all produced hydrogen is directed to the methanol plant, this target is achieved with a hydrogen plant using 10% of the NG used to produce methanol. If 80% of the hydrogen is exported and only 20% used in the SR, the hydrogen
25 plant size in terms of natural gas consumption must be half of the petrochemical plant to achieve the same goal.

It follows that the product G*H, in the design and operation of a hydrogen plant integrated with a methanol plant according to embodiments, can be chosen to advantageously reduce greenhouse
30 gas emissions from a methanol plant.

Embodiments include a number of modifications and variations to the above described techniques.

35 For example, embodiments are not restricted to a hydrogen production plant being integrated with a methanol plant and the hydrogen plant may alternatively be integrated with other types of plant, such as one or more of a nitrogen production plant, Fischer-Tropsch synthesis plant, an oil refinery, an air-separation plant or petrochemical plant.

The size of the gas-heated reformer in terms of natural gas usage may be 0.5-30% of a typical world scale methanol plant, alternatively 1-20%, further alternatively 1.5-15%.

5 The product G^*H may be at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2.

Figure 3 shows hydrogen and carbon dioxide being separated for a gas mixture in the separated process 13 and 15. Embodiments also include the hydrogen being separated from the gas mixture before the carbon dioxide is separated from the gas mixture, or the hydrogen and carbon dioxide
10 may be separated from the gas mixture at the same time in a single process. The separated carbon dioxide may be used, stored and/or deposited in a geological reservoir.

Embodiments include the following numbered clauses:

15 1. A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons; and

20 performing reforming processes so as to generate hydrogen in dependence on the feed gas;

wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and

25 heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

2. The method according to clause 1, further comprising:

30 saturating the received feed gas with water;

adding a hydrogen rich stream to the gas; and

pre-reforming the gas;

35 wherein the reforming processes are performed on the pre-reformed gas.

3. The method according to clauses 1 or 2, further comprising:

performing a water-gas-shift on the gas output from the reforming processes; and

5 separating hydrogen from the shifted gas.
4. The method according to clause 3, further comprising compressing and, optionally, liquifying the separated hydrogen.
- 10 5. The method according to clause 3 or 4, further comprising separating carbon dioxide from the shifted gas.
6. The method according to clause 5, further comprising compressing and, optionally, liquifying the separated carbon dioxide.
- 15 7. The method according to any of clauses 2 to 6, further comprising removing sulfur from the received feed gas prior to saturating the received feed gas with water.
8. The method according to any preceding clause, wherein the feed gas is natural gas.
- 20 9. The method according to any of clauses 1 to 7, wherein the feed gas is a hydrocarbon rich gaseous stream from or within an oil refinery, or a petrochemical plant.
10. The method according to clause 7 or any clause dependent thereon, further comprising
25 using ZnO to remove sulfur from the feed gas.
11. The method according to any preceding clause, wherein the method is performed in a hydrogen production plant.
- 30 12. The method according to any of clauses 2 to 10, wherein the method is performed in a hydrogen production plant and one or more further processing plants separate from the hydrogen production plant; and

one or more of saturating the received feed gas with water, adding a portion of a hydrogen rich stream to the gas and pre-reforming the gas is performed by a further processing plant.

- 5 13. The method according to clause 12, wherein the one or more further processing plants include a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.
- 10 14. The method according to clause 13, wherein the added hydrogen rich stream is obtained from a synthesis loop in a methanol synthesis plant.
- 15 15. The method according to any preceding clause, wherein the temperature of gas output from the autothermal reforming process is in the range 900-1100 °C, and preferably between 1000 and 1050 °C.
16. The method according to any preceding clause, wherein the temperature of gas output from the gas-heated reformer is in the range 400-800 °C, and preferably 450-700 °C, and further preferably 500-600 °C.
- 20 17. The method according to any preceding clause, further comprising providing the autothermal reforming process with:
- oxygen from an air separation unit; and/or
- 25 oxygen or oxygen enriched air from a membrane air separation unit.
18. The method according to clause 12 or any clause dependent thereon, wherein the autothermal reforming process is supplied with oxygen from an auxiliary air separation unit that is part of a methanol synthesis plant or a nitrogen production plant.
- 30 19. The method according to clause 3 or any clause dependent thereon, wherein the water-gas-shift is performed in both a high-temperature-shift reactor and a low-temperature shift reactor.
- 35 20. The method according to any of clauses 3 to 18, wherein the water-gas-shift is performed in one reactor

21. The method according to clause 3 or any clause dependent thereon, wherein hydrogen is separated by one or more of a PSA unit, a membrane that is optionally a Pd-membrane and/or a membrane in which the permeate side of the membrane is flushed by steam.
- 5 22. The method according to clause 5 or any clause dependent thereon, wherein carbon dioxide is separated by cryogenic processes and/or a solvent that is optionally methanol.
23. The method according to clause 5 when dependent on clause 3, or any clause dependent on clause 5, wherein hydrogen and/or carbon dioxide is liquified using excess cooling capacity from an auxiliary processing plant, optionally the auxiliary processing plant is an air-separation plant and the excess cooling capacity is in the form of cold oxygen and/or nitrogen.
- 10 24. The method according to clause 3 or any clause dependent thereon, wherein all, or part of, the separated hydrogen is used to adjust the stoichiometric number of a methanol synthesis plant so that the stoichiometric number is 2.0 or slightly above 2.
- 15 25. The method according to clause 3 or any clause dependent thereon, wherein all, or part of, the separated hydrogen is used to reduce carbon dioxide emission from an auxiliary processing plant, optionally the hydrogen being added to burners of a fired heater and, optionally, the burners are part of a steam reformer.
- 20 26. The method according to clause 13 or any clause dependent thereon, wherein the hydrogen production plant is integrated with a methanol synthesis plant; and
- 25 the product $G \cdot H$ is at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2;
- wherein:
- 30 G is the natural gas consumption in the hydrogen plant relative to the methanol plant; and
- H is the fraction of hydrogen produced by the hydrogen production plant that is directed to the methanol synthesis plant for consumption in burners therein.
- 35 27. A hydrogen production plant arranged to perform the method of any preceding clause.

28. A hydrogen production plant and one or more further processing plants arranged to perform the method of clause 12 or any clause dependent thereon.

5 29. A hydrogen production plant and one or more further processing plants according to clause 28, wherein the one or more further processing plants include a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.

10 In a particularly preferred embodiment, a hydrogen production plant is integrated with a further process plant, such as a methanol production plant, as described throughout the present document.

In another particularly preferred embodiment, a hydrogen production plant comprises a method of
15 producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; the method further comprising saturating the
20 received feed gas with water; and pre-reforming the gas to generate pre-reformed gas; wherein the reforming processes are performed on the pre-reformed gas.

The hydrogen production plant according to the present embodiment may be a standalone hydrogen production plant or integrated with a further processing plant, such as a methanol
25 production plant, as described throughout the present document. The hydrogen production plant according to the present embodiment, and when included the further processing plant, may include any of the features of a hydrogen production plant and/or further processing plant as set out in the above numbered clauses and/or described throughout the present document.

30 In another particularly preferred embodiment, a hydrogen production plant comprises a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is
35 supplied to the gas-heated reforming process; the method further comprising: performing a water-gas-shift on the gas output from the reforming processes; and separating hydrogen from the shifted

gas; wherein the process of separating hydrogen from the shifted gas comprises generating a rest gas; and the method further comprises using at least part of the rest gas.

5 Preferably, at least part of the rest gas is used as a fuel for one or more of: pre-heating one or more of the feed gas, the gas input to a pre-treatment process, the gas input to a pre-reforming process and the gas input to the gas-heated reforming process; generating steam for use in a pre-reforming process and/or for adding to the gas stream input to a water gas shift reactor; and powering a gas turbine.

10 Preferably, at least part of the rest gas is fed into the autothermal reforming process and gas-heated reforming process.

15 The hydrogen production plant according to the present embodiment may be a standalone hydrogen production plant or integrated with a further processing plant, such as a methanol production plant, as described throughout the present document. The hydrogen production plant according to the present embodiment, and when included the further processing plant, may include any of the features of a hydrogen production plant and/or further processing plant as set out in the above numbered clauses and/or described throughout the present document.

20 The flow charts and descriptions thereof herein should not be understood to prescribe a fixed order of performing the method steps described therein. Rather, the method steps may be performed in any order that is practicable. Although the present invention has been described in connection with specific exemplary embodiments, it should be understood that various changes, substitutions, and alterations apparent to those skilled in the art can be made to the disclosed embodiments without
25 departing from the spirit and scope of the invention as set forth in the appended claims.

Claims:

1. A method of producing hydrogen, the method comprising:
5 receiving a feed gas comprising hydrocarbons; and

performing reforming processes so as to generate hydrogen in dependence on the feed gas;

10 wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;

15 wherein the method is performed in a hydrogen production plant that is integrated with one or more further processing plants.
2. The method according to claim 1, further comprising:
20 optionally saturating the received feed gas with at least water; and

pre-reforming the gas to generate a pre-reformed gas;

25 wherein the reforming processes are performed on the pre-reformed gas.
3. The method according to claim 2, further comprising adding a hydrogen rich stream to the received feed gas before the feed gas is input to the pre-reforming process.
- 30 4. The method according to any preceding claim, further comprising:

performing a water-gas-shift on the gas output from the reforming processes; and

separating hydrogen from the shifted gas.
35
5. The method according to claim 4, further comprising compressing and, optionally, liquifying the separated hydrogen.

6. The method according to claim 4 or 5, further comprising separating carbon dioxide from the shifted gas.
7. The method according to claim 6, further comprising compressing and, optionally, liquifying the separated carbon dioxide.
8. The method according to any of claims 2 to 7, further comprising removing sulfur from the received feed gas prior to saturating the received feed gas with water.
9. The method according to claim 8, wherein ZnO is used to remove sulfur from the feed gas.
10. The method according to any preceding claim, wherein the feed gas is natural gas.
11. The method according to any of claims 1 to 9, wherein the feed gas is a hydrocarbon rich gaseous stream from, or within, an oil refinery and/or a petrochemical plant.
12. The method according to any preceding claim, wherein the one or more further processing plants include any of a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.
13. The method according to any of claims 2 to 12, wherein the method is performed in a hydrogen production plant that is integrated with a methanol synthesis plant; and
- one or both of saturating the received feed gas with water and pre-reforming the gas is performed by the methanol synthesis plant; and
- the method comprises supplying at least part of the feed gas that is saturated with water, and/or at least part of the pre-reformed gas, from the methanol synthesis plant to the hydrogen plant.
14. The method according to any of claims 3 to 13, wherein the hydrogen rich stream that is added to the feed gas is generated by a synthesis loop in a methanol synthesis plant.
15. The method according to any preceding claim, further comprising:
- supplying at least part of any product that is generated in the hydrogen production plant to at least one of the one or more of the further processing plants that the hydrogen

production plant is integrated with such that the supplied product can be used by the at least one of the one or more of the further processing plants; and/or

5 supplying at least part of any product that is generated in at least one of the one or more of the further processing plants that the hydrogen production plant is integrated with to the hydrogen production plant such that the supplied product can be used by the hydrogen production plant.

10 16. The method according to any preceding claim, wherein the temperature of gas output from the autothermal reforming process is in the range 900-1100 °C, and preferably between 1000 and 1050 °C.

15 17. The method according to any preceding claim, wherein the temperature of gas output from the gas-heated reformer is in the range 400-800 °C, and preferably 450-700 °C, and further preferably 500-600 °C.

18. The method according to any preceding claim, further comprising providing the autothermal reforming process with:

20 oxygen from an air separation unit such as a cryogenic air separation unit;

oxygen or oxygen enriched air from a membrane air separation unit; and/or

25 oxygen from a pressure or vacuum swing adsorption unit.

19. The method according to any preceding claim, wherein the autothermal reforming process is supplied with oxygen from an auxiliary air separation unit that is part of a methanol synthesis plant or a nitrogen production plant.

30 20. The method according to claim 4 or any claim dependent thereon, wherein the water-gas-shift is performed in both a high-temperature-shift reactor and a low-temperature shift reactor.

35 21. The method according to any of claims 4 to 19, wherein the water-gas-shift is performed in a single reactor.

22. The method according to claim 4 or any claim dependent thereon, wherein hydrogen is separated by one or more of a PSA unit, a membrane that is optionally a Pd-membrane and/or a membrane in which the permeate side of the membrane is flushed by steam.
- 5 23. The method according to claim 6 or any claim dependent thereon, wherein carbon dioxide is separated by cryogenic processes and/or a solvent that is optionally methanol.
24. The method according to claim 6 or any claim dependent thereon, wherein hydrogen and/or carbon dioxide is liquified using the excess cooling capacity of an auxiliary processing plant, wherein optionally the auxiliary processing plant is an air-separation plant and the excess cooling capacity is in the form of cold oxygen and/or nitrogen.
- 10 25. The method according to claim 4 or any claim dependent thereon, wherein the further processing plant is a methanol synthesis plant and all, or part of, the separated hydrogen is used to adjust the stoichiometric number of the methanol synthesis plant so that the stoichiometric number is 2.0 or slightly above 2.
- 15 26. The method according to claim 4 or any claim dependent thereon, wherein, in use, all, or part of, the separated hydrogen is used to reduce carbon dioxide emission from an auxiliary processing plant, optionally the hydrogen being added to burners of a fired heater and, optionally, the burners are part of a steam reformer.
- 20 27. The method according to claim 4 or any claim dependent thereon, wherein the process of separating hydrogen from the shifted gas comprises generating a rest gas; and
- 25 the method further comprises using at least part of the rest gas.
28. The method according to claim 27, wherein at least part of the rest gas is used as a fuel for one or more of:
- 30 pre-heating one or more of the feed gas, the gas input to a pre-treatment process, the gas input to a pre-reforming process and the gas input to the gas-heated reforming process;
- 35 generating steam for use in a pre-reforming process and/or for adding to the gas stream input to a water gas shift reactor; and
- powering a gas turbine.

29. The method according to claim 27 or 28, wherein at least part of the rest gas is fed into the autothermal reforming process and/or the gas-heated reforming process.
30. The method according to any preceding claim, wherein the hydrogen production plant is
5 integrated with a methanol synthesis plant; and
the product $G \cdot H$ is at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2;
- 10 wherein:

G is the natural gas consumption in the hydrogen plant relative to the methanol plant; and

H is the fraction of hydrogen produced by the hydrogen production plant that is directed to
15 the methanol synthesis plant for consumption in burners therein.
31. A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons; and
20 performing reforming processes so as to generate hydrogen in dependence on the feed gas;

wherein the reforming processes comprise both a gas-heated reforming process and an
25 autothermal reforming process; and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;
- 30 the method further comprising saturating the received feed gas with water; and

pre-reforming the gas to generate pre-reformed gas;

wherein the reforming processes are performed on the pre-reformed gas.
35
32. A method of producing hydrogen, the method comprising:
receiving a feed gas comprising hydrocarbons; and

performing reforming processes so as to generate hydrogen in dependence on the feed gas;

5 wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;

10 the method further comprising:

performing a water-gas-shift on the gas output from the reforming processes; and

15 separating hydrogen from the shifted gas;

wherein the process of separating hydrogen from the shifted gas comprises generating a rest gas; and

20 the method further comprises using at least part of the rest gas.

33. A hydrogen production plant arranged to perform the method of claim 31 or claim 32.

34. A hydrogen production plant and one or more further processing plants arranged to perform the method of any of claims 1 to 32.

25

35. A hydrogen production plant and one or more further processing plants according to claim 34, wherein the one or more further processing plants include any of a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.

30

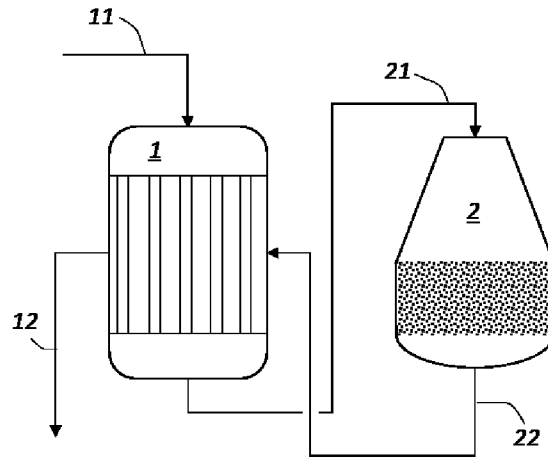


Figure 1

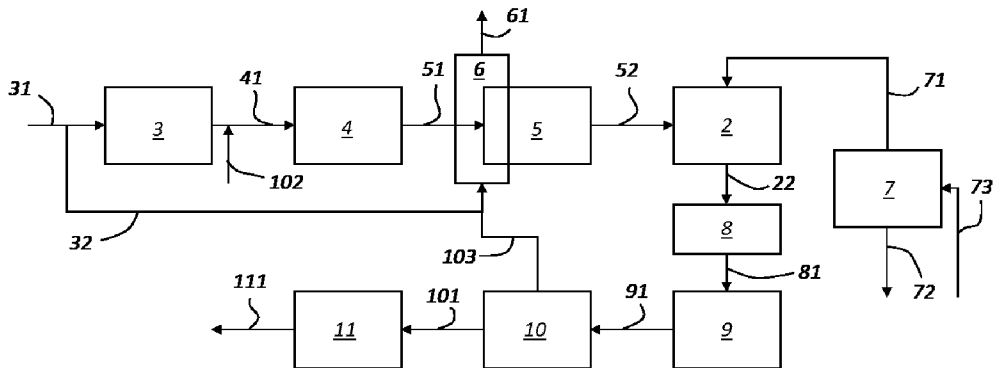


Figure 2

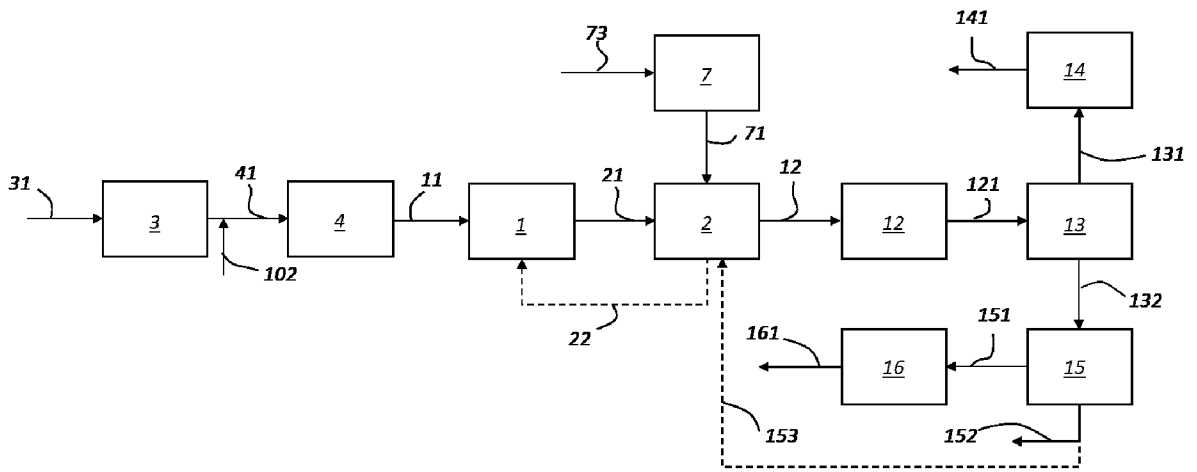


Figure 3

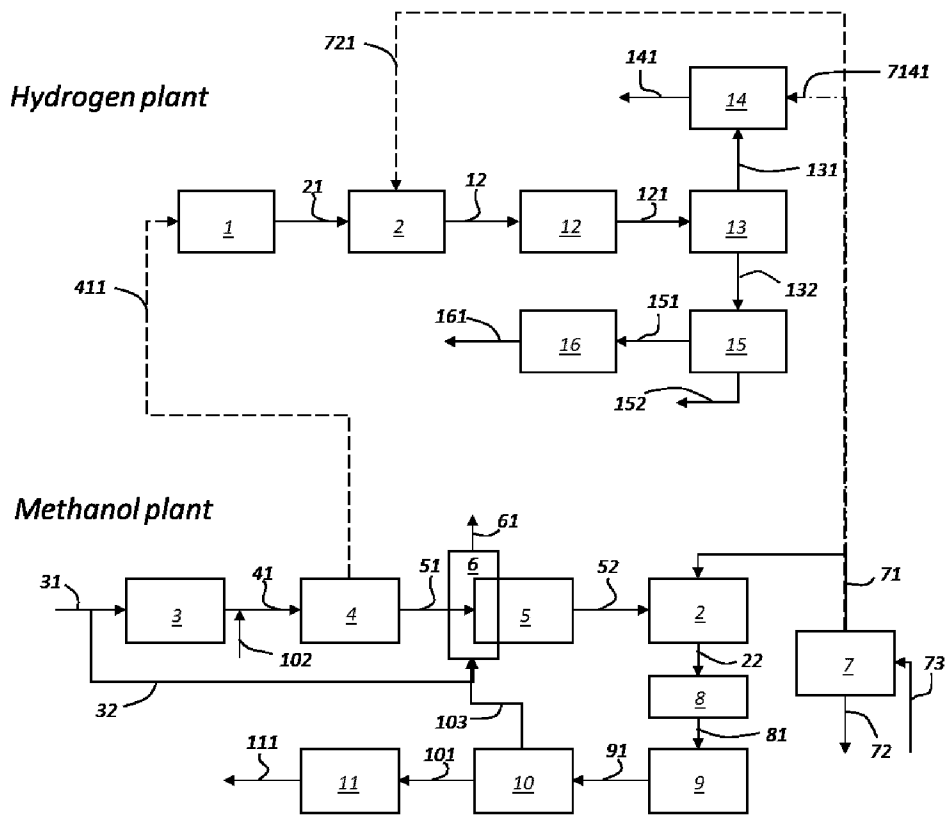


Figure 4

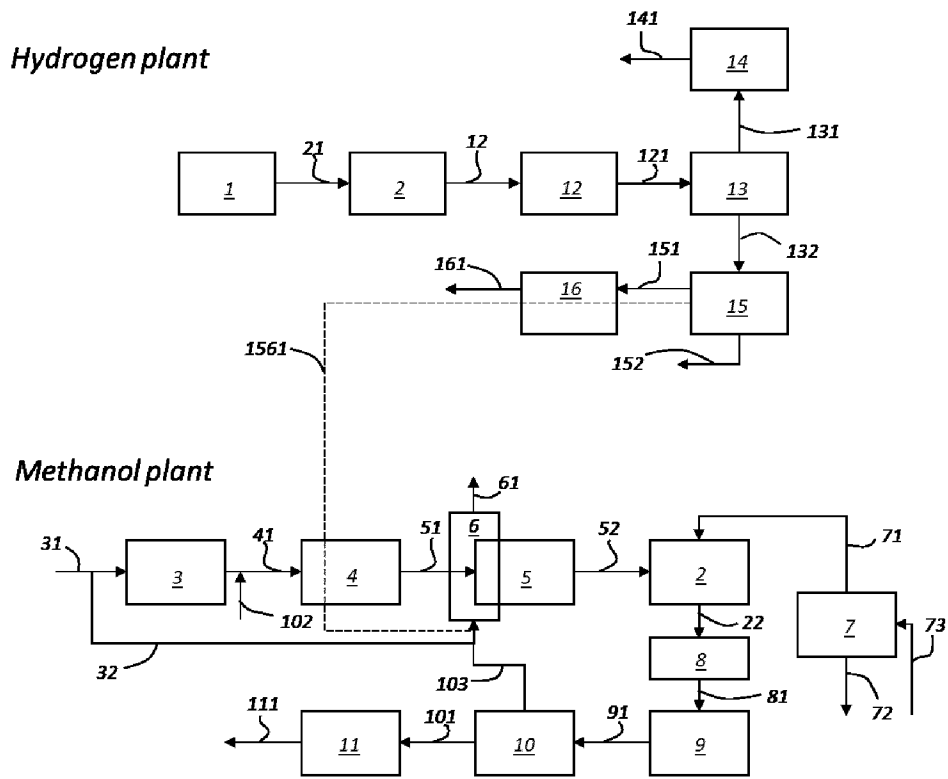


Figure 5

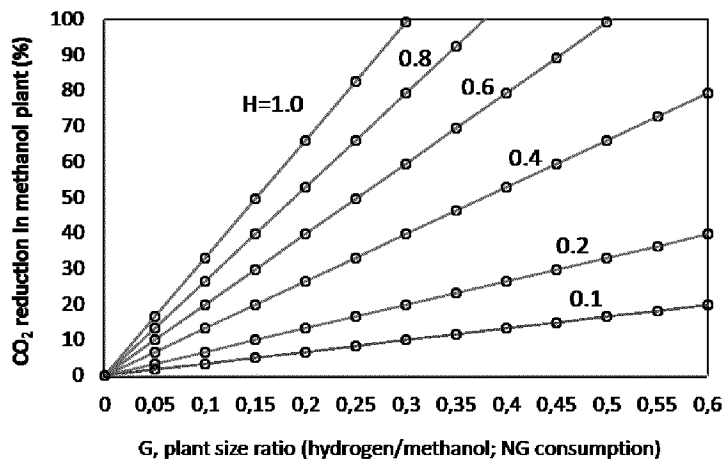


Figure 6