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REVIEW **Open Access**

Methanation of CO_2 - storage of renewable energy in a gas distribution system

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Abstract

This article presents some crucial findings of the joint research project entitled «Storage of electric energy from renewable sources in the natural gas grid-water electrolysis and synthesis of gas components». The project was funded by BMBF and aimed at developing viable concepts for the storage of excess electrical energy from wind and solar power plants. The concept presented in this article suggests the conversion of CO_2-containing gases into methane in a pressurized reactor using hydrogen produced via electrolysis. The produced gas can be upgraded to synthetic natural gas (SNG) and fed into the well-developed German natural gas grid. This concept benefits from the high storage capacity of the German gas grid and does not require any extensions of the current gas or power grid. The reaction heat released by the exothermic methanation reaction leads to a temperature rise of the gas in the fixed bed catalyst of the reactor. The conversion of carbon dioxide is limited in accordance to the chemical equilibrium which depends strongly on temperature and pressure. For maximum carbon dioxide conversion, it is convenient to split the methanation into several stages adding cooling sections in between. This article focuses on the methanation process and its transfer onto an industrial scale evaluating the different plant capacities and feedstock mixtures used. The methanation takes place in a staged fixed bed reactor. This staged reactor concept is an in-house development based on know-how from the sulfuric acid production technology.

Keywords: Chemical storage; Fixed-bed staged reactor; Methanation

Review

Background

Huge efforts are currently being made to replace the conventional energy sources such as nuclear power or fossil fuels by renewable energy sources such as wind or solar energy. However, most of the renewable energy sources cannot provide base load electric power due to their intermittent nature (e.g., wind energy). To overcome this problem, storage systems have to be integrated in the power grid.

There are various possibilities of storing this excess energy: A direct storage of the electrical energy can for instance be realized with supercapacitors and superconducting magnetic energy storage (SMES). By the use of pumped storage power plants, electric energy is converted to potential energy. Compressed air reservoirs or flywheel energy storage systems buffer electricity as mechanical energy, whereas batteries enable storage of electricity via chemical energy, which is however convertible in electricity via an electrochemical way. Furthermore, electrical energy can be converted into chemical energy by transferring it into fuels such as hydrogen, synthetic natural gas (SNG), or methanol.

A comparison of the described storage technologies with regard to their storage capacity and their characteristic charge/discharge times is shown in Figure 1 [1]. A crucial requirement for storage technologies in the context of the present article (storage of energy from renewable resources) is an elevated storage capacity combined with high charge/discharge periods. Only chemical secondary energy carriers such as hydrogen and carbon-based fuels (SNG) fulfill this requirement. Storage technologies such as flywheels and batteries, on the other hand, are strongly limited regarding their capacity and charge duration. Therefore, these technologies are only used for compensating short-term fluctuations by supplying electric energy over a time period of several minutes up to several hours.

Besides high capacity and charge/discharge cycles, the process efficiency is another important characteristic.

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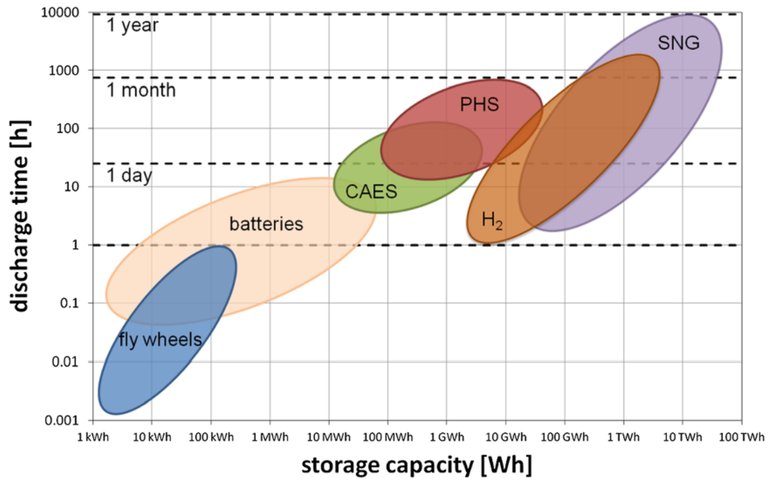


Figure 1 Charge/discharge period and storage capacity of different electricity storage systems. CAES, compressed air energy storage; PHS, pumped hydro storage; SNG, substitute natural gas.

Figure 2 illustrates the efficiency losses of described typical power to gas process.

The conversion of electrical energy into hydrogen causes efficiency losses of about 20% due to the internal cell resistance which will be realized as heat losses. The subsequent transformation of hydrogen in the methanation step reduces the efficiency down to 64%. For the whole process from renewable energy to the storage in the gas grid, an efficiency of approximately 63.6% can be reached [2]. At this stage, the highly developed natural gas grids in Germany can be used for the transport of excess energy. The German network for natural gas offers a huge storage capacity taking into account the high energy density of compressed methane. Moreover, the gas grid allows for a nearly time-independent storage. The natural gas grid is hence very well suited for balancing the transport bottlenecks of the power grid caused by excess energy production in the northern part of Germany and an elevated energy demand in southern Germany. In contrast to this, a mere expansion of the German power grid cannot efficiently reduce the bottlenecks: It has been shown in surveys that additional 3,600 km of high-voltage power lines are needed until 2020 to eliminate the transport bottlenecks in Germany. Up to now, only 200 km of new power lines have been built because of tedious planning and approval processes and because of strong opposition to high-voltage power lines and their pylons in the population [3,4].

Project description

The joint research project «Storage of electric energy from renewable sources in the natural gas grid-water electrolysis and synthesis of gas components» focused on a concept for the conversion of electrical energy from renewable sources into methane (power to gas). A schematic overview of the whole concept is shown in Figure 3. Comprehensive studies and investigations into this concept taking into account technical and economical aspects have been carried out by a consortium consisting of various scientific research institutes and industrial partners.

This article focuses on the synthesis step (see Figure 3), thus the conversion of carbon dioxide containing gases

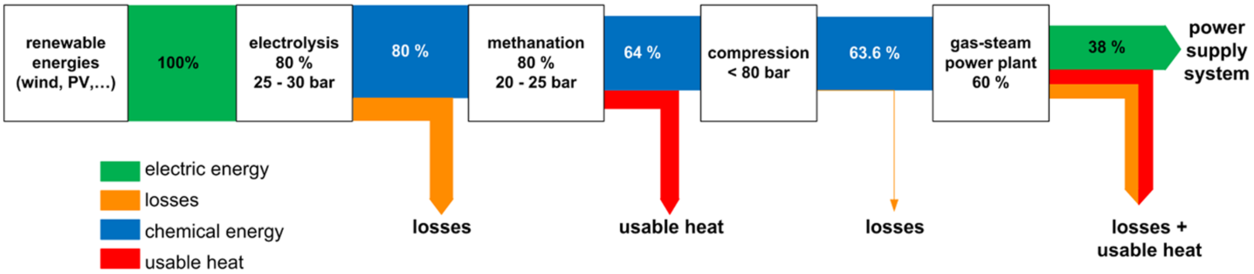


Figure 2 Sankey diagram for 'power to gas' storage technology.

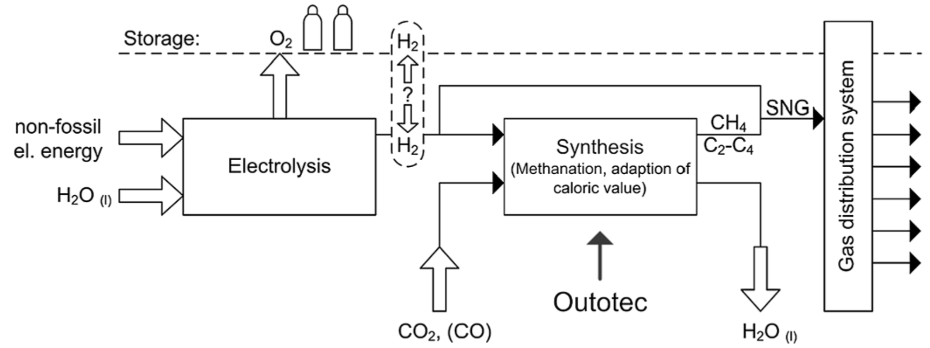


Figure 3 **Concept for the storage of renewable energy in a gas distribution system.**

to SNG. This reaction shall be carried out in a pressurized methanation reactor. Carbon dioxide is taken from biogenous or other sources. The produced gas can be upgraded to SNG to be fed into the natural gas grid.

The present article is basically split into two main parts: In the first part, the results of a detailed experimental investigation into the methanation process are presented. A lab-scale pilot plant was used to determine both the suited catalysts, which are primarily designed for CO methanation, and the optimum operation conditions for the methane synthesis step for CO_2 in a fixed bed adiabatic reactor. This data cannot be found in the literature.

The second part then addresses the scaling-up of the methanation process from the lab-scale to an industrial scale. Different plant concepts have been compared to each other taking into consideration technical and economical aspects. This part also includes rough cost estimations.

Methanation process

Fundamentals

The methanation reactions of carbon monoxide and carbon dioxide were discovered at the beginning of the 19th century [5]. Nowadays, these reactions are widely applied in ammonia synthesis plants to remove traces of carbon monoxide that acts as a catalyst poison for the ammonia synthesis catalyst [6]. Also refineries and hydrogen plants make use of the methanation reactions for the purification of hydrogen (removing the carbon monoxide) [7]. With today's increasing interest in producing SNG from (cheap) coal via gasification, the perception of the methanation process has changed completely: Originally considered as a pure gas cleaning technology, it is today viewed at as a major chemical synthesis process. Another reason for the increasing importance of the methanation process is the need for storing excess electrical energy from renewable sources.

Many applications that were developed to remove carbon monoxide converting to methane can be easily modified into processes where carbon dioxide and hydrogen are used as a feedstock, such as the Fischer-Tropsch synthesis, the methanol synthesis, or the methanation [8-10].

The methanation of carbon dioxide is an exothermic catalytic reaction and is typically operated at temperatures between 200°C and 550°C depending on the used catalyst:

$$\mathrm{CO_2} + 4\mathrm{H_2} \leftrightarrows \mathrm{CH_4} + 2\mathrm{H_2O}\; \Delta_r\mathrm{H} = -165\ \mathrm{kJ/mol} \tag{1}$$

A two-step reaction mechanism is assumed for this reaction. In the first step, carbon dioxide and hydrogen are converted to carbon monoxide and water via the water-gas shift reaction:

$$\mathrm{CO_2} + \mathrm{H_2} \leftrightarrows \mathrm{CO} + \mathrm{H_2O}\; \Delta_r\mathrm{H} = 41\ \mathrm{kJ/mol} \tag{2}$$

In the subsequent reaction, methane is formed from carbon monoxide and hydrogen:

$$\mathrm{CO} + 3\mathrm{H_2} \leftrightarrows \mathrm{CH_4} + \mathrm{H_2}O\; \Delta_r H = -206\ \mathrm{kJ/mol} \tag{3}$$

Besides methane and water, also higher saturated hydrocarbons can be found in the products [11]. The most stable C_{2+} hydrocarbon is ethane and it is formed according to

$$\mathrm{CO_2} + 3.5\mathrm{H_2} \leftrightarrows 0.5\mathrm{C_2H_6} + 2\mathrm{H_2}O\; \Delta_r H = -132\ \mathrm{kJ/mol} \tag{4}$$

Under certain process conditions, carbon precipitation can occur according to following reaction mechanism:

$$\mathrm{CO_2} + 2\mathrm{H_2} \leftrightarrows C + 2\mathrm{H_2}O\; \Delta_r H = -90\ \mathrm{kJ/mol} \tag{5}$$

A suitable quantity to estimate which of the above products can be expected at a certain process temperature is the Gibbs free energy ΔG. Figure 4 summarizes the development of the Gibbs enthalpy with temperature for all reactions introduced above. The lines in the diagram have been calculated using the software tool HSC Chemistry.

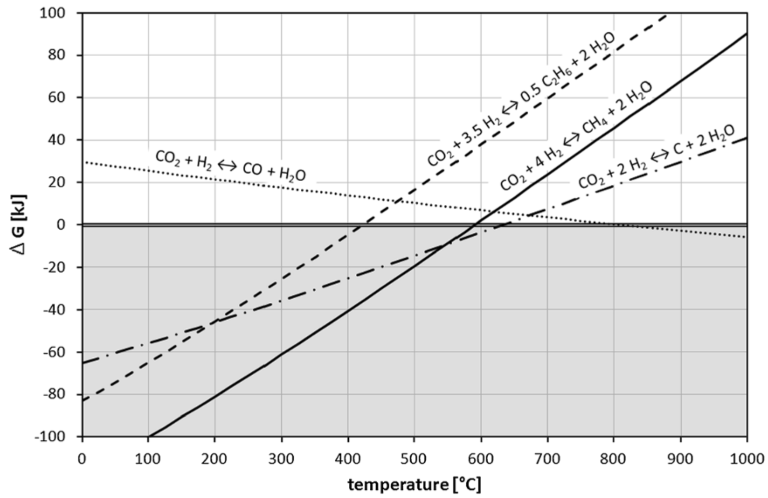


Figure 4 **Gibbs free energy as a function of temperature.**

A reaction is in equilibrium, if $\Delta G = 0$. For $\Delta G < 0$ (gray area in the diagram), the corresponding reaction is favored and the equilibrium is shifted towards the products. If $\Delta G > 0$, the equilibrium is shifted towards the reactants. It can be seen that methane formation from carbon dioxide and hydrogen is favored up to a maximum temperature of about 600°C. Carbon monoxide formation from carbon dioxide, on the other hand, is favored at temperatures above 800°C. Thus, the process should be run with multiple stages to keep the temperature and consequently the concentration of carbon monoxide low (methanation reaction is exothermic). As the formation of ethane is not favored at temperatures above 400°C, low ethane selectivity is expected at elevated temperatures.

Apart from the discussed temperature influence, also the pressure dependence of the methanation reaction has to be taken into account. Figure 5 visualizes the conversion of carbon dioxide at an equilibrium affected by the methanation reaction (Equation 1) as a function of temperature and pressure.

A glance at Figure 5 clearly shows that the conversion of carbon dioxide increases with increasing pressure and decreasing temperature. At an atmospheric pressure of 1 bar and a reaction temperature of 450°C for instance, a carbon dioxide conversion of 78% could be achieved. However, the methane synthesis process presented here requires higher carbon dioxide conversions. With a simple one-stage process, elevated conversions can only be achieved at lower temperatures or elevated pressures. By

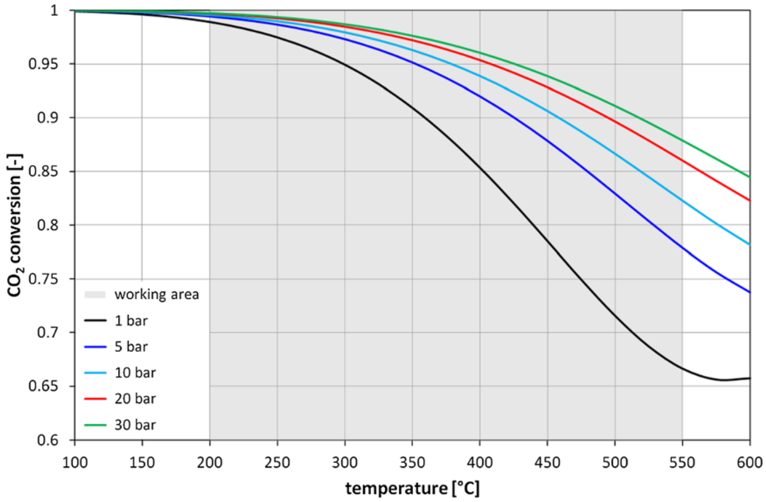


Figure 5 **CO_2 conversion as a function of temperature and pressure.** CO2/H2 = 1/4.

increasing the pressure to 20 barg and keeping the temperature at 450°C, the carbon dioxide conversion reaches approximately 93%. A further increase of the operating pressure does not significantly increase the methane yield.

Apart from these purely thermodynamic considerations, the choice of catalysts has a significant influence on the methanation reaction. The state-of-the-art catalyst is based on nickel because of the high activity and the comparatively low price of nickel.

The nickel catalyst, however, has to meet some important conditions: The material must be able to withstand fast temperature changes between 50°C and 100°C occurring within a few seconds and caused by changes of the operating point [12].

Operating temperatures below 200°C are not allowed in the presence of a nickel-based catalyst because of the potential formation of highly toxic nickel carbonyl from carbon monoxide. The operating temperature should, on the other hand, never exceed 550°C to avoid deactivation of the catalyst by sintering or carbon formation [12]. For these reasons, the range of possible temperatures in the methanation reactor is clearly defined. Figure 5 visualizes the catalyst's operating temperature range by a gray shaded box. To avoid the catalyst's degradation by catalyst poisons, such as sulfur or siloxane, a gas cleaning strategy upstream the methanation reactor is needed [13].

Methanation reactor design

Due to the highly exothermic nature of the methanation reaction, the design of the reactor is crucial to be able to have thermal control over the system. There are basically two state-of-the-art reactor types that can be used for this process: two-phase fixed bed reactors and fluidized bed reactors. Whatever reactor design is chosen, the generated heat of the methanation reaction has to be continuously removed from the reactor. For the methanation of carbon dioxide (reaction Equation 1), an increase of the methane's molar gas fraction of about 1% in the product gas induces a temperature rise of about 60 K.

An effective way to reduce temperatures in the reactor is the reduction of the reactive feed via a controlled dilution of the reactor inlet gas stream. This can be carried out by cooling down and recirculating a portion of the reactor's outlet gas stream. Cooling down the product gas, however, causes undesired energy losses.

An alternative solution is the isothermal operation of the reactor. In this case, a cooled reactor is needed transferring the reaction heat from the reaction zone to a cooling medium [12]. However, owing to the strong exothermic nature of the methanation reaction and the limited radial and axial heat transfer in a fixed bed reactor, it is difficult to operate a single fixed bed reactor under isothermal conditions. For a good control of the reaction temperature in a fixed bed reactor, at least two adiabatic reactors have to be connected in series. Temperature control can be realized by recirculation of the reactor outlet gas streams (as discussed above) and by intermediate gas cooling steps [12,14,15].

As an alternative to the fixed bed reactors, also fluidized bed reactors were considered in this article. In these reactors, the methanation reaction takes place within a fluidized bed of catalyst particles. Due to the very good mixing of gas and solid catalyst particles in the fluidized bed, high mass and heat transfer and almost isothermal conditions can be achieved. A further advantage of the fluidized bed reactors is the very good process control. However, abrasion and entrainment of catalyst particles in the gas flow are challenging issues, if this reactor type is chosen [16,17].

Table 1 summarizes already realized reactor concepts for the methanation process along with some operational data [2,15,18,19]. All presented processes used coal or naphta as a feedstock. Major developments in the field of SNG production from coal or naphtha date back to a time between the sixties and eighties.

Processes using fixed bed reactors were all realized with at least two stages. The processes (a), (b), (d), and (g) use a partial product gas recirculation with intermediate cooling steps for a better temperature control inside the reactors. The process (i) is composed of a first, isothermal fixed bed reactor with an indirect heat exchanger and a second adiabatic fixed bed reactor aimed at increasing the total methane yield. Process (c) is a so-called «one through» process with between four and six fixed bed reactors in series. Gas recirculation is not necessary, because the cold feed gas can be split and fed to the first four reactor stages at different ratios. A high-temperature methanation process consisting of three adiabatic reactors in series and gas cooling in between was developed by ICI (h).

The US Bureau of Mines developed two different fluidized bed reactors which are equipped with different gas feeding systems (k): The first reactor of an inner diameter of 19 mm had only one gas inlet. The second reactor of an inner diameter of 25.4 mm contained three gas inlets located at the bottom. The fluidized bed methanation reactors of (j), on the other hand, contained two feed inlets and two in-tube heat exchanger bundles. The methanation reactor of (j) had a diameter of 0.4 m and was operated for several hundred hours between 1977 and 1981. In 1982, a pre-commercial reactor of a diameter of 1 m was built and commissioned. Thereby, the process concept could be demonstrated on an industrial scale with a production rate of 2,000 m^3/h of synthetic natural gas [2,15,18,19].

Table 1 Already developed processes for fixed bed and fluidized methanation

Process number	Process/company	Reactor type	Process stages	Operation range		Feed
				p (bar)	*T* (°C)	
(a)	TREMP/Haldor Topsøe	Fixed bed	3	30	300…700	Coal, petrol coke, biomass
(b)	Hicom/British Gas Corp.	Fixed bed	4	25…70	230…640	Coal
(c)	RMP/Ralph M. Parson Co.	Fixed bed	4…6	1…70	315…780	Coal, heavy fuel
(d)	SuperMeth, ConoMeth/Conoco	Fixed bed	4/4	Approximately 80	n. s.	Coal
(e)	CRG/British Gas Corp.	Fixed bed	2	Approximately 25	300	Naphtha (refinery residue)
(f)	Hygas/Institute of Gas Technology	Fixed bed	2	70	280…480	Coal
(g)	Lurgi, Sasol/Lurgi GmbH	Fixed bed	2	18	Approximately 450	Coal
(h)	ICI, Koppers/Imperial Chemical Industries	Fixed bed	3		400…700	Coal
(i)	Linde/Linde AG	Fixed bed	2	n. s.	n. s.	Coal
(j)	Bi-Gas/Bituminous Coal Res. Inc	Fluidized bed	1	86	n. s.	Coal
(k)	Bureau of Mines/US department of the Interior	Fluidized bed		20	200…400	
(l)	Comflux/Thysengas GmbH	Fluidized bed	1	20…60	400…500	Coal (biomass)

Technological as well as economical challenges did not allow for a wide-spread commercialization of the above described reactor concepts. Worldwide, only one commercial methanation plant has been built so far. It was commissioned in 1984 in North Dakota (United States) by Lurgi GmbH (g). Originally, the plant was designed for a synthetic natural gas production of 3.54 Mio m^3/day. A continuous process optimization during the nineties finally increased the production to 4.81 Mio m^3/day. The plant is still in operation [20-22].

Other concepts, such as catalytic tube wall reactors, adiabatic parallel-plate or hybrid reactors were brought to commercialization [15].

Recent research activities

Some countries' growing desire for independence from natural gas imports along with the growing prices for natural gas have strongly revived activities in the field of synthetic natural gas production from coal and biomass. Especially in the United States and China, huge efforts have been made to increase SNG production. For China, the production of SNG is expected to reach around 20 billion m^3/a (at 0°C and 1 atm) until 2015 [15,19].

In the United States, some new methanation process concepts, such as the hydromethanation process [23] and alternative fluidized bed reactors or concepts without catalysts have been developed over the last years [15,18].

The development history of SNG synthesis processes based on biomass is much shorter than the respective history of SNG production based on coal. Due to the increasing importance of a sustainable use of natural resources, synthetic natural gas production via biomass with its carbon-neutral character is a very promising approach. However, if biomass is chosen as a feedstock for synthetic natural gas production, new challenges such as strongly varying chemical feed compositions and feed gas impurities (e.g., organic sulfur compounds) have to be overcome. Different reactor concepts (e.g., multitubular reactors) for the methanation of biomass are currently being developed in Europe [16,18,19].

The present and future need for the storage of renewable energy from wind and solar power plants opens up even new markets for innovative methanation process designs. Some current research activities in this field include liquid-phase methanation with novel cooling agents [24], biological methanation [25], and innovative reactor concepts using so-called comb catalysts [2].

Experimental work

The first part contains the results of a comprehensive experimental study of the methanation process in a lab-scale pilot plant aimed at determining the optimum operation conditions and finding appropriate commercial catalysts for the carbon dioxide methanation.

The methanation test plant was designed and commissioned to investigate the catalytic methanation of carbon dioxide and hydrogen. The process flow diagram of the plant is shown in Figure 6.

A mixture of different gases was fed to the evaporator to add water vapor to the gas mixture. Downstream, the water containing gas was fed to a heated fixed bed reactor. Heating as well as proper insulation of the reactor was necessary to minimize heat losses and to achieve quasi-adiabatic process conditions. The reactor outlet gas was cooled to condense the water contained in the off-gas. A pressure valve was installed in the product gas line to control the pressure in the reactor. The composition of the product gas was analyzed after leaving the

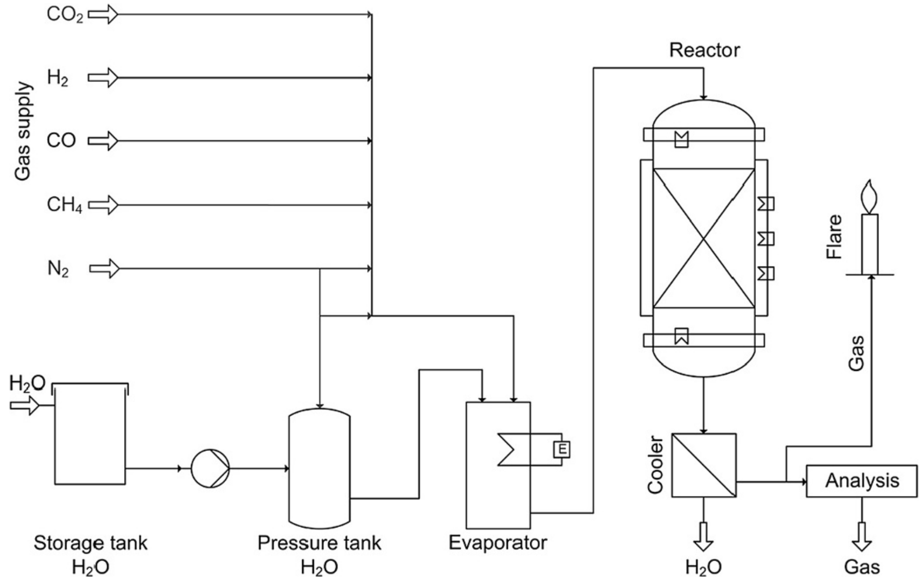


Figure 6 **Process scheme of the methanation test plant.**

reactor: For this purpose, a small portion of the off-gas was sent through a series of gas analyzers continuously measuring the concentrations of methane (CH_4), hydrogen (H_2), carbon dioxide (CO_2), and carbon monoxide (CO). The major part of the off-gas was directly burnt by a flare.

A series of experiments was carried out to evaluate the performance of different catalysts varying the inlet and outlet gas temperatures as well as the catalyst space velocities (NGHSV).The pressure was kept at 20 barg for all experiments.

A cross-sectional view of the fixed bed reactor is shown in Figure 7.

The catalyst layer is placed between two layers of inert material to achieve a uniform gas distribution. Three heating elements are placed at the outer walls of the reactor to ensure an individual temperature control. A multipoint temperature sensor is applied in the center of the reactor bed with the highest measurement point density being within the region of the catalyst layer.

In the experiments, the gas temperature after the catalyst layer (T_{128} in Figure 7) is controlled by adjusting the methane content in the reactor inlet gas stream. The following quantities were fixed for all experiments: the height of the catalyst layer, the molar ratio between hydrogen and carbon dioxide (was kept stoichiometric at $H_2/CO_2 = 4$), and the water vapor content of the in-gas (30 vol.% to prevent carbonizing effects).

In Figure 8, three temperature profiles along the reactor for different temperatures of the catalyst are shown. The electric power of the three distinct heating zones was chosen in a way to achieve approximately adiabatic conditions within the packed bed of the catalyst. The key parameter to be controlled, however, was the gas temperature at the lower end of the packed catalyst bed. The control of this temperature was done by adjusting the methane content in the in-gas. In an industrial process, this adjustment of the methane content at the reactor's inlet would be best realized by a partial recirculation of the (methane-rich) product gas.

The temperature at the inlet of the reactor was kept at approximately 250°C for all experiments.

The temperature profile clearly shows that the reaction was already completed in the first centimeters of the catalyst bed, at the point where the maximum temperature was reached.

A typical evolution of the product gas composition with time during a test run is shown in Figure 9 (solid line). Additionally, also the evolution of the temperature at the lower end of the packed catalyst bed is plotted in the diagram (dashed line).

To reach steady state conditions, each experiment was run for about 24 h. Before the start of each experiment, the catalyst was first heated up to 250°C, while the reactor was purged with nitrogen. The experiment was started by changing the gas mixture to the desired composition. Due to the thermal inertia of the catalyst bed, some time is needed for the catalyst to reach its final temperature.

Figure 10 shows the experimentally determined carbon dioxide conversion of different test runs as a function of the adjusted temperature after the catalyst layer (T_{128} in Figure 7). Experiments were performed for different inlet gas compositions and gas space velocities. The solid lines

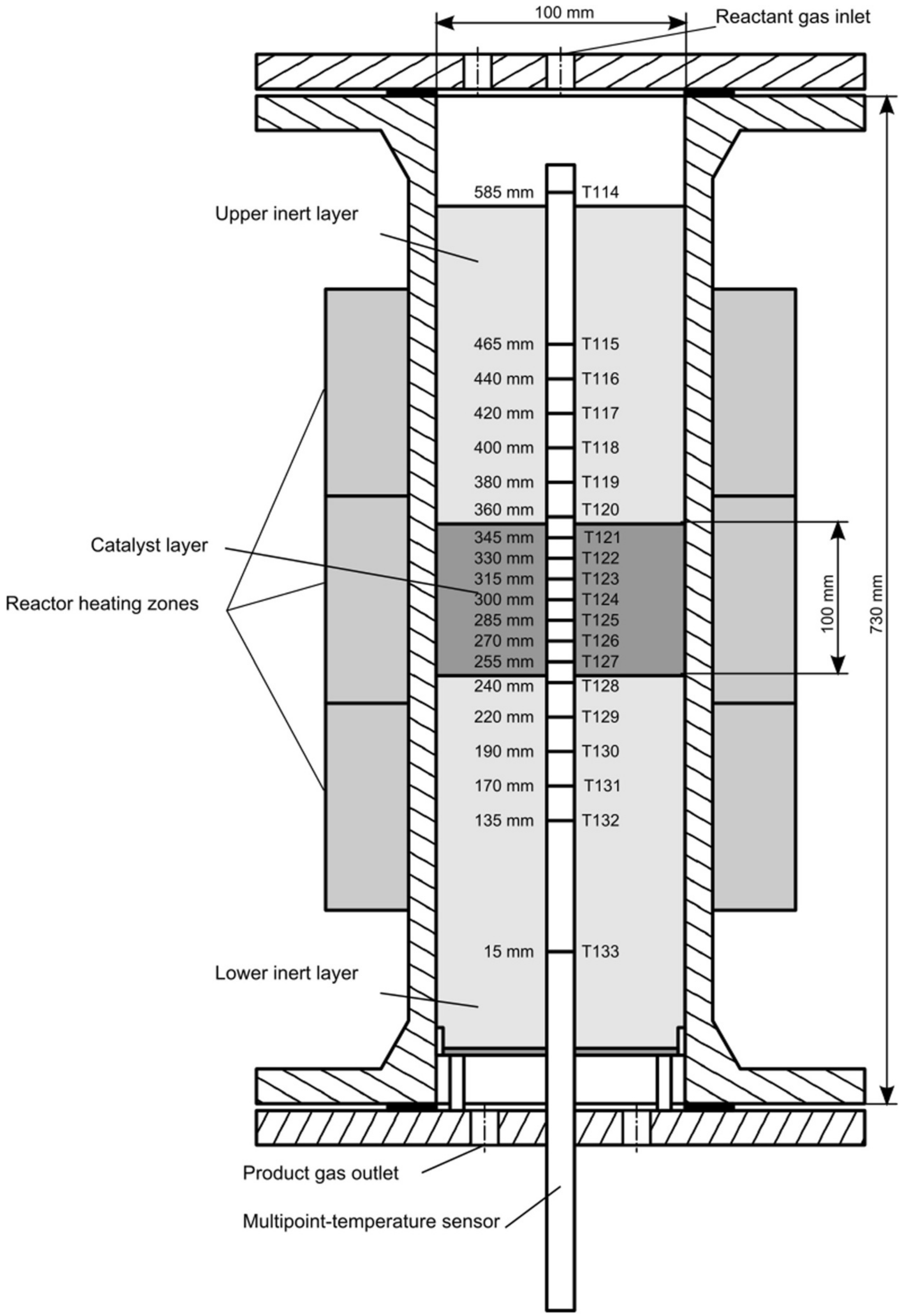


Figure 7 Cross section of the methanation reactor.

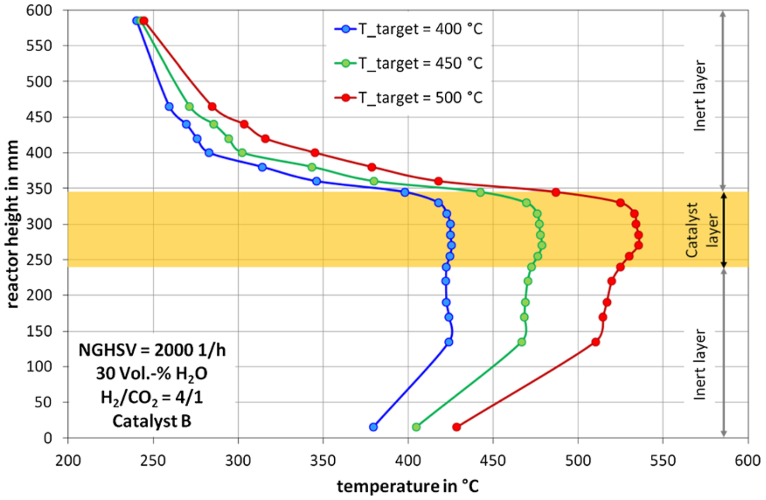


Figure 8 **Temperature profiles over the height of the reactor for different gas outlet temperatures.**

in Figure 10 represent calculated values of carbon monoxide conversions at chemical equilibrium for the corresponding inlet gas compositions.

Higher methane contents in the feed gas generally lead to a lower carbon dioxide conversion, if the temperature is kept constant. However, as the catalyst temperature in the experiments decreased with increasing methane feed gas concentration, higher carbon dioxide conversions were reached at higher methane concentrations. An ideal reactor stage would show carbon dioxide conversions lying on the solid curves in the diagram above. The experimental values are slightly below these equilibrium curves. However, the experimental data follows the trend of the equilibrium curve very well. The results indicate that the experimental conversion is close to equilibrium for the investigated range of gas space velocities and that the presented catalyst is suitable for the carbon dioxide methanation. Different tested catalysts show similar results in terms of temperature profiles and carbon dioxide conversion [26,27].

In addition to the online gas analytics, the reactor outlet gas was also analyzed by a gas chromatograph (GC). Unlike the online gas analysis, the GC also analyzed the concentrations of higher hydrocarbons such as ethane. The results of both measurement methods are compared in Table 2.

The comparison of both analytic methods indicates good agreement. Furthermore, the measured gas compositions at the reactor outlet also reflect the temperature dependence of the Gibbs free energies for the involved

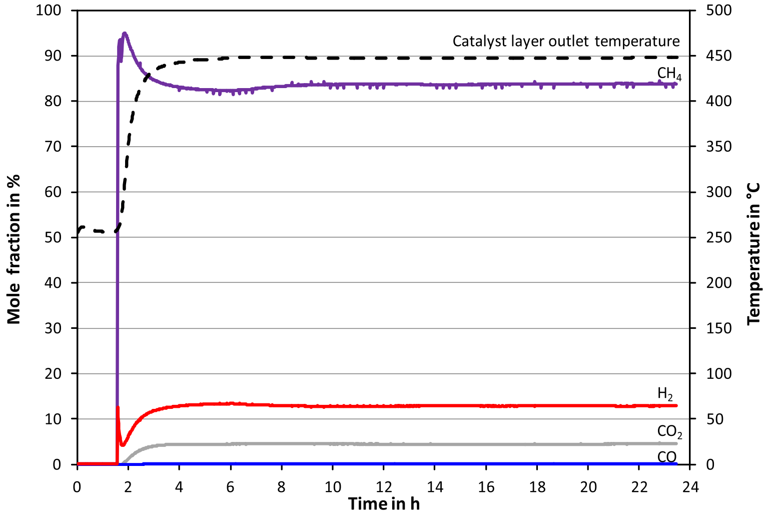
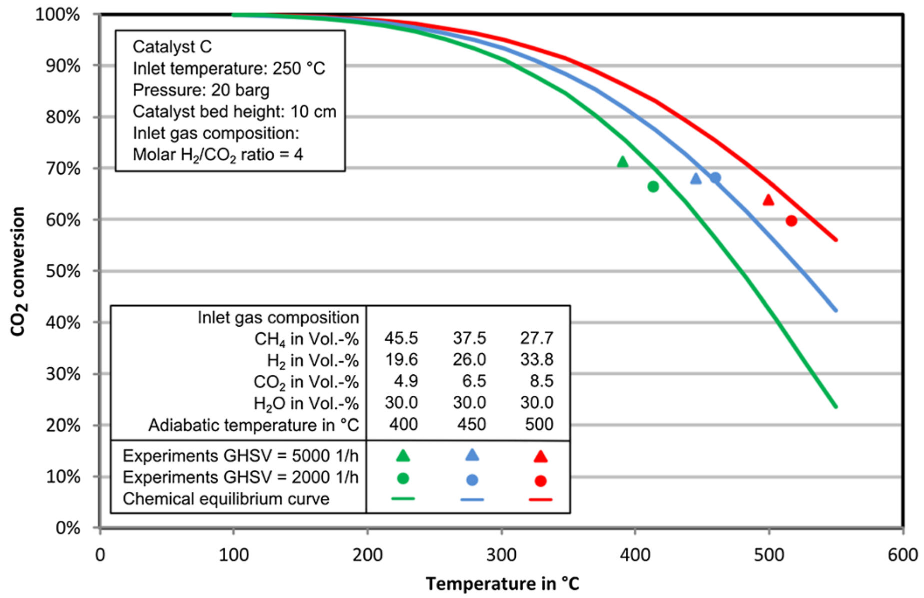


Figure 9 **Time-dependent product gas composition during the test run.**



Inlet gas composition			
CH_4 in Vol.-%	45.5	37.5	27.7
H_2 in Vol.-%	19.6	26.0	33.8
CO_2 in Vol.-%	4.9	6.5	8.5
H_2O in Vol.-%	30.0	30.0	30.0
Adiabatic temperature in °C	400	450	500
Experiments GHSV = 5000 1/h	▲	▲	▲
Experiments GHSV = 2000 1/h	●	●	●
Chemical equilibrium curve	—	—	—

Figure 10 Experimentally determined carbon dioxide conversion of different test runs. CO2 conversion in temperature-dependent experiments after the packed catalyst bed for different gas space velocities and inlet gas compositions. The solid lines represent the calculated equilibrium curves for the respective compositions.

reactions (see Figure 4): The formation of carbon monoxide (water-gas shift reaction, Equation 2) and ethane (Equation 4) should both be impeded ($\Delta G > 0$) within the investigated temperature range. These theoretical considerations were confirmed in the experiments by the low fractions of these components found in the off-gas. Analysis of the product gas stream by gas chromatography showed no formation of higher hydrocarbons such as heptanes or hexanes for the investigated catalysts and operation conditions.

Above all experimental data obtained in this study were compared to theoretical values at chemical equilibrium due to the lack of literature data in the field of carbon dioxide methanation in fixed bed adiabatic reactors.

Theoretical work

In this second part, the scaling-up of a methanation process from a lab-scale to an industrial scale is discussed.

Table 2 Comparison of GC and online analytics for the off-gas composition

Component	Analytic method	
	Online analytic (vol.%)	GC analytic (vol.%)
Methane (CH4)	82.8	81.3
Hydrogen (H_2)	12.87	14.64
Carbon dioxide (CO_2)	4.31	4.01
Carbon monoxide (CO)	0.02	0.03
Ethane (C_2H_6)	-	0.02

The work done for this part included considerations on process design and process calculations based on AspenPlus simulations as well as cost estimations for the determination of suitable plant sizes.

The industrial-scale methanation plant shall consist of a staged fixed bed catalyst reactor similar to the reactor design used for the sulfur dioxide (SO_2) oxidation process of sulfuric acid plants. This prerequisite allows for the use of existing expertise and know-how of our company in the field of sulfuric acid plants. This approach generates beneficial synergies, because both processes (methanation and sulfur dioxide oxidation) are characterized by strongly exothermic chemical reactions and are based on gaseous reactants and products.

Two different plant capacities with methane productions of 1,000 m^3/h and 10,000°m^3/h methane were considered. Hydrogen for the feed gas is produced by water electrolysis. For the carbon dioxide feed, on the other hand, two different concepts were evaluated depending on plant capacity: For the 10,000 m^3/h plant, pure carbon dioxide from either a power plant or an ammonium synthesis plant can be used. The carbon dioxide for the smaller methanation unit (1,000 m^3/h) is best taken from a biogenous source such as a biogas plant offering a mixture of approximately 50 vol.% carbon dioxide and 50 vol.% methane. Minor components and impurities such as organic sulfur were neglected in the process calculations. To prevent carbon formation on the catalyst's surface, 30 vol.% water vapor has to be added to the feed gas [26-28]. The requested product gas purity for a gas to be fed into the German natural gas grid is defined by [29-31] and summarized in Table 3.

For both defined plant capacities, flow-sheet calculations were carried out using the simulation tool AspenPlus. These calculations served as basis for different plant concepts. In what follows, two different plant concepts for the 10,000 m^3/h plant are presented in more detail.

Plant concept I

Figure 11 illustrates the process scheme of the first plant concept: To achieve high yields of methane in the product gas, the methanation reactor is divided into four serial reaction stages interrupted by intermediate gas coolers. The first step of the reaction takes place in the single fixed bed reactor (C1). The subsequent three stages are included in one single reactor (C2) being thus called a stage reactor.

Hydrogen and water vapor are supplied at a pressure level of 20 barg. Water vapor is supplied only for starting up the plant. During steady-state operation, the water produced in the reactors C1 and C2 is partially separated in the separators B1 and B2 and recirculated to be fed again to C1. As a result of this, the reaction temperatures in C1 and C2 are reduced. The amount of water in the feed has to be sufficient to prevent carbon formation on the catalyst surface. The carbon dioxide has to be pressurized to the operating pressure level by a four-stage compressor prior to be fed to the reactor (C1). The water in the off-gas of C1 is partially removed in the first water separator B1 after having passed the cooler W3. The amount of water, which has to be removed from the gas stream, is defined by the desired gas outlet temperature after the first stage of the reactor C2. A temperature of 550°C should never be exceeded. Before being fed to the reactor C2, the gas is heated up to 220°C in the heat exchanger W5. Reactor C2 contains two intermediate heat exchangers cooling the gas down to 220°C before entering the next reactor stage. Further gas drying after C2 is realized in a flash (B2) and a molecular sieve (B3).

The required recirculation stream from the outlet of the reactor (C1) back to its inlet increases the dimensions of the reactor, and hence, also the investment costs significantly. In order to keep the reaction temperature below 550°C, about 70% of the reactor outlet gas must be recirculated.

Table 3 Requested product gas purity

Component	Fraction
Methane (CH_4)	>96 vol.%
Hydrogen (H_2)	<2 vol.%
Carbon dioxide (CO_2)	<3 vol.%
Carbon monoxide (CO)	<30 ppm
Water (H_2O)	Dew point < −8°C (70 bar)

The efficiency of the process can be increased by an internal exchange of thermal energy between different heat exchangers. The excess heat generated in an exothermic reaction can for instance be used to heat up a medium somewhere else in the process. The method to detect the energy integration potential of a process is called the pinch analysis. The method not only considers the amount of thermal energy that is exchanged by heating and cooling in a process but also the corresponding temperature level of all heat sources and sinks. The pinch method is able to calculate the amount of thermal energy that can be interchanged between different internal process streams (=integrated heat) without the need of providing external heating or cooling media.

The methanation process of Figure 11 is characterized by a total generated process heat of 30 MW due to the exothermic reactions involved. The energy integration analysis by the pinch method shows that a portion of 11 MW can be used for heating up the feed of the reactors and for producing electricity for the plant operation via a steam turbine. Another 12 MW are available for other purposes, such as steam generation or district heating. The rest of 7 MW must be removed by the use of cooling water due to the low temperature level of this energy.

Plant concept II

The second plant concept is basically an improvement of plant concept I. Technical and economical aspects were taken into consideration to simplify the process and to decrease costs. The result of these optimizations is shown in Figure 12.

The obvious difference between plant concept I and plant concept II is the merging of the two originally individual methanation reactors C1 and C2 to one single reactor (C1*). Six stages are required to reach the requested product gas specification. The process of concept I was able to reach the requested specification with only four reaction stages. Furthermore, the new plant concept is also characterized by a modified carbon dioxide feeding concept: Carbon dioxide is now fed to the process at four different locations marked with numbered squares in Figure 12. The four-stage feeding system S1 distributes the carbon dioxide in defined fractions to keep the maximum temperature after each reactor stage below 550°C. The new configuration does not require any recirculation gas stream for the first reactor stage any more. In addition to this, also the compressor V2 used in concept I can be omitted. However, in case 2, steam has to be provided to the process also during steady-state operation.

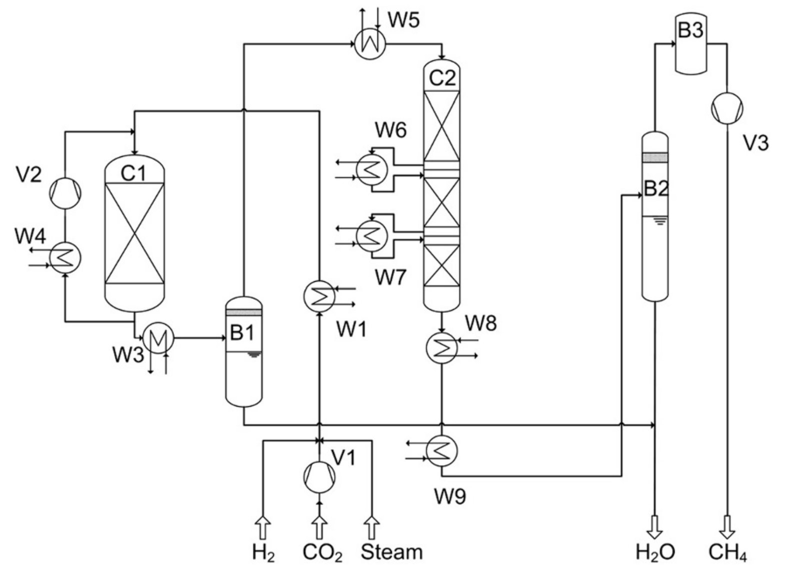


Figure 11 Process scheme of plant concept I.

The coolers W2 and W4 to W8 between the reaction stages have to remove 46 MW of thermal energy. For the water vapor production as well as for heating up the feed gas to a temperature of 220°C in the heat exchangers W1 and W3, only approximately 15 MW of the available 46 MW are needed. Hence, after energy integration, there are still about 31 MW left for further use. The portion of this energy that is at a high temperature level can be used for electricity generation via steam turbines. This allows for running the plant without any additional energy supply. The removed process heat at medium temperatures between 90°C and 240°C can be used for district heating. The remaining 9 MW of low-temperature thermal energy (lower than 90°C) must be removed by cooling water.

Conclusions

Some results of the joint research project entitled «Storage of electric energy from renewable sources in the natural gas grid-water electrolysis and synthesis of gas components» are presented in this article. The article focuses on the methanation process as one of the crucial steps in the conversion of electric energy from renewable sources to synthetic natural gas (power to gas). In a first section of the article, results of experimental investigations on a lab-scale

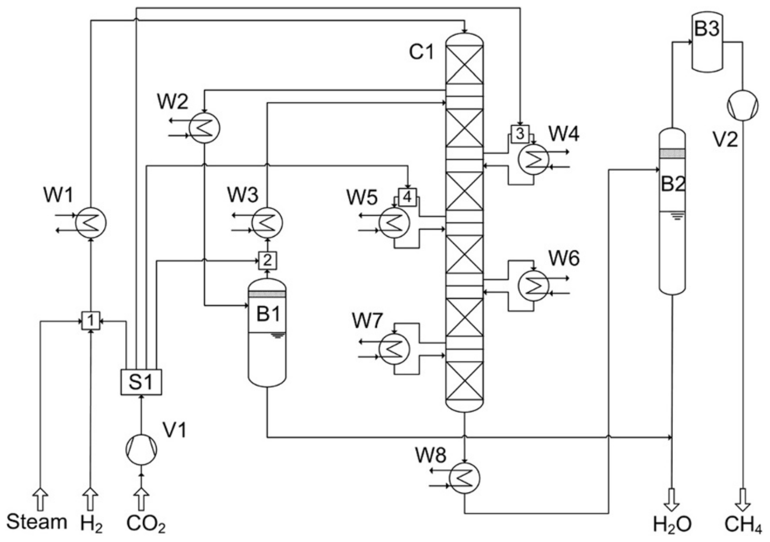


Figure 12 Process scheme of plant concept II.

methanation pilot plant are presented. The second part then addresses different plant concepts for the scaling-up of the investigated methanation process to an industrial scale.

A lab-scale pilot plant was designed and commissioned to investigate commercial fixed bed catalysts for the carbon monoxide methanation. The experiments are carried out under different operation conditions varying the gas hourly space velocity (GHSV), the reactor inlet gas temperature, and the reaction temperature. The experimental results show that all catalysts tested in this study can be applied in the carbon dioxide methanation. The experiments showed carbon dioxide conversions being slightly below equilibrium but following the expected trends. Lower reaction temperatures in the packed catalyst bed led to higher carbon dioxide conversion rates. A maximum carbon dioxide conversion of 70% could be reached within one single reaction stage.

Based on the knowledge from these experiments, two different concepts for methanation plants on an industrial scale were developed. The product gas quality was given as a specification. The first plant concept consists of two reactors. The first reactor requires a recirculation of a portion of the reactor outlet gas for the control of the reactor temperature. The second reactor includes three subsequent reaction stages. The first reactor has large dimensions due to the recirculation of product gas proposed for this reactor. This leads to high costs also due to the required amount of catalyst for this reactor.

The second plant concept only proposes one single methanation reactor consisting however of six reaction stages. The dimensions of the first reaction stage can be reduced, because no recirculation of product gas is necessary any more.

If energy integration is strictly applied, the energy demand of both proposed processes can be completely covered by the heat generated in the process. The excess thermal energy can be used in various ways (e.g., electricity generation via steam turbine, district heating, etc.)

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

The article was jointly prepared by all authors. All authors read and approved the final manuscript.

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