

DEVICE AND METHOD FOR PRODUCING SYNTHETIC GAS

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a device and method for producing synthetic gas. It applies, in particular, to the field of producing synthetic natural gas or "SNG" (Synthetic Natural Gas).

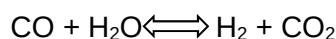
STATE OF THE ART

Biomethane, which is an "SNG" (Synthetic Natural Gas), can be produced by utilizing Power-to-SNG (abbreviated to "P2G") methods, designed to convert water, CO₂ and electrical energy into a combustible gas of a quality similar to that of natural gas.

To achieve a satisfactory economic return, P2G is based on using electrical energy from a renewable source during periods when there is an overproduction of this energy. Consequently, the methanation technology requires great operational flexibility in terms of power, or flow rate, and processing.

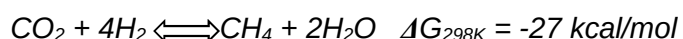
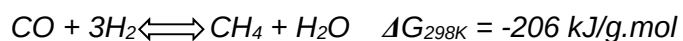
Several technological options exist within this sector.

The first option consists of directly co-electrolyzing water, in the form of vapor, and anthropogenic CO₂ to produce CO and H₂. This conversion generally takes place at high temperature, and the gas produced is a syngas whose compositional characteristics are close to those from biomass gasification (CO, H₂, CO₂ and H₂O). The main difference lies in better control of the H₂/CO ratio without a gas-to-water reaction step, abbreviated to "WGS" (for Water Gas Shift) and referred to as the "Dussan reaction". The formula for this WGS reaction is



The second option consists of converting the water by alkaline or polymer electrolyte membrane electrolysis to produce H₂ at the cathode and O₂ at the anode. The H₂ produced in this way is then mixed with CO₂ to form syngas, which is the source of the synthetic natural gas.

The production of biomethane from the syngas is based on the catalytic methanation (or hydrogenation) reaction of the CO or CO₂, called the "Sabatier reaction". Methanation consists of converting the carbon monoxide or dioxide in the presence of hydrogen and a catalyst, generally based on nickel or any other more or less noble transition metal, to produce methane. It is governed by the following competitively balanced hydrogenation reactions:



To produce SNG from syngas, the first option utilizes a methanation reaction of the CO and residual CO₂ whereas the second option utilizes a CO₂ methanation reaction.

The methanation reaction is an exothermic reaction with a reduction in the number of moles; according to Le Chatelier's principle, the reaction is encouraged by increasing the pressure and discouraged by increasing the temperature.

These highly exothermic balanced reactions require good control of the cooling of the reactor in which they take place.

The heat generated during CO conversion is approximately 2.7 kWh during the production of 1 Nm³ of methane. Controlling the temperature inside the reactor, and therefore removing the heat produced by the reaction, is one of the keys to minimizing the deactivation of the catalyst, by sintering, and maximizing the methane conversion rate.

Profitable reuse of the heat produced during methanation, either within the actual unit or by selling heat, is one of the keys to the technical and economic balance of the SNG production method. The production of steam is a conventional way to obtain this reuse.

The methanation reactions, which have rapid kinetics at the temperatures utilized, are characterized by very high exothermicity.

To maximize the production of CH₄ by carbon monoxide hydrogenation, the H₂ and CO should have a stoichiometric ratio of about 3:1. Even by respecting to this ratio, the reaction remains incomplete because of the chemical balances.

Among the methanation reactor technologies, some utilize a dense fluidized-bed reactor, the bed being formed by the methanation reaction catalyst. The heat produced by the reaction is therefore removed by exchangers immersed in the fluidized bed. However, because of the very high exothermicity of the reaction, the amount of heat to be removed, and therefore the exchange surface areas required, is very great. Therefore, the volume occupied by this exchanger leads to an overall over-dimensioning of the reactor size, and above all to making its design more complex.

The utilization of a fluidized bed is a simple solution for limiting the reaction temperature. Fluidization of the catalyst by the reactant mixture enables almost perfect homogenization of the temperatures at all points of the catalyst layer and the reactor can be assimilated to an isothermal reactor. The removal of the heat produced by the reaction is achieved by means of exchangers immersed within the fluidized bed. The thermal exchange coefficients between the fluidized layer and a wall immersed into the bed are very high (of the order of 400 to 600 watts per kelvin per square meter, expressed as W/K.m², comparable to those between a liquid and a wall) and make it possible to minimize the dimensions of the exchanger, and therefore the overall size of the reactor.

In the temperature range utilized in the fluidized-bed methanation reactors, the kinetics of the methanation reaction are very rapid and, as a result, the amount of catalyst

required just for the chemical reaction is small. Consequently, the size of the reactor and the amount of catalyst used stem from the overall dimensions of the exchanger installed within the fluidized bed and from the required transfer surface area.

At temperatures below 230°C, nickel, constituting the catalyst or present in the material making up the reactor walls, is likely to react with the carbon monoxide to form nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$), a highly toxic compound. For this reason, it is essential that all portions of the reactor in contact with CO are always at a temperature above 150°C and preferably above 230°C.

Because of the thermal exchange and the fluidization regime, a major drawback is attributable to this technology for high-pressure operation. The reduction in the gas volume due to increased pressure leads to a smaller cross-sectional area available for positioning the exchanger (for equivalent power). However, solutions of the person skilled in the art exist for overcoming the adjustment of the effective surface area or the fluidization regime. For example, the non-exhaustive solutions are:

- reducing the number of tubes and, as a result, increasing the height of the catalyst layer, with a height limit linked to the slugging phenomenon with reduced thermal exchange properties, slugging being the movement of solids in packets with, between two packets, a gaseous pocket that fills the entire cross-sectional area of a reactor, which has the effect of producing an alternation between solid and gaseous packets instead of a mixture of gas and solids, as expected; and

- modifying the physical characteristics of the catalyst (particle size, density of the support) to preserve an equivalent fluidization for a lower volumetric flow rate.

To optimize operational flexibility, the fluidized bed naturally allows greater flexibility in terms of reactor flow rate and therefore power with regard to sizing conditions.

The solutions currently proposed for this technological family are not really differentiated from each other by conversion efficiency, but mainly by the methodology utilized to cool the reactor.

The overall schematic diagram for current P2G systems therefore comprises the following steps:

- co-electrolysis of the water vapor and CO_2 ;
- CO methanation by the hydrogen co-produced in the co-electrolysis; and
- adjustment to specifications, to separate the H_2O and residual H_2/CO_2 .

The function of the adjustment to specifications step is to separate the constituents of the gas produced by methanation in order to obtain a synthetic methane meeting the specifications for injection into the natural gas grid. This separation therefore generates the sub-products H_2O , CO_2 and H_2 . It is usually carried out in separate equipment with sometimes very different operating conditions.

Before the SNG produced is processed and injected, a significant fraction of the residual H_2 from the methanation reaction has to be removed in order to meet specifications. The technique used most frequently for this separation is membrane permeation, which can present a non-trivial level of complexity and costs, in terms of capital expenditure and operation, with a considerable impact on the value chain.

The composition of the raw SNG on output from the reactor is closely related to the operating conditions of the reactor, in terms of pressure, temperature, adiabatic or isothermal operating mode of the reactor, these conditions governing the chemical balances of the methanation reactions. These reactions generally form water, and consequently this species needs to be separated. With regard to the other species (CO , CO_2 and H_2), their respective concentrations can be modified by acting first on the operating mode of the reactor (adiabatic or isothermal) and second on the temperature or pressure. A high pressure and a low temperature will therefore allow the concentrations of these compounds to be reduced considerably. When the operation is carried out in an “adiabatic” reactor, a series of steps is also necessary to achieve an equivalent conversion quality to the isothermal reactor. In any event, the composition of the gas produced is generally incompatible with regard to the specifications for the injection or use of natural gas, and improvement steps are necessary to remove the CO_2 and/or the residual H_2 . Therefore, the operating mode forms a block to simplifying the chain of methods.

Systems are known such as those described in document US 2013/0317126. In these systems, an adiabatic methanation reactor is utilized and a portion of the methanation products is recirculated in the input to said reactor.

This recirculation of methanation products is aimed, according to this document, at adjusting the temperature of the reagents input into the adiabatic methanation reactor so as to moderate the exothermicity of the adiabatic reaction occurring in the reactor.

In these solutions, the temperature reached on input to the methanation reactor is of the order of 310 to 330°C and the temperature on output from this reactor is of the order of 620°C, which results in a somewhat inefficient conversion limited by the thermodynamics of the reaction and therefore the presence of undesirable compounds, for example excess H_2 , CO , CO_2 in the flow output from the reactor. This presence of undesirable compounds, especially hydrogen, makes a hydrogen separation step necessary downstream from the reactor to meet, for example, the specifications for injection into the natural gas distribution or transport grid.

The flow is said to meet injection specifications when the following characteristics of the flow:

- high heating value (“HHV”);
- Wobbe index; and

- hydrogen content

are within predefined value ranges corresponding to the particular characteristics of the natural gas distribution or transport grid.

Systems such as those described in document US 3 967 936 are also known. In these systems, a series of adiabatic methanation reactors is utilized and a portion of the methanation products is recirculated in the input to each reactor of the series.

This recirculation of methanation products is aimed, according to this document, at adjusting the temperature of the reagents input into the adiabatic methanation reactor so as to moderate the exothermicity of the adiabatic reaction occurring in the reactor.

In the same way, these solutions require the separation, downstream from the reactor, of undesirable compounds such as hydrogen to meet, for example, the specifications for injection into the natural gas distribution or transport grid.

Systems are known such as those described in document US 2009/0247653. In these systems, a series of three adiabatic methanation reactors is utilized, the last reactor in the series being designed to produce additional synthetic methane. In these systems, a portion of the methanation products CO and H₂ is recirculated after the second reactor towards the input flow of the first reactor in the series so as to adjust the CO and H₂ ratio and adjust the temperature of the input flow of the first reactor in order to moderate the exothermicity of the adiabatic reaction occurring in the first reactor.

However, these solutions also require the separation, downstream from the reactor, of undesirable compounds such as hydrogen.

The adiabatic reactors, while they do not assume cooling within the methanation reactor, have several drawbacks:

- a plurality of reactors in series is necessary to obtain a satisfactory methanation yield; and
- in the case of CO methanation, a specific composition of the synthetic gas, by adding a so-called gas-to-water catalyst step, is necessary to obtain a satisfactory stoichiometry.

On the other hand, the design of adiabatic reactors is simpler, since they basically consist of a chamber having to resist generally high pressures (>30 bars) to achieve a satisfactory conversion.

In the case of methanation in an isothermal reactor, the operating pressure does not need to be as high (<20 bars), but requires the arrangement of surfaces immersed in the catalyst layer, which generates a complex design and additional cost linked to the cooling system.

In conclusion, the current techniques of the state of the art do not enable satisfactory control of the exothermicity of the methanation reaction and do not give the device

satisfactory flexibility with regard to power fluctuations linked directly to the over-production of electricity. In addition, these current techniques require a systematic separation of H_2 and/or CO_2 , when the operating pressure is less than 40 bars, to meet, for example, the specifications for the injection or use as a substitute for natural gas in the grid.

Therefore, the current systems do not make the adjustment to specifications for injection into the natural gas distribution or transport grid possible without a hydrogen separation step, downstream from the methanation step, taking place.

SUBJECT OF THE INVENTION

The present invention aims to remedy all or part of these drawbacks.

To this end, according to a first aspect, the present invention envisages a synthetic natural gas production device, which comprises:

- a means for high-temperature co-electrolysis of a carbon dioxide and water mixture in order to produce a syngas comprising carbon monoxide, carbon dioxide, water, and hydrogen;
- an isothermal methanation reactor comprising:
 - an inlet, for syngas produced by the co-electrolysis means, connected to a syngas supply channel, and
 - an outlet for synthetic natural gas;
- a water separation means comprising:
 - an inlet for synthetic natural gas and
 - an outlet for dehydrated synthetic natural gas; and
- a bypass for a portion of the dehydrated synthetic natural gas from the outlet of the water separation means to the syngas supply channel in order to provide a mixture of the syngas and the bypassed synthetic natural gas to the reactor.

As the water separation means cools the synthetic natural gas, supplying a portion of this synthetic natural gas on input to the reactor allows the syngas to be cooled and means the reactor does not require a heat exchanger. The design of such a reactor, especially in terms of sizing, is made even simpler. In addition, the supply of dehydrated synthetic natural gas in the supply channel improves the Wobbe index and HHV of the methanation reaction products through the favorable modification of the reaction balances. Therefore, the device that is the subject of the present invention allows a simplified sizing of the reactor and the simplification of the adjustment to specifications requiring separation of the carbon dioxide before processing for injecting into a gas grid.

In addition, the utilization of an isothermal reactor makes it possible to have a single methanation step to obtain an efficient synthetic natural gas conversion and obtain a gas of a

quality close to the specifications for injection into the natural gas distribution or transport grid.

In some embodiments, the device that is the subject of the present invention comprises a means for separating carbon dioxide from the synthetic natural gas, this separation means being positioned downstream from the bypass.

These embodiments improve the adjustment to specifications of the methanation reaction products.

In some embodiments, the device that is the subject of the present invention comprises a means for separating carbon dioxide from the synthetic natural gas, this separation means being positioned upstream from the bypass.

These embodiments further improve the simplification of the adjustment to specifications of the methanation reaction products.

In some embodiments, the device that is the subject of the present invention comprises, upstream from the syngas supply channel, a means for high-temperature co-electrolysis of a carbon dioxide and water mixture.

In some embodiments, the device that is the subject of the present invention comprises:

- a means for injecting a purge gas for cleaning an anode of the co-electrolysis means;
- a means for separating water from co-electrolysis products; and
- a means for recovering oxygen or oxygen-enriched air on output from the separation means.

These embodiments enable the injected vapor to achieve a backpressure relative to the cathode operating pressure of the co-electrolysis means.

In some embodiments, the device that is the subject of the present invention comprises a means for compressing carbon dioxide intended to be mixed with the water.

These embodiments make it possible to improve the operation of the co-electrolysis means utilized.

In some embodiments, the device that is the subject of the present invention comprises, upstream from the input to the reactor, a means for cooling the mixture to a temperature higher than the dew point temperature of the mixture, to prevent any pre-condensation of the water of the mixture, and lower than the operating temperature of the reactor, to allow the reactor to be cooled.

These embodiments make it possible to bring the syngas into line with the operating temperatures of the methanation reactor.

In some embodiments, the mixture cooling means cools this mixture to a temperature between 150°C and 300°C.

In some embodiments, the mixture cooling means cools this mixture to a temperature higher than 230°C and less than the operating temperature of the reactor.

In some embodiments, the device that is the subject of the present invention comprises:

- a sensor of a temperature inside or on output from the reactor; and
- a recirculator of natural gas input into the bypass, controlled as a function of a value of the temperature measured.

These embodiments make it possible to regulate the flow rate of reaction products recirculated as a function of the temperature measured. If the measured temperature is above a predefined temperature, corresponding to optimum methanation reaction conditions, the flow rate of recirculated products is increased to cool the reaction medium of the reactor. Conversely, if the measured temperature is below the predefined temperature, the flow rate of recirculated products is reduced.

In some embodiments, the device that is the subject of the present invention comprises a bypass channel, for a portion of the hot methanation reaction products, comprising:

- an inlet positioned between the outlet from the reactor and the water separation means; and
- an outlet positioned upstream from the inlet to the reactor and downstream from the cooling means.

These embodiments make it possible to regulate the flow rate input to the reactor so as to give the device great flexibility, regardless of the quantity of electrical energy produced upstream.

In some embodiments, the device that is the subject of the present invention comprises:

- a means for measuring the flow rate of the syngas downstream from the mixing location and upstream from the methanation reactor; and
- a recirculator of hot methanation reaction products input into the bypass channel, controlled as a function of syngas flow rate measured.

These embodiments make it possible to regulate the flow rate input to the reactor as a function of the syngas flow rate measured.

In some embodiments, the water separation means is configured to cool the synthetic natural gases to a temperature between -5°C and +60°C.

In some embodiments, the water separation means is configured to cool the synthetic natural gases to a temperature below the dew point temperature at the operating conditions of the reactor.

These embodiments make it possible to separate almost all of the water contained in the SNG on output from the methanation reactor.

In some embodiments, the isothermal reactor is a fluidized-bed reactor.

In some embodiments, the device that is the subject of the present invention comprises at least one heat exchange surface positioned in the fluidized bed.

These embodiments make it possible to regulate the temperature inside the methanation reactor.

These embodiments allow the temperature in the catalyst layer of the isothermal reactor to be made uniform simply.

According to a second aspect, the present invention envisages a method for producing synthetic natural gas, which comprises:

- a step of high-temperature co-electrolysis of a carbon dioxide and water mixture in order to produce a syngas comprising carbon monoxide, carbon dioxide, water, and hydrogen;
- a methanation reaction step, comprising:
 - a step of inputting syngas, output from the co-electrolysis step, into an isothermal methanation reactor by means of a syngas supply channel, and
 - a step of outputting synthetic natural gas;
- a step of separating water, comprising:
 - a step of inputting synthetic natural gas and
 - a step of outputting dehydrated synthetic natural gas;
- a step of bypassing a portion of the dehydrated synthetic natural gas output from the water separation step to the syngas supply channel in order to provide a mixture of the syngas and the bypassed synthetic natural gas to the reactor.

The method that is the subject of the present invention corresponding to the device that is the subject of the present invention, the particular features, advantages and aims of this method are similar to those of the device that is the subject of the present invention. These features, advantages and aims are not repeated here.

In some embodiments, the method that is the subject of the present invention comprises a step of separating carbon dioxide from the dehydrated synthetic natural gas output from the water separation step.

In some embodiments, the method that is the subject of the present invention comprises a step of bypassing a portion of the hot methanation reaction products, to upstream of the methanation step.

BRIEF DESCRIPTION OF THE FIGURES

Other advantages, aims and particular features of the invention will become apparent from the non-limiting description that follows of at least one particular embodiment of the device and method for producing synthetic natural gas that are the subjects of the present invention, with reference to drawings included in an appendix, wherein:

- figure 1 represents, schematically, a first particular embodiment of the device that is the subject of the present invention;
- figure 2 represents, schematically, a second particular embodiment of the device that is the subject of the present invention;
- figure 3 represents, schematically and in the form of a logical diagram, a particular series of steps of the method that is the subject of the present invention;
- figure 4 represents, in the form of a curve, the Wobbe index of synthetic gas obtained by the first and second embodiments of the device and the method that are the subjects of the present invention;
- figure 5 represents, in the form of a curve, the HHV of synthetic gas obtained by the first and second embodiments of the device and the method that are the subjects of the present invention;
- figure 6 represents, in the form of a curve, the relative reduction of the hydrogen molar flow inside the reactor during the utilization of the first and second embodiments of the device, compared to a comparable device without recirculation;
- figure 7 represents, in the form of a curve, the exothermicity of the methanation reaction during the utilization of the first and second embodiments of the device and the method that are the subjects of the present invention; and
- figure 8 represents, schematically, an example of system utilized in the state of the art.

DESCRIPTION OF EXAMPLES OF REALIZATION OF THE INVENTION

The present description is given as a non-limiting example, each characteristic of an embodiment being able to be combined with any other characteristic of any other embodiment in an advantageous way.

It is now noted that the figures are not to scale.

Figure 8 shows a schematic view of an example of system 80 utilized in the state of the art.

In these systems 80, methanation reagents enter into a methanation reactor 805, which can be part of a series (not shown) of such reactors.

On output from the methanation step, the water is separated from the methanation products by a means 825 for separating this water, such as a heat exchanger for example.

The dehydrated synthetic natural gas is then processed by a means 845 for separating carbon dioxide.

Lastly, the synthetic natural gas is processed by a means 855 for separating hydrogen so that this synthetic natural gas meets the specifications for injection into the natural gas distribution grid.

The steps of separating water, carbon dioxide and hydrogen can be carried out in any order.

Figure 1, which is not to scale, shows a schematic view of a first embodiment of the device 10 that is the subject of the present invention. This synthetic natural gas production device 10 comprises:

- a means 805 for high-temperature co-electrolysis of a carbon dioxide and water mixture in order to produce a syngas comprising carbon monoxide, carbon dioxide, water, and hydrogen;
- an isothermal methanation reactor 105 comprising:
 - an inlet 110, for syngas produced by the co-electrolysis means, connected to a syngas supply channel 115, and
 - an outlet 120 for synthetic natural gas;
- a water separation means 125 comprising:
 - an inlet 130 for synthetic natural gas,
 - an outlet 135 for dehydrated synthetic natural gas; and
- an outlet 127 for the water separated from the synthetic natural gas, and a bypass 140 for a portion of the dehydrated synthetic natural gas from the outlet of the water separation means to the syngas supply channel 115 in order to provide a mixture of the bypassed syngas and synthetic natural gas to the reactor.

The water, H_2O , and the CO_2 are co-electrolyzed at a high temperature, of the order of 750 to 850°C, to produce syngas comprising CO , CO_2 , H_2O and H_2 which results, by catalytic reaction, in hydrocarbons in the reactor 105. This system uses both electrical energy and heat to electrolyze the molecules of CO_2 and H_2O .

The reactor 105 is, preferably, an isothermal fluidized-bed methanation reactor operating at a predefined temperature. Fluidization of the catalyst by the reactant mixture enables almost perfect homogenization of the temperatures at all points of the catalyst layer and the reactor can be assimilated to an isothermal reactor. In some variants, this reactor 105 can be a boiling water reactor, known to the person skilled in the art under the abbreviation "BWR" (for Boiling Water Reactor). In other variants, this reactor 105 can be a wall-cooled reactor or an exchanger reactor.

In some embodiments, the reactor 105 comprises at least one heat exchange surface 106 positioned in the fluidized bed of the isothermal reactor 105.

This surface 106 is, for example, a tube configured to form a loop for circulating a fluid from the outside the reactor 105 to the inside of this reactor 105, the fluid being cooled outside the reactor 105.

This fluid is, for example, superheated or saturated water vapor.

This reactor 105 is configured to carry out the methanation of the carbon monoxide and/or carbon dioxide.

This reactor 105 comprises the inlet 110 for syngas which is, for example, an aperture of the reactor 105 equipped with a connector (not shown) compatible with the syngas supply channel 115.

The synthetic natural gases leave the reactor 105 through the outlet 120 from the reactor. This outlet 120 is, for example, an aperture connected to a connector (not shown) making it possible to connect a sealed channel for transporting synthetic natural gas.

The water separation means 125 is, for example, a heat exchanger for cooling the synthetic natural gases to a temperature below the dew point temperature of the water. This temperature is preferably between -5°C and $+60^{\circ}\text{C}$. Preferentially, this temperature is between 5°C and 40°C . Preferably, this temperature is lower than the dew point temperature of the water under the operating conditions of the present invention, to prevent any pre-condensation of the water of the mixture, and lower than the operating temperature of the reactor, to allow the reactor 105 to be cooled.

The water separated in this way is collected by an outlet 127 for water and can be injected into the vapor production means 830, used by an external device, or heated to be transformed into water vapor that can, as indicated below, be injected into the compression means 825.

The water separation means 125 comprises the inlet 130 for synthetic natural gas. This inlet 130 is, for example, an aperture associated with a connector (not shown) to be connected to a sealed channel for transporting synthetic natural gas output from the reactor 105.

The water separation means 125 comprises the outlet 135 for dehydrated synthetic natural gas. This outlet 135 is, for example, an aperture associated with a connector (not shown) to be connected to a sealed channel (not shown) transporting dehydrated synthetic natural gas.

The bypass 140 is, for example, a sealed channel connected to the transport channel for dehydrated synthetic natural gas in order to capture a portion of the flow passing through this transport channel.

This bypass 140 injects the dehydrated synthetic natural gases into the syngas supply channel 115.

In this way, the syngas and the dehydrated synthetic natural gas, cooled by the water separation process, form a mixture which, in the reactor 105, reduces the exothermicity of the methanation reaction and also improves the specifications of the synthetic natural gas output from the reactor 105.

In particular, the mixture produced makes it possible to avoid the downstream separation of H_2 in the SNG.

The supply channel 115 is sealed and receives, for example, CO, CO_2 , H_2O and H_2 output from a means for co-electrolyzing water and carbon dioxide.

In some preferred embodiments, such as that shown in figure 1, the device 10 comprises

- a means 810 for injecting a purge gas, such as water vapor or a mixture of air and water vapor, for cleaning an anode of the co-electrolysis means 805;
- a means 815 for separating water from co-electrolysis products;
- a means 820 for recovering oxygen or oxygen-enriched air on output from the separation means 815.

The injection means 810 is, for example, a channel connected to an injection valve enabling an anode of the co-electrolysis means 805 to be cleaned.

This injection channel is supplied with water from a water vapor production means 830.

The oxygen produced during the co-electrolysis is removed from the co-electrolysis means 805 by a different channel from the channel connected to the supply channel 115. This oxygen removal channel traverses the means 815 for separating water from co-electrolysis products. This water separation means is, for example, a heat exchanger for cooling the oxygen and water or the enriched air and water to a temperature below the dew point temperature of the water. The water separated in this way is directed towards the tank that supplies water to the vapor injection means 810.

The means 820 for recovering oxygen or enriched air is, for example a channel connected to the water vapor production means 830.

In some preferred embodiments, such as that shown in figure 1, the device 10 comprises a means 825 for compressing carbon dioxide intended to be mixed with the water. The compression means can be any type known to the Person Skilled in the Art.

Preferably, the compression means 825 is, for example, an ejector utilizing vapor as transporting fluid. This vapor comes, for example, from the vapor injection channel that forms the vapor injection means 810.

In some preferred embodiments, such as that shown in figure 1, the device 10 comprises, upstream from the inlet of the reactor 105, a means 160 for cooling the mixture to

a temperature higher than the dew point temperature of the mixture and lower than the operating temperature of the reactor.

In some preferred embodiments, such as that shown in figure 1, the mixture cooling means 160 cools this mixture to a temperature between 150°C and 300°C and preferably higher than or equal to 230°C to prevent the formation of toxic compounds such as, for example, nickel tetracarbonyl.

This cooling means 160 is, for example, a heat exchanger for cooling the syngas.

In addition, the device 10 can comprise, in these embodiments, a temperature sensor 162 of the mixture downstream from the cooling means 160. The temperature of the cooling means 160 varies as a function of the captured temperature and a predefined temperature setpoint. If the captured temperature is higher than the temperature setpoint, the power of the cooling means 160 is increased. Conversely, the power of the cooling means 160 is reduced when the captured temperature is below the temperature setpoint.

In some preferred embodiments, such as that shown in figure 1, the device 10 comprises:

- a sensor 150 of a temperature inside or on output 120 from the reactor 105; and
- a recirculator 155 of hot methanation reaction products input into the bypass channel, controlled as a function of the captured temperature.

The sensor 150 is positioned inside or outside the reactor 105. This sensor 150 captures the temperature of the catalyst forming the fluidized bed, the atmosphere of the reactor 105 and/or the wall of the reactor 105 and/or the temperature of the outlet 120 of the reactor 105.

The recirculator 155 aims to offset the load, or pressure, losses successively in:

- the preheating means 160, the reactor 105, the water separation means 125 particularly for the device 10 described with reference to figure 1, and
- the preheating means 260, the reactor 205, the water separation means 225 and the carbon dioxide separation means 245 for the device 20 described with reference to figure 2

and all the connecting channels of these various items of equipment.

Such a load loss is estimated to be between 200 and 800 mbars, for example. The recirculator 155 is, for example, a fan, compressor or ejector. In the case of an ejector, the fluid used to realize the ejection mechanism is, for example, water vapor to enable the WGS taking place in the reactor 105.

If the measured temperature is above a predefined temperature, corresponding to optimum methanation reaction conditions, the flow rate of recirculated products is increased to cool the reaction medium of the reactor 105. Conversely, if the measured temperature is below the predefined temperature, the flow rate of recirculated products is reduced.

In some preferred embodiments, such as that shown in figure 1, the device 10 comprises a bypass channel 170, for a portion of the hot methanation reaction products, comprising:

- an inlet 175 positioned between the outlet from the reactor 105 and the water separation means 125; and
- an outlet 180 positioned upstream from the inlet 110 to the reactor 105 and downstream from the cooling means 160.

The bypass channel 170 is, for example, a sealed channel. The inlet 175 is, for example, an aperture emerging at the interior of the synthetic natural gas transport channel, upstream from the water separation means 125. The outlet 180 is, for example, an aperture for injecting synthetic natural gas into the mixture, downstream from the cooling means 160.

The synthetic natural gases, being hot, make it possible to keep the flow rate constant in the reactor 105.

The flow rate of the syngas is entirely a function of the quantities of electrical energy available. In order to maintain conversion stability during the methanation operation, the hydrodynamic conditions must be kept as constant as possible. However, if the available electrical power is insufficient and, as a result, the syngas flow rate is reduced, it is necessary to maintain a constant overall flow rate input to the reactor 105 or opt for a very flexible technology. Even in the case of the fluidized bed able to operate in a flow rate range of one to six, flow rates that are too low can cause degradation of the cooling, and therefore of the conversion. To overcome this difficulty, in the event of a significant drop in the syngas flow rate, the flow rate on output from the cooling means 160 is supplemented by a hot recirculation coming directly from the outlet 120 of the reactor 105 by means of the bypass channel 170. The fact of using a hot recirculation fluid does not cause a thermal imbalance of the reactor 105 but allows the device 10 to be made very flexible.

In some preferred embodiments, such as that shown in figure 1, the device 10 comprises:

- a means 185 for measuring the flow rate of the syngas downstream from the mixing location and upstream from the reactor 105; and
- a recirculator 190 of the natural gas input into the bypass channel 170, controlled as a function of the flow rate measured.

The flow rate measurement means 185 can be any type known to the person skilled in the art that is suitable for measuring the flow rate of gases, such as an anemometer, Coriolis effect flowmeter, vortex effect flowmeter, or electromagnetic flowmeter, for example.

The recirculator 190 is similar to the recirculator 155 in structural terms. This recirculator 190 is controlled as a function of the flow rate measured by the flow rate measurement means 185 and a flow rate setpoint value 187. If the measured flow rate is

below a predefined flow rate setpoint 187, the recirculator 190 is actuated so as to make up the difference between the measured flow rate and the flow rate setpoint 187 by an equivalent flow rate of synthetic natural gas.

In some preferred embodiments, the device 10 comprises a means 145 for separating carbon dioxide from the synthetic natural gas positioned downstream from the bypass 140. The utilization of the device 10 that is the subject of the present invention makes it possible to obtain synthetic gas close to the specifications of the gas grid requiring few additional operations.

In addition, the device 10 can also be utilized for a pressure range of between one bar and one hundred bars, and a range of predefined temperatures of between 230°C and 700°C.

Figure 2, which is not to scale, shows a schematic view of a second embodiment of the device 20 that is the subject of the present invention. This synthetic gas production device 20 is similar to the device 10 described with reference to figure 1. Therefore, references 205, 210, 215, 220, 225, 227, 230, 235, 240, 250, 255, 260, 262, 270, 275, 280, 285, 287, 290, 905, 910, 915, 920, 925 and 930 of device 20 correspond respectively to references 105, 110, 115, 120, 125, 127, 130, 135, 140, 150, 155, 160, 162, 170, 175, 180, 185, 187, 190, 805, 810, 815, 820, 825 and 830 of device 10.

The device 20 also comprises a means 245 for separating carbon dioxide from the synthetic natural gas positioned upstream from the bypass 240. This separation means 245 can be positioned upstream or downstream from the water separation means 225.

Figure 3 shows, in the form of a logical diagram of steps, a particular embodiment of the method 30 that is the subject of the present invention. This synthetic natural gas production method 30 comprises:

- a means 340 for high-temperature co-electrolysis of a carbon dioxide and water mixture in order to produce a syngas comprising carbon monoxide, carbon dioxide, water, and hydrogen;
- a methanation reaction step 305, comprising:
 - a step 310 of inputting syngas, output from the co-electrolysis step 340, into an isothermal methanation reactor by means of a syngas supply channel, and
 - a step 315 of outputting synthetic natural gas;
- a step 320 of separating water, comprising:
 - a step 325 of inputting synthetic natural gas and
 - a step 330 of outputting dehydrated synthetic natural gas;
- a step 335 of bypassing a portion of the dehydrated synthetic natural gas output from the output step of the water separation step to the syngas supply channel in order to

provide a mixture of the syngas and the bypassed synthetic natural gas to the reactor;

- preferably, a step 345 of separating carbon dioxide contained in the dehydrated synthetic natural gas, which separation step 345 can be performed between the reaction step 305 and the water separation step 320 or downstream from the water separation step 320; and
- preferably, a step 350 of bypassing a portion of the hot methanation reaction products, to upstream of the methanation step.

This method 30 is utilized, for example, by a device 10 or 20 that is the subject of the present invention and described with reference to figure 1 and 2.

It is noted that figures 4 to 7 are the result of simulations carried out to determine the impact of the device and method that are the subject of the present invention. These results are compared to a simulation of a case of recirculation without dehydration. The aim of the device and method that are the subjects of the present invention is also to minimize the steps of adjustment to specifications while operating a single-stage methanation at moderate pressure that is acceptable in terms of costs. For the same reasons, the SNG is preferably compressed at the end of the production chain after the separations required for injection into the grid. The simulations carried out and presented below were carried out at 8 bars and a methanation temperature of 320°C.

Figures 4 and 5 respectively show the Wobbe index and HHV of the SNG before H₂ separation for the reference configuration with recirculation of the humid SNG, recirculation of the dehydrated SNG and recirculation of the dehydrated, decarbonated SNG.

These results are presented as a function of the recirculation rate, which corresponds to the ratio of the volume flow rates under normal pressure and temperature conditions of the recirculated flow to the syngas flow. For the “reference configuration”, the recycled flow is replaced by a humid SNG flow rate equivalent to the flow passing through the bypass channel.

Figure 4 shows, on the x-axis, the Wobbe index of the synthetic natural gas produced by the device, 10 or 20, as a function of the recirculation rate, on the y-axis, and of the nature of the recirculated synthetic natural gas on input to the methanation reactor, 105 or 205.

It is noted, in particular, that the recirculation of humid synthetic natural gas 405 has no effect on the Wobbe index of the synthetic natural gas produced by the device.

It is noted, lastly, that the recirculation of dehydrated, decarbonated synthetic natural gas 415 improves the Wobbe index of the synthetic natural gas produced by the device, even with a recirculation rate of less than one.

It is also noted that the recirculation of dehydrated synthetic natural gas 410 further improves the Wobbe index of the synthetic natural gas produced by the device.

Figure 5 shows, on the x-axis, the HHV of the synthetic natural gas produced by the device, 10 or 20, as a function of the recirculation rate, on the y-axis, and of the nature of the recirculated synthetic natural gas on input to the methanation reactor, 105 or 205.

It is noted, in particular, that the recirculation of humid synthetic natural gas 505 has no effect on the HHV of the synthetic natural gas produced by the device.

It is noted, lastly, that the recirculation of dehydrated, decarbonated synthetic natural gas 515 improves the HHV of the synthetic natural gas produced by the device, even with a recirculation rate of less than one.

It is also noted that the recirculation of dehydrated synthetic natural gas 510 further improves the HHV of the synthetic natural gas produced by the device.

According to the results obtained in terms of the Wobbe index and HHV, the recirculation rate of the humid gas, ie the reference configuration, has no impact on the quality of the gas and shows that the separation of the H_2 is essential to achieve the injection specifications. Recirculation after dehydration alone or with decarbonation leads to a larger or smaller increase in the Wobbe index and the HHV. These improvements may be interpreted as the result of a simple dilution, but figure 6 highlights a real improvement in the reaction balances, with a dramatic reduction in the H_2 molar flow on output from device 10 or 20.

Figure 6 shows, on the x-axis, the relative H_2 molar flow on output from device, 10 or 20, as a function of the recirculation rate, on the y-axis, and of the nature of the recirculated synthetic natural gas on input to the methanation reactor, 105 or 205, relative to a device with the recirculation of humid synthetic natural gas or without recirculation.

It is noted, in particular, that the recirculation of humid synthetic natural gas 605 has no effect on the H_2 molar flow on output from the device.

It is also noted that the recirculation of dehydrated synthetic natural gas 610 causes a reduction in the H_2 molar flow on output from the device.

It is noted, lastly, that the recirculation of dehydrated, decarbonated synthetic natural gas 615 also causes a reduction in the H_2 molar flow on output from the device.

Despite the dilution by recirculation, the CO/H_2O ratio after recirculation is maintained on input to the reactor relative to the initial CO/H_2O ratio without recirculation. Therefore, the risk linked to deactivation of the methanation catalyst through coking remains relatively low. Between the two devices, 10 and 20, decarbonation downstream from the recirculation of the synthetic natural gas appears more effective in terms of molar reduction of the H_2 . Thus, to comply with the injectability criteria, the recirculation flow rate needs to be two to three times lower for dehydration alone than in the solution with decarbonation. For the operating conditions used for the simulation, and when only dehydration is applied before recirculation, the minimum recirculation rate required to avoid H_2 separation is estimated to be 0.4. When

dehydration is supplemented by a decarbonation step, the required rate is 1. These respective rates effectively make it possible to meet the constraints related to injection, yet still require an internal system for cooling the reactor to maintain isothermality and, in that case, cannot be applied to non-cooled fixed bed technologies. With regard to exchanger reactors - boiling water or fluidized-bed reactor - this new feature, under these operating conditions, allows the exchanger surface area to be reduced by 15% and 5% respectively.

Figure 7 makes it possible to see the change in the reactor's normalized exothermicity, ie the heat to be removed compared to a case without recirculation, as a function of the recirculation rate for the reference configuration and the two devices, 10 and 20, described above.

Figure 7 shows, on the x-axis, the exothermicity of the methanation reactor of the device, 10 or 20, as a function of the recirculation rate, on the y-axis, and of the nature of the recirculated synthetic natural gas on input to the methanation reactor, 105 or 205.

It is noted, in particular, that the recirculation of humid synthetic natural gas 705 reduces the exothermicity of the methanation reactor.

It is also noted that the recirculation of dehydrated synthetic natural gas 710 also reduces the exothermicity of the methanation reactor.

It is noted, lastly, that the recirculation of dehydrated, decarbonated synthetic natural gas 715 also reduces the exothermicity of the methanation reactor.

It appears that increasing the recirculation rate leads to a linear reduction in the exothermicity of the reactor. Here, the recirculated SNG plays the role of heat accumulator, which is more marked in the presence of H_2O because of a higher heat capacity. Obtaining a recirculation level corresponding to an ideal operating temperature of the devices, 10 and 20, makes it possible to be liberated from the internal exchanger of the reactor and the H_2 separation for adjustment to specifications. Further, the reactor is allothermal and therefore requires a heat supply to maintain the reactions.

The change in the molar fractions of the H_2 , CO_2 , CO and CH_4 species as a function of the recirculation rate for the different configurations simulated is in the direction of improved SNG quality. However, the molar fraction of CO increases with the dehydrated SNG recirculation device 10. For the operating conditions considered, however, the setpoint value is never exceeded. In this case, dehydration alone leads to the CO_2 content being concentrated on input to the reactor and shifts the balance of the WGS reaction towards the production of CO and consumption of H_2 . For the device 20, the CO_2 extraction incorporated into the recirculation loop allows the WGS reaction to be encouraged towards the production of H_2 , which is then converted into CH_4 .

CLAIMS

1. Synthetic natural gas production device (10, 20) characterized in that it comprises:
 - a means (805, 905) for high-temperature co-electrolysis of a carbon dioxide and water mixture in order to produce a syngas comprising carbon monoxide, carbon dioxide, water, and dihydrogen;
 - an isothermal methanation reactor (105, 205) comprising:
 - an inlet (110, 210), for syngas produced by the co-electrolysis means, connected to a syngas supply channel (115, 215), and
 - an outlet (120, 220) for synthetic natural gas;
 - a water separation means (125, 225) comprising:
 - an inlet (130, 230) for synthetic natural gas and
 - an outlet (135, 235) for synthetic natural gas;
 - a bypass (140, 240) for a portion of the dehydrated synthetic natural gas from the outlet of the water separation means to the syngas supply channel in order to provide a mixture of the bypassed syngas and synthetic natural gas to the reactor.
2. Device (10) according to claim 1, which comprises a means (145) for separating carbon dioxide from the synthetic natural gas, this separation means being positioned downstream from the bypass (140).
3. Device (20) according to one of claims 1 or 2, which comprises a means (245) for separating carbon dioxide from the synthetic natural gas, this separation means being positioned upstream from the bypass (240).
4. Device (10, 20) according to one of claims 1 to 3, which comprises a means (825, 925) for compressing carbon dioxide intended to be mixed with the water.
5. Device (10, 20) according to one of claims 1 to 4, which comprises, upstream from the inlet of the reactor (105, 205), a means (160, 260) for cooling the mixture to a temperature higher than the dew point temperature of the mixture, to prevent any pre-condensation of the water of the mixture, and lower than the operating temperature of the reactor, to allow the reactor (105, 205) to be cooled.
6. Device (10, 20) according to claim 5, wherein the mixture cooling means (160, 260) cools this mixture to a temperature between 150°C and 300°C.
7. Device (10, 20) according to claim 6, wherein the mixture cooling means (160, 260) cools this mixture to a temperature higher than 230°C and less than the operating temperature of the reactor (105, 205).
8. Device (10, 20) according to claim 7, which comprises a bypass channel (170, 270), for a portion of the hot methanation reaction products, comprising:

- an inlet (175, 275) positioned between the outlet from the reactor (105, 205) and the water separation means (125, 225); and
 - an outlet (180, 280) positioned upstream from the inlet to the reactor and downstream from the cooling means (160, 260).
9. Device (10, 20) according to one of claims 1 to 8, which comprises:
- a sensor (150, 250) of a temperature inside or on output from the reactor (105, 205); and
 - a recirculator (155, 255) of hot methanation reaction products input into the bypass channel (140, 240), controlled as a function of the captured temperature.
10. Device (10, 20) according to claim 9, which comprises:
- a means (185, 285) for measuring the flow rate of the syngas downstream from the mixing location and upstream from the methanation reactor (105, 205); and
 - a recirculator (190, 290) of the natural gas input into the bypass channel (170, 270), controlled as a function of the syngas flow rate measured.
11. Device (10, 20) according to one of claims 1 to 10, which comprises:
- a means (810, 910) for injecting a purge gas for cleaning an anode of the co-electrolysis means (805, 905); and
 - a means (815, 915) for separating water from co-electrolysis products;
 - a means (820, 920) for recovering oxygen or oxygen-enriched air on output from the separation means.
12. Device (10, 20) according to one of claims 1 to 11, wherein the separation means (125, 225) is configured to cool the synthetic natural gases to a temperature between -5°C and +60°C.
13. Device (10, 20) according to one of claims 1 to 12, wherein the water separation means (125, 225) is configured to cool the synthetic natural gases to a temperature below the dew point temperature at the operating conditions of the reactor.
14. Device (10, 20) according to one of claims 1 to 13, wherein the isothermal reactor (105) is a fluidized-bed reactor.
15. Device (10, 20) according to claim 14, which comprises at least one heat exchange surface (106) positioned in the fluidized bed.
16. Method (30) for producing synthetic natural gas, characterized in that it comprises:
- a means (340) for high-temperature co-electrolysis of a carbon dioxide and water mixture in order to produce a syngas comprising carbon monoxide, carbon dioxide, water, and hydrogen;
 - a methanation reaction step (305), comprising:
 - a step (310) of inputting syngas, output from the co-electrolysis step, into an isothermal methanation reactor by means of a syngas supply channel, and

- a step (315) of outputting synthetic natural gas;
- a step (320) of separating water, comprising:
 - a step (325) of inputting synthetic natural gas and
 - a step (330) of outputting dehydrated synthetic natural gas; and
- a step (335) of bypassing a portion of the dehydrated synthetic natural gas output from the water separation step to the syngas supply channel in order to provide a mixture of the syngas and the bypassed synthetic natural gas to the reactor.

17. Method (30) according to claim 16, which comprises a step (340) of separating carbon dioxide from the dehydrated synthetic natural gas output from the separation step (320).

18. Method (30) according to one of claims 16 or 17, which comprises a step of bypassing a portion of the hot methanation reaction products, to upstream of the methanation step (305).