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Review

Renewable Power-to-Gas: A technological and economic review

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ABSTRACT

The Power-to-Gas (PtG) process chain could play a significant role in the future energy system. Renewable electric energy can be transformed into storable methane via electrolysis and subsequent methanation.

This article compares the available electrolysis and methanation technologies with respect to the stringent requirements of the PtG chain such as low CAPEX, high efficiency, and high flexibility.

Three water electrolysis technologies are considered: alkaline electrolysis, PEM electrolysis, and solid oxide electrolysis. Alkaline electrolysis is currently the cheapest technology; however, in the future PEM electrolysis could be better suited for the PtG process chain. Solid oxide electrolysis could also be an option in future, especially if heat sources are available.

Several different reactor concepts can be used for the methanation reaction. For catalytic methanation, typically fixed-bed reactors are used; however, novel reactor concepts such as three-phase methanation and micro reactors are currently under development. Another approach is the biochemical conversion. The bioprocess takes place in aqueous solutions and close to ambient temperatures.

Finally, the whole process chain is discussed. Critical aspects of the PtG process are the availability of CO_2 sources, the dynamic behaviour of the individual process steps, and especially the economics as well as the efficiency.

1. Introduction

In its Renewable Energy Roadmap 21, the European Commission has proposed a target of 20% renewable energy in the EU's overall energy mix by 2020 [1]. Thereby, wind and solar energy play an important role. In 2013, wind power had already comprised a high share of the electricity supply. In Denmark (34%) and Spain (21%), wind energy has become the largest source of electricity; also Portugal (>20%), Ireland (>16%), and Germany (9%) have reached high shares [2]. The total world installed wind capacity increased from 17,400 MW in 2000 to 318,105 MW in 2013 [3]. However, wind and solar energy are fluctuating and intermittent and have to be balanced for electric grid stability purposes. Consequently, long term and large capacity electricity storage is required, as well as reserve production capacity. In Germany, e.g., the residual power capacity is estimated to be 30–60 GW.

The Power-to-Gas (PtG) technology might contribute to tackling this issue. The PtG process links the power grid with the gas grid by converting surplus power into a grid compatible gas via a two-step process: H_2 production by water electrolysis and H_2 conversion with an external CO or CO_2 source to CH_4 via methanation (Fig. 1). The resulting CH_4, known as substitute natural gas (SNG), can be injected into the existing gas distribution grid or gas storages, used as CNG motor fuel, or it can easily be utilised in all other well-established natural gas facilities. The total world storage capacity of natural gas is > 3600 TWh [4] (total world power production from wind and solar power in 2012: 639 TWh [5]).

The importance of PtG for handling high shares of renewable energies is being discussed at length [6–10]. The scope of this review paper is to describe the technological and economic difficulties, thus the general necessity of PtG will not be the subject of this article. Due to the large number of papers on Power-to-Gas, this review focuses on Power-to-Methane. An alternative would be direct injection of H_2 into the gas grid. However, the amount of H_2 in the gas grid is limited by country specific standards and regulations to a maximum of 0–12 vol.% [11].

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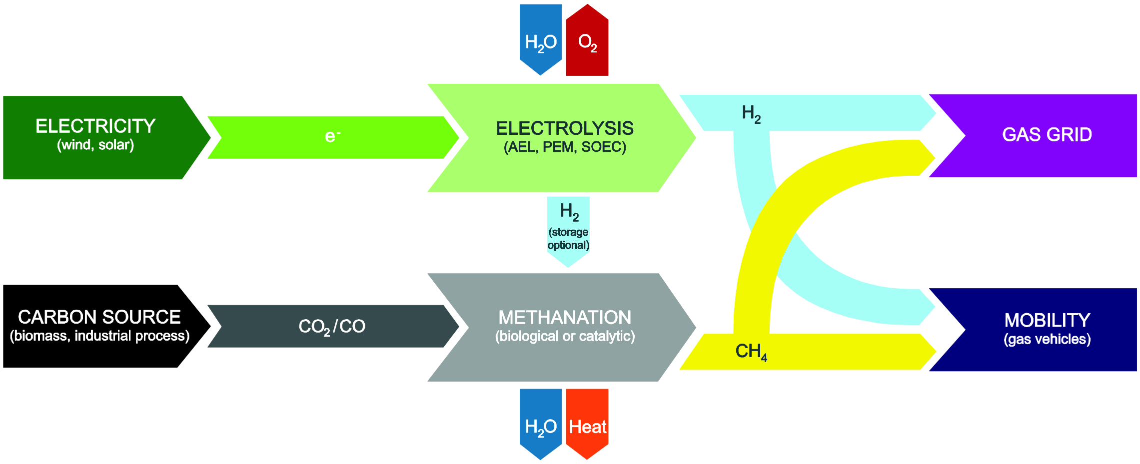

Fig. 1. Exemplary Power-to-Gas process chain.

The main drawbacks of Power-to-Gas are a relatively low efficiency and high costs. These aspects will be discussed in Section 5.

The Power-to-Gas process chain was first proposed in Japan in the 1980s–1990s [7]. Hashimoto et al. proposed a global CO_2 recycling using sea water and built a pilot plant in 2003 [8]. A broader interest in Power-to-Gas has begun to grow (especially in Europe) in recent years driven by the increasing share of wind and solar power [12–17]. In the meantime, there is a significant amount of Power-to-Gas research in different countries. Some examples are Switzerland, Denmark, France, Japan, and Germany where pilot plants are under construction or even in operation (see Sections 3.2 and 5.4).

An alternative to SNG is the production of liquid energy carriers such as methanol, dimethyl ether (DME), and Fischer-Tropsch products or the production of chemicals [18–21]. In the future, the photocatalytic conversion of CO_2 and H_2O to methane or other fuels could be an interesting alternative to the proposed PtG chain [22]. However, this technology is still in an early development stage.

2. Hydrogen supply

2.1. Fundamentals

Water electrolysis to yield H_2 and O_2 (Eq. (1)) is an electrochemical reaction which can be segmented into 2 steps. At the negatively charged cathode the reduction reaction takes place (Eq. (2)), while the oxidation reaction occurs at the positively charged anode (Eq. (3)). Depending on the technology, the charge carrier can be OH^-, H_3O^+, or O^{2-} (see Table 1).

$$H_2O(l) \rightarrow H_2(g) + ½O_2(g) \quad \Delta H_r^0 = +285.8\ \mathrm{kJ/mol} \qquad \text{Eq. 1}$$

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \qquad \text{Eq. 2}$$

$$O^{2-} \rightarrow ½O_2 + 2e^- \qquad \text{Eq. 3}$$

For calculating equilibria (Fig. 2), the Gibbs free energy of water electrolysis ΔG_r^0 is expressed by the equilibrium cell voltage (Eq. (4)), where n is the number of transferred electrons counted in moles and F is the Faraday constant, converting electric properties into thermodynamic and vice versa:

$$\Delta G_r^0 = nFE_V^0 \quad \Delta G_r^0 = +237.1\ \mathrm{kJ/mol} \qquad \text{Eq. 4}$$

As depicted in Fig. 2, temperature has a positive influence on the water electrolysis reaction, while pressure has a negative influence.

The most important parameters of the electrolysis technologies are efficiency, flexibility, and lifetime. The different technologies will be discussed in Section 2.2.

2.2. Water electrolysis

Excess electrical energy can be used to produce hydrogen via water electrolysis. H_2 can be converted into methane with a suitable carbon source or it can be directly injected into the gas grid or used for fuel cell vehicles. Water electrolysis is a well understood technology. Thereby, developments in fuel cell technology also helped to improve water electrolysis technologies. Three different electrolysis technologies are of interest for PtG process chains: alkaline electrolysis (AEL), polymer electrolyte membranes (PEM), and solid oxide electrolysis (SOEC). The key operational parameters of the three electrolysis technologies are summarized in Table 1.

2.2.1. Alkaline electrolysis (AEL)

Of the three types of electrolysis technologies considered for PtG plants, alkaline electrolysis is the most mature and well understood technology (commercially available for decades [23]). In AEL, an aqueous alkaline solution (KOH or NaOH) is used as the electrolyte. AEL works either atmospherically or under elevated pressure. According to Smolinka et al. [24], pressurized alkaline electrolysers have a lower efficiency and produce a lower purity product than atmospheric AEL. The foremost advantage of pressurized AEL compared to atmospheric AEL is that it produces compressed hydrogen (either for grid injection or further use) with less additional energy input [25]. This is a result of the fact that the reduction in electric efficiency of the electrolysis with increased pressure (see Fig. 2) is lower than the energy needed to compress the produced hydrogen.

According to manufacturers, AEL electrolysers can be operated between 20 and 100% of the design capacity, and overload operation up to 150% is possible. This operation window makes AEL a good choice for systems such as PtG which are coupled with a fluctuating and intermittent power supply. However, Gahleitner [26] reports problems with intermittent and fluctuating power sources. One problem is that it takes 30–60 min to restart the system following a shutdown [27]. Continuous operation of AEL systems is advised [27]. The biggest disadvantage of AEL is that the utilised electrolytes (alkaline solution, e. g. 20–30 % potassium hydroxide solution) are highly corrosive, thus necessitating high

Table 1
Summary of the key operational parameters of Alkaline, PEM, and Solid Oxide Electrolysis.

	Alkaline electrolysis	PEM electrolysis	Solid oxide electrolysis
State of development	Commercial [23]	Commercial [35,36]	Laboratory [30]
H_2 production in m^3/h (STP, per system)	<760 [34] ≈2.7 MW	Up to ≈ 450 [36] ≈1.6 MW	–
Electrolyte	Alkaline solution	Solid polymer membrane (Nafion)	ZrO_2 ceramic doped with Y_2O_3
Charge carrier	OH^-	H_3O^+/H^+	O^{2-}
Cell temperature in °C	40–90 [30]	20–100 [30]	800–1000 [39]
Cell voltage in V	1.8–2.4 [24]	1.8–2.2 [24]	0.91 [29]–1.3 [37]
System power consumption (current) in kWh/m^3 H_2 (H_S)[a]	4.5–7 [24] 4.7–5.4 [33] 5.4–8.2 [46]	4.5–7.5 [24] 5.2–7.1 [33] 4.9–5.2 [46]	–
System power consumption (future) in kWh/m^3 H_2 (H_S)	4.3–5.7 [24]	4.1–4.8 [24]	–
Cold start time	Minutes–hours [24,27,33]	Seconds–minutes [24,31,33]	–
Advantages	Available for large plant sizes, cost, lifetime [29,47]	No corrosive substances, high power densities, high pressure > 100 bar, dynamics [24,30,33,34]	High electrical efficiency, integration of waste heat possible [37,38,48]
Disadvantages	Low current density, maintenance costs (system is highly corrosive) [24,30,33,34]	Expensive, fast degradation [30–34]	Limited long term stability of the cells [29], not suited to fluctuating systems [24], expensive [29,37]
Transient operation	Possible, but leads to problems [26,27]; reduction up to 20% load possible; overload operation possible [33,34]	Better than AEL [26], dynamic adjustment possible, partial (down to 5%) and overload operation possible [24,27,31,33]	Not well suited [24]
Renovations/lifetime	Renovations stack: 8–12 a [24] Lifetime: up to 30 a [28]	Lifetime: 5 a [26], shorter lifetime than AEL [29]	–

[a] Further data from suppliers and demo plants are given in Refs. [26,29].

maintenance costs. A general overhaul of the system is necessary every 7–12 years [24]. According to [28], the expected lifetime for an alkaline electrolyser is currently about 30 years, which is high compared to the other considered electrolyser types. In recent years, AEL has been optimised, especially with respect to efficiency and total investment.

2.2.2. Polymer electrolyte membrane (PEM) electrolysis

Compared to AEL, PEM is a relatively new technology, with the first commercial PEM electrolyser available for purchase in 1978 [29]. The technology is based on solid polymer membranes [30]. According to [26], the main advantages of PEM include faster cold start, higher flexibility, and better coupling with dynamic and intermittent systems. Furthermore, the purity of the produced H_2 is very high [31]. The minimum load is reported to be 5% [24,27]. However, this technology is currently more expensive than AEL systems (due to the costs for the membrane and the use of a noble metal catalyst), and the limited life expectancy is also disadvantageous [30–34]. PEM electrolysers in the MW scale have recently become available (Proton Onsite and Siemens) [35,36].

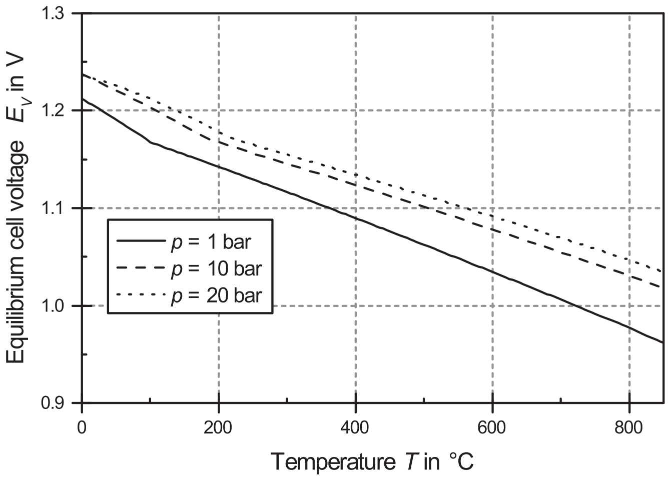

Fig. 2. Equilibrium cell voltage as function of temperature for different pressure levels.

2.2.3. Solid oxide electrolysis (SOEC)

Solid Oxide Electrolysis (also known as high temperature electrolysis) is the most recently developed electrolysis technology and is still at the laboratory stage. In SOEC, ZrO_2 doped with 8 mol% Y_2O_3 is used as the electrolyte, which at high temperatures is highly conductive for oxygen ions (charge carrier), and has good thermal and chemical stability [37,38]. The high temperature reduces the equilibrium cell voltage (see Section 2.1) and therefore the electricity demand [39]; however, the heat demand increases with increasing temperature. The low electricity demand is the most significant advantage of SOEC systems. Theoretically, electrical efficiencies above 100% could be achieved (endothermic mode) [38,39]. In particular, the combination with exothermal reactions in PtG and PtL process chains leads to a higher overall efficiency [34,40–44]. According to [45], the heat utilisation is not reasonable for PtG as electrical energy storage. The specific cell area and the investment per hydrogen unit produced increase with increasing heat integration. Due to the low capacity utilisation, electrical energy storage requires a low investment.

The biggest challenges for SOEC systems are the fast material degradation and the limited long term stability, both of which are due to high temperature operation [29]. Furthermore, the high temperature level means that the product stream from the electrolyser is a mixture of hydrogen and steam, and requires additional processing; thereby further increasing the capital costs. Moreover, SOEC systems are not stable against fluctuating and intermittent power sources [24,29].

2.2.4. Cost analysis

Currently, capital expenditures for AEL are predicted to be significantly lower than for PEM. Fig. 3 compares the specific investment for hydrogen production indicating the significant differences between the electrolysis technologies. According to [33,34,37,49], currently the investment for PEM systems is at least two times that of AEL systems. The investment for AEL is on the order of magnitude of 1000 €/kW (equivalent to 5060 €·h/(m^3 H_2) for 70% electrical efficiency), whereby the costs depend on the specific conditions (e.g. pressure and size) [28,33,49]. According to Siemens (reported in Ref. [33]), PEM electrolysis will be available for < 1000 €/kW already in 2018, whereas in Ref. [49] a PEM price of 1250 €/kW is expected for 2020.

For SOEC systems, limited information is available. Mougin et al. [37] estimated the price for manufacturing and selling a SOEC system which can produce 46.4 m^3/h (100 kg/day) of H_2. An annual production scale of 100 systems was used for the calculation. A selling price of approximately 11,200 € h/(m^3 H_2) was calculated and compared to selling prices of comparable AEL and PEM systems. According to them, estimated SOEC prices are comparable to the upper range of prices estimates for PEM systems. In Refs. [49], SOEC specific costs of 1000 €/kW are predicted for 2030 (equivalent to 3540 €·h/(m^3 H_2) for 100% electrical efficiency).

2.3. Hydrogen storage

Another challenge for PtG systems is the temporary storage of hydrogen necessitated by the fluctuating power supply and consequent intermittent operation of the electrolyser. For the hydrogen storage, the size and necessary peripheral equipment is highly variable and depends on the configuration and the operating parameters of the system [26].

Several probable methods exist for the hydrogen storage: compressed gas tanks, cryogenic compressed liquid hydrogen tanks, metal hydride storage, physical storage, and underground storage (e.g. salt caverns). Storage of hydrogen as a cryogenic liquid is a technical challenge as well as energetically inefficient [50]. The unstable pressure, continuous leakage of gas, and expensive insulation, make cryogenic liquid hydrogen storage a poor choice for PtG applications.

Another option for hydrogen storage is the physical storage of hydrogen in underground caverns. Although this option is the cheapest option of all storage methods mentioned here, this storage is better suited for high capacity, long term hydrogen storage [46,51]. Thus, it is not a viable option for PtG systems, which require small scale, onsite, and temporary hydrogen storage.

The two best options for the temporary hydrogen storage are high pressure gas tanks (350–700 bar) or metallic hydride tanks.

According to Gahleitner [26], hydrogen storage within PtG systems (both planned and realised in 2012) in high pressure gas cylinders is the current and future method of choice. As an alternative, metal hydride tanks were installed in 12% of the PtG plants included in the study. However, they are more expensive.

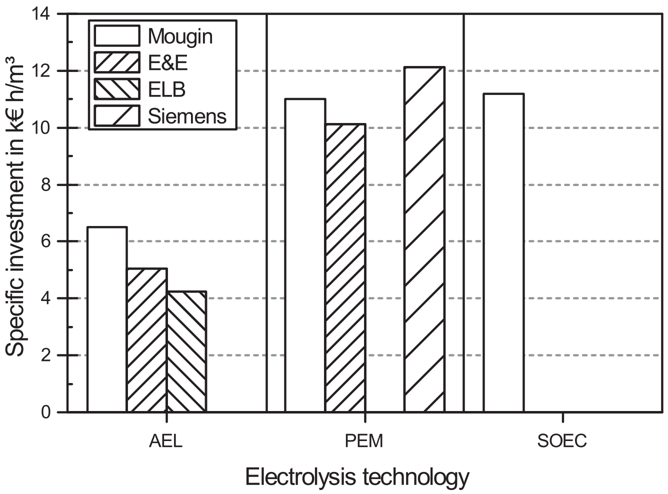

Fig. 3. Comparison of the current selling prices of AEL, PEM, and SOEC systems ([37,49], data for ELB Elektrolysetechnik and Siemens from Ref. [33]).

3. Methanation for Power-to-Gas applications

3.1. Fundamentals

Methanation can be done both in biological and catalytic methanation reactors (see Fig. 4). To compare the methanation technologies, different parameters have been chosen:

- Achievable gas quality of the product gas
- Reactor volume needed to reach the required gas quality and volumetric flow
- Complexity of the process setup

One possible approach to compare reactor performance is to compare the Gas Hourly Space Velocity (*GHSV*) of different reactor concepts. Therefore, a definition according to Eq. (5) is used. In this case, $F_{V,G,in}$ is the volumetric flow rate (STP) of the feed gas without any inert gases and with a stoichiometric H_2/CO_2-ratio. V_R is the reactor volume. If the concept is based on a series of reactors, then the sum of all reactor volumes is used.

$$GHSV = \frac{F_{V,G,in}}{V_R} \qquad \text{Eq. 5}$$

The properties of SNG produced in a PtG chain must be similar to the properties of natural gas distributed in the gas grid. Typically, natural gas contains more than 80% CH_4 [52]. Further important components are higher hydrocarbons, e. g. ethane, propane, and butane which increase the calorific value compared to pure methane. On the other hand, inert components such as CO_2 or N_2 can be found in natural gas and have a corresponding lowering effect on the calorific value.

Typically, CO_2 methanation on nickel catalysts has a selectivity of almost 100% [53–59]. The lack of higher hydrocarbons in the SNG may result in a calorific value of SNG produced from CO_2 methanation that is lower than the calorific value of natural gas.

Fig. 5 shows that a CO_2 conversion of almost 98% is required to achieve a methane content of >90%, whereas a CO_2 conversion of 99% correlates with a methane content of 95%. Inert gases or hyperstoichiometric H_2/CO_2 ratios make it impossible to achieve high methane contents. As a consequence, the requirements for the methanation reactor are very high.

3.1.1. Thermodynamics

Several reactions play a role in the methanation process: the CO (Eq. (7)) and the CO_2 hydrogenation (Eq. (6)) are accompanied by other reactions such as the reverse water gas shift reaction (Eq. (8)) and the Boudouard reaction (Eq. (9)). The CO_2 hydrogenation can be seen as the combination of CO hydrogenation and reverse water-gas shift.

$$CO_2(g) + 4\,H_2(g) \rightleftharpoons CH_4(g) + 2\,H_2O(g) \quad \Delta H_r^0 = -165.1\ \text{kJ/mol} \qquad \text{Eq. 6}$$

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \quad \Delta H_r^0 = -206.3\ \text{kJ/mol} \qquad \text{Eq. 7}$$

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad \Delta H_r^0 = +41.2\ \text{kJ/mol} \qquad \text{Eq. 8}$$

$$2\,CO(g) \rightleftharpoons C(s) + CO_2(g) \quad \Delta H_r^0 = -172.5\ \text{kJ/mol} \qquad \text{Eq. 9}$$

CO and CO_2 hydrogenation are highly exothermic reactions with the consequence that high temperatures limit the CO and especially

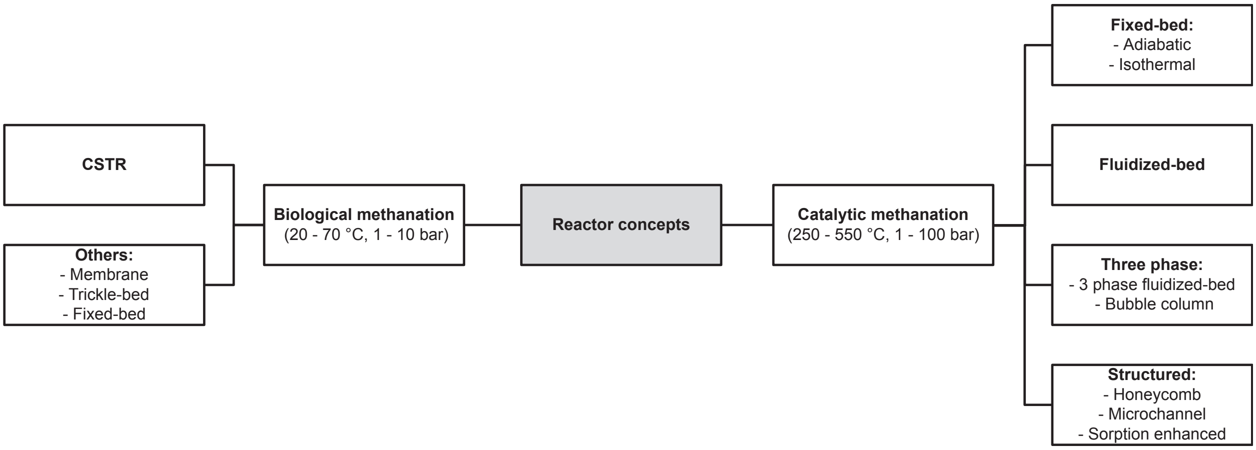

Fig. 4. Reactor concepts for the production of SNG.

the CO_2 conversion. As illustrated in Fig. 6, a temperature below 225 °C (1 bar) or 300 °C (20 bar) is required to reach a CO_2 conversion of at least 98%. Additionally, the positive effect of pressure, as previously addressed, is apparent from the results shown in Fig. 6. Consequently, an elevated pressure should be used for the methanation.

3.2. Catalytic methanation

3.2.1. Reactor concepts

The catalytic methanation reaction has been known since 1902 [60]. Since the oil crisis in the 1970s, the use of methanation for the production of SNG from synthesis gas has gained increasing interest [56]. CO_2 methanation for SNG production has also been investigated for decades [54,61–63]. Several reactor concepts (mostly fixed-bed) for large scale coal-to-gas plants have been developed [64]. However, the PtG chain requires novel concepts which are optimised for smaller plant sizes and intermittent or dynamic operation.

Catalytic methanation reactors are typically operated at temperatures between 200 °C and 550 °C and at pressures ranging from 1 to 100 bar. Several metals such as Ni, Ru, Rh, and Co may be used as the catalyst for the methanation reaction. However, most often Ni is considered to be the optimum catalyst choice due to its relatively high activity, good CH_4 selectivity, and low raw material price [56,65]. However, nickel based catalysts require a high purity of the feed gas (with respect to halogeneous and sulphurous compounds, among others) [66,67].

The methanation reaction is highly exothermic. Assuming a *GHSV* of 5000 h^{-1} and a total CO_2 conversion, approx. 2 MW heat per m^3 catalyst bed need to be removed (methanol synthesis: approx. 0.6 MW/m^3). As a consequence, a significant issue in a methanation reactor is to realise good temperature control in the reactor in order to prevent thermodynamic limitation and catalyst sintering. In order to meet this essential objective, several steady-state reactor concepts have been developed, namely fixed-bed, fluidized-bed, three-phase and structured reactors. Fluidized-bed reactors as well as fixed-bed reactors are established technologies, while the other reactor concepts are in the development phase. The development of these methanation reactor concepts has already been reviewed elsewhere [64,68]. A list of research groups working on the different concepts can be found in Table 2, where almost 30 groups were identified indicating a large interest in methanation. Each of these reactor concepts offers a different approach to overcome the issue related to the reaction heat removal.

For **adiabatic fixed-bed reactors**, the usual approach relies on a series of adiabatic reactors, typically 2–5, with intercooling and sometimes with gas recirculation [69,70]. Due to the adiabatic

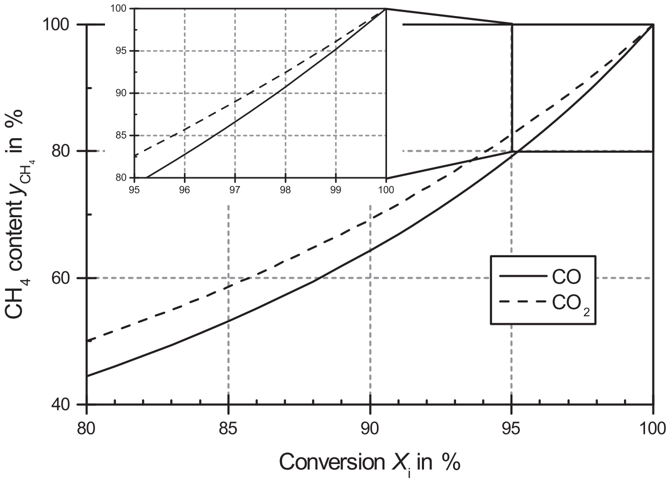

Fig. 5. Relationship between CO or CO_2 conversion and methane content in the dry SNG (no inert gas; $H_2/CO = 3$ and $H_2/CO_2 = 4$, respectively; 100% selectivity).

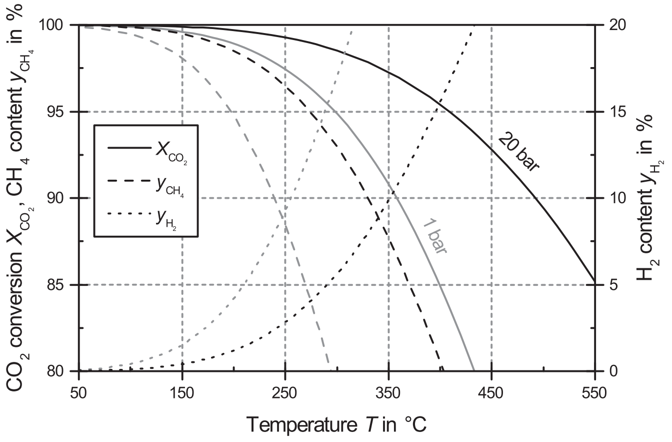

Fig. 6. Equilibrium conversion as well as H_2 and CH_4 content for CO_2 methanation ($(H_2/CO_2)_{in} = 4$, no inert gases).

Table 2
Overview of research groups working on catalytic methanation reactor concepts (sorted by country in alphabetical order).

Fixed-bed	Fluidized-bed	Three-phase methanation	Structured reactor
Montan Universität, Leoben, Austria [86]	Beijing University of Chemical Technology, China [87]	Chinese Academy of Sciences, Taiyuan, China [77]	Montan Universität, Leoben, Austria [86]
Unité de Catalyse et de Chimie du Solide, Villeneuve d'Ascq, France [88]	Chinese Academy of Sciences, Beijing, China [87,89]	DVGW and KIT, Karlsruhe, Germany [58,59,75]	Tsinghua University, China [82]
Deutsches Biomasseforschungszentrum, Leipzig, Germany [70]	Engie SA (former GDF Suez), Paris, France [90]		Brandenburg University of Technology, Cottbus, Germany [55]
DVGW and KIT, Karlsruhe, Germany [41]	Paul Scherrer Institute, Villigen, Switzerland [72,73]		DVGW and KIT, Karlsruhe, Germany [91]
Friedrich-Alexander-Universität, Erlangen-Nürnberg, Germany [92]			Karlsruhe Institute of Technology (KIT), Germany [81]
TU Clausthal, Germany [93]			Energy Research Centre of the Netherlands, Petten, Netherlands [85]
TU München, Germany [94]			Instituto Superior Técnico, Portugal [95]
Zentrum für Sonnenenergie-und Wasserstoff-Forschung, Stuttgart, Germany [28]			Zurich University of Applied Sciences with Laboratory for Hydrogen & Energy, Switzerland [84]
Tokyo Institute of Technology, Japan [96]			Colorado School of Mines, Golden, USA [83]
Energy Research Centre of the Netherlands, Petten, Netherlands [97]			Columbia University, USA [80]
HSR Hochschule für Technik Rapperswil, Switzerland [98]			Pacific Northwest National Laboratory, Richland, USA [83]
Pacific Northwest National Laboratory, Richland, USA [99]			

mode of operation, the catalyst must be able to withstand a broad temperature range (250–700 °C). The main concerns for the catalyst are possible cracking or sintering [67]. Detailed information about two methanation concepts for PtG plants based on fixed-bed methanation can be found in Ref. [68]. Alternatively, cooled fixed-bed reactors can be applied for methanation. Usually, such a reactor contains cooling tube bundles; a further possibility is the use of cooled plates [34,64,71]. Due to the cooling, the process setup is simpler than for adiabatic reactors, however, the reactor itself is more expensive.

In **fluidized-bed reactors**, the mixing of fluidized solids leads to almost isothermal conditions in the reactor facilitating the control of the operation. Offering more effective heat removal is the major advantage of this concept, which allows for using one single reactor with a rather simplified design [72–74]. Nevertheless, due to high mechanical load resulting from fluidization, attrition processes take place in relation to the catalyst as well as the wall of the reactor. As a consequence, the catalyst is eventually deactivated [67]. A further disadvantage can be the incomplete CO_2 conversion caused by bubbling. In addition, a fluidized-bed reactor is limited by superficial gas velocity within the reactor: it cannot be too low in order to assure minimum fluidization conditions and cannot be too high in order to avoid catalyst elutriation.

Other concepts are based on the use of **three-phase reactors** for methanation [59,75–78]. Generally, a slurry reactor is filled with a liquid phase (e. g. heat transfer oils such as Dibenzyltoluene), in which fine catalyst particles are suspended as a result of the gas flow. The presence of the liquid phase with high heat capacity allows for effective and accurate temperature control: the heat of reaction can be completely removed and the reactor can operate almost isothermally, leading to a simple process design. The challenges with the use of slurry reactors are a result of gas liquid mass-transfer resistances and the decomposition and evaporation of the suspension liquid [58,59,75,79].

Structured reactors such as monolith reactors have been developed to tackle the drawbacks of adiabatic fixed-bed reactors, namely temperature hot spots and high pressure drops. Due to their internal metallic structure, monolith reactors feature an enhancement of radial heat transport by two to three orders of magnitude due to heat conduction through the metallic structure (depending on the metallic material) [80]. A special structured reactor concept is embodied by micro structured reactors which are very compact reactors with a high surface-to-volume ratio. They combine high heat transfer and a small pressure drop [55,81–83]. Drawbacks of structured reactors are the more complicated catalyst deposition on the metallic structure, as well as the difficulty of replacing the deactivated catalyst: once the catalyst has been deactivated, the whole reactor has to be equipped with a new catalyst coating.

A further development of structured reactors is the sorption enhanced methanation reaction concept. The water produced by the methanation reaction is removed from the gas phase by the catalyst carrier showing adsorbent functionality. Thereby, thermodynamic limitation of the conversion rate (see section 3.1) is reduced. For the subsequent water removal, temperature swing and/or pressure swing with or without purge gas can be applied. A further development of the Zurich University of Applied Sciences combines this water removal with a regeneration step where the applied materials can undergo catalytic and microstructure regeneration [84,85].

3.2.2. *Specific catalyst and reactor requirements*

Two operation strategies can be developed for a methanation reactor that is used for PtG applications. The methanation reactor can be operated either under steady-state or under dynamic conditions. For steady-state operation, a H_2-storage with high capacity is required to allow for a constant H_2 flow to the methanation reactor. However, this augments the PtG facility costs (see Section 5.3). Consequently, the methanation reactor has to be operated dynamically.

Dynamic operation significantly changes the methanation catalyst and reactor requirements. One aspect is the stand-by operation of the reactor. According to Mutz et al. [100], the methanation catalyst showed a fast bulk-like oxidation in a CO_2 atmosphere. For the catalyst stability, a H_2 atmosphere would be advantageous during stand-by operation.

Under dynamic operation, the reactor temperature can severely change if the reactor heating or cooling cannot be adapted quickly enough. This strong temperature variation can lead to catalyst cracking or sintering which diminishes the catalyst lifetime [67].

One way to overcome this problem is to develop catalysts that can withstand high temperature variations over a long operation time. Nevertheless, as far as is known, no research has been done in this direction.

Another way to overcome the temperature variation issue is to adapt methanation reactor concepts for dynamic temperature regulation. Rönsch et al. simulated the temperature increase of an adiabatic methanation reactor with outlet gas cooling and recirculation [101]. They showed that, even with an adaptive increase in gas recirculation, a catalyst temperature increase of more than 30 °C cannot be prevented after a strong increase in inlet gas flow. Isothermal reactor concepts may show better temperature regulation under dynamic conditions. Lefebvre et al. investigated the dynamic behaviour of a lab-scale three-phase methanation reactor and showed that the reactor temperature does not change even though the gas load at the reactor inlet was varied between 25 and 100% [59]. Consequently, the liquid phase makes the three-phase reactor less sensitive to fluctuating feed streams.

If the H_2 production from the electrolyser is not sufficient, the methanation reactor may have to be shutdown. In this case, a reactor with rapid start-up and shut-down is required. ZSW, Germany investigated the start-up and shut-down behaviour of a micro methanation reactor with an oil cooling system [28]. Reactor stand-by mode was set at 260 °C and pure H_2 atmosphere, while the methanation operating conditions were set at 650 °C (hot spot temperature) and 4000 m^3 reactant/(m^3 catalyst h). They alternated between methanation operating conditions (12 min) and shutdown (8 min) for more than 900 cycles. They could not observe any catalyst deactivation and also reached high CO_2 conversion, which is a promising result for PtG technology.

3.3. *Biological methanation*

Biological methanation (BM) is another option for the PtG process chain. Thereby, methanogenic microorganisms serve as biocatalysts. In a typical biogas plant, the first step is the hydrolysis of an organic substrate (biomass) to simple monomers (monosaccharide, amino acids, and fatty acids). Subsequently, theses monomers are converted to acetate, carbon dioxide, and hydrogen (acidogenesis, acetogenesis). Lastly, the methane is produced by aceticlastic methanogenesis (depletion of acetate) and hydrogenotrophic methanogenesis (CO_2 reduction with H_2) [102,103]. The production of methane directly from CO_2 and H_2 is done by microorganisms (cell type: archea), which obtain the energy for growth by anaerobically metabolising hydrogen and carbon dioxide. This biological reaction has been known since 1906 [104] and the metabolic pathways are shown by Thauer et al. [105]. In BM, methane is produced via hydrogenotrophic methanogenesis from CO_2 and H_2.

3.3.1. *Overview*

Biological methanation proceeds under anaerobic conditions at temperatures between 20 and 70 °C (mesophil and thermophil) and mostly at ambient pressure (Table 3). However, the technical implementation is still an issue. Important parameters for evaluating the reactor efficiency are the methane formation rate (*MFR*, Eq. (10)), the *GHSV* (Eq. (5)) and the methane content in the product gas. The efficiency depends, among other things, on the type of microorganism, cell concentration, reactor concept, pressure, pH-value, and temperature.

$$MFR = \frac{F_{V,CH_4,out} - F_{V,CH_4,in}}{V_R} \qquad \text{Eq. 10}$$

Since the microorganisms are present in a fermentation broth, the methanation reaction takes place within the aqueous solution. Hence, there is an additional gas liquid mass transfer resistance compared to 2-phase catalytic methanation reactors. The gas liquid mass transfer to the microorganisms can be described by Eq. (11). According to this equation, the effective reaction rate $r_{i,eff}$ can be increased by enhancing the mass transfer coefficient $k_L a$ (e. g. stirring) or by increasing the solubility c^*_{iL} (e. g. by an increase in pressure).

$$r_{i,eff} = \frac{F_{(n,i,G|L)}}{V_R} = (k_L a)_i \cdot \left(c^*_{i,L} - c_{i,L}\right) = (k_L a)_i \cdot \left(\frac{p_i \cdot \rho_L}{H_{i,L}} - c_{i,L}\right) \qquad \text{Eq. 11}$$

The Henry's law coefficient for hydrogen in water at 60 °C is ${}^{V}H_{H2,H2O} = 1408$ bar l/mol, while the Henry's law coefficient for carbon dioxide in water is ${}^{V}H_{CO2,H2O} = 36$ bar l/mol [106]. Thus, carbon dioxide is nearly 23 times more soluble than hydrogen in the aqueous fermentation liquid. Due to the poor solubility of hydrogen in the broth (mainly water), improving the hydrogen supply to the microorganisms by enhancing the mass transfer (increasing $k_L a$) presents a big engineering challenge.

Mostly, continuous stirred-tank reactors (CSTR) are used to study BM. By increasing the stirring rate, $k_L a$ increases and the transfer of hydrogen to the liquid can be improved [107]. As a consequence of the increased stirrer frequency, the energy consumption for the agitation is higher. At elevated pressure and for a stoichiometric gas mixture ($H_2/CO_2 = 4$), the H_2 and CO_2 mass transfer to the broth increases (Eq. (11)). Due to the improved supply of hydrogen, the *MFR* increases [108,109]. Furthermore, the CO_2 concentration in the broth is higher and therefore the pH value decreases. To ensure adequate conditions for the microorganisms, an effective method for controlling the pH value in pressurised reactors needs to be developed.

3.3.2. *Process concepts*

Two main process concepts are possible for BM: methanation in situ digester and methanation in a separate reactor. Both process concepts are the focus of academic research as well as the focus of companies working on BM (Table 4).

Table 3
Reactor performance of separate biological methanation reactors during continuous operation; the composition of the reactant gas is a stoichiometric mixture of $(H_2/CO_2)_{in} = 4$ (for more data see supplementary data).

Author	*T* in °C	*p* in bar	Reactor concept	*MFR* in h^{-1}	CH_4 content in %	*GHSV* in h^{-1}
Martin, 2013 [109]	60	1	CSTR	1.4[a]	82.7	8.6[a]
		1.22		2[a]	81	12[a]
Nishimura et al., 1992 [108]	65	3	CSTR	28.7[a]	13.4	300[a]
Seifert, 2014 [111]	65	1	CSTR	21.3[a]	60	120[a]
				5.6[a]	85	29[a]
Burkhardt, 2014 [112]	37	1	Trickle-bed	0.05[b]	98	0.3[b]
Jee et al., 1988 [113]	65	1	Fixed-bed	4.6[b]	34	30[b]

[a] Based on the liquid volume.
[b] Based on the bed volume.

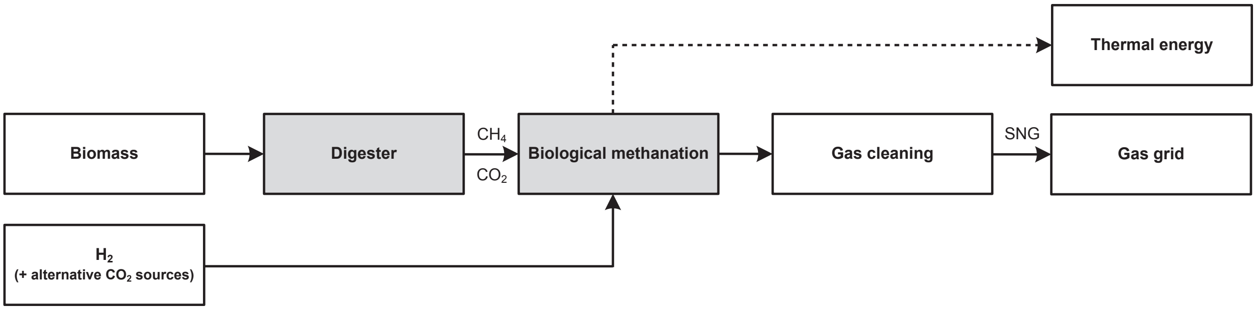

Fig. 7. Process flow diagram for biological methanation in a separate reactor.

3.3.2.1. Biological methanation in a separate reactor. In a separate BM reactor, pure gases are converted by methanogen cultures into CH_4 (Fig. 7). This concept offers the possibility to increase the calorific value of biogas, but it is not limited to biogas as a carbon source [110]. Another advantage is that the process conditions and the reactor design can be adjusted with respect to the requirements of the hydrogenotrophic methanogens. Currently, several reactor concepts are being developed to increase the *MFR* by specifically reducing the gas–liquid mass transfer limitations. In addition to CSTR, fixed-bed, trickle-bed, and membrane reactors are also being investigated, in which the microorganisms are immobilized.

The range of reported reactor performance is wide (Table 3). Comparatively high *MFRs* of 21.3 and 28.7 h^{-1} were achieved by Refs. [111] and [108] using CSTRs operated at a *GHSV* of 120 and 300 h^{-1}, respectively. However, the product gas has a methane content of 60 and 13.4%, respectively. This gas is ineligible to replace natural gas due to the low CH_4 content. Seifert et al. [111] reached a methane content of 85% in the reactor outlet by reducing the *GHSV* by a factor of 4. Thereby, the *MFR* also decreased by nearly 75%. A methane concentration of 98% in the product gas is reached by using a trickle-bed reactor [112]. This high concentration is obtained at a relatively low *GHSV* of 0.3 h^{-1}. Furthermore the MFR is comparably low. Another approach for BM is using a fixed-bed reactor. The studies of Jee et al. [113] show a *MFR* of 4.6 h^{-1} and a pure product yield of 34%. Compared with the *MFR* in CSTRs, the *MFR* obtained in trickle-bed or fixed-bed reactors are lower. On the other hand a stirrer is unnecessary and therefore the energy consumption is lower.

For all investigated reactor designs, the supply of hydrogen to the microorganisms is the rate limiting step. Therefore, the biggest challenge for BM is the delivery of the gaseous hydrogen to the microorganisms. Hence, there is significant potential for process development with respect to the method of hydrogen delivery.

3.3.2.2. In situ biological methanation. Digesters of biogas plants can be used for the PtG process chain (Fig. 8). Thereby, hydrogen is fed directly to the biogas digester. A part or all of the CO_2 produced by the aceticlastic methagonese is then in situ converted to CH_4 resulting in a biogas with a higher methane content and calorific value. The methane formation rate of the biological methanation is limited by the CO_2 production rate of the biogas plant. Therefore, only small *MFRs* of <0.1 h^{-1} are possible [115]. Furthermore, the process conditions cannot be adapted to optimal conditions for the hydrogenotrophic methanogens (e. g. elevated *T* and *p*). Nevertheless, no further reactor is necessary which results in a lower investment.

Bensmann et al. [116] modelled the steady-state and the dynamic behaviour of in situ biological methanation. They assumed ideal mixing for the liquid phase and plug flow behaviour for the gas phase. Due to the assumption of a dispersion free gas phase, the results can be regarded as a best-case approximation with respect to achievable H_2 conversion rates.

Achieving a total conversion of the produced CO_2 is very difficult. For biogas plants using energy crops as feedstock, the methane content can be increased from 52 to 75 % (values are reported by MicrobEnergy GmbH, Germany). Luo et al. [110,117] studied the in situ conversion of the produced CO_2 by addition of H_2 in a small scale CSTR ($V_L = 3.5$ l) under ambient pressure at a temperature of 55 °C. They reached a H_2 conversion of approx. 80% and decreased the CO_2 content in the product gas from 38 % to 15 %. Due to the relatively low H_2 conversion, the H_2 content in the product gas is 20%. By increasing the hydrogen utilisation (improved gas liquid mass transfer), the H_2 and CO_2 content could be further decreased.

Table 4
Overview of research groups and companies working on biological methanation (sorted by country in alphabetical order).

Institution	Concepts	Country
Institute of Chemical Engineering, Division Biochemical Engineering, Vienna University of Technology [111]	Separate reactor	Austria
Department of Enviromental Engineering, Technical University of Denmark	In situ digester Separate reactor	Denmark
Faculty of Environmental Science and Process Engineering, Brandenburg University of Technology Cottbus [114]	Separate reactor	Germany
State Institute of Agricultural Engineering and Bioenergy, University of Hohenheim	In situ digester Separate reactor	Germany
Krajete GmbH	Separate reactor	Austria
Electrochaea GmbH	Separate reactor	Germany, Denmark, USA
MicrobEnergy GmbH	In situ digester Separate reactor	Germany
MicroPyros GmbH	Separate reactor	Germany

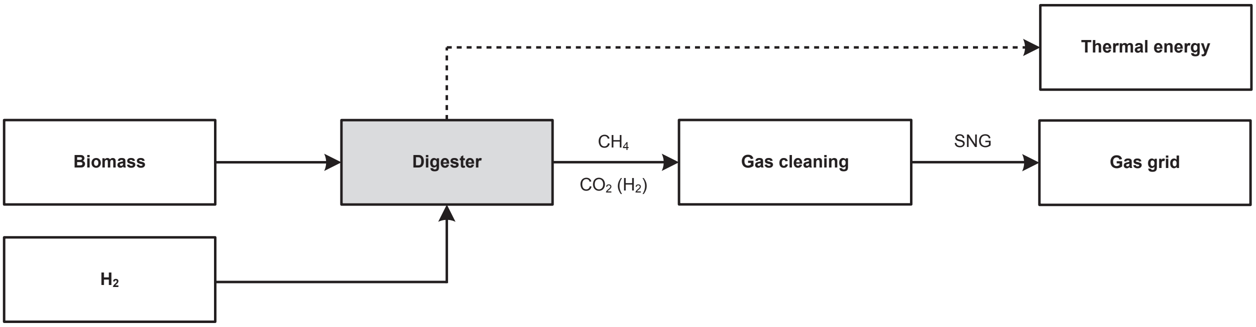

Fig. 8. Process flow diagram for in situ biological methanation.

4. Comparison of methanation technologies

4.1. Comparison of technical parameters

In this section, the biological methanation in a separate reactor will be compared with the most common catalytic methanation concept, adiabatic fixed-bed methanation. Furthermore, data for three-phase methanation are given. A summary of the results discussed in this section is given in Table 5.

4.1.1. Required reactor volume (characterised by the GHSV)

It is of interest to compare the required reactor size of biological methanation with catalytic methanation since reactor size is a crucial aspect regarding the investment. A direct comparison of the required reactor volume is possible by comparing the *GHSV* (Eq. (5)). However, the *GHSV* is only comparable if similar conversion rates are also compared. In this case, a high conversion leading to a methane content of >90% in the product gas (dry basis) is assumed.

In comparison to biological methanation, catalytic CO_2 methanation in a fixed-bed reactor proceeds at a much faster rate, followed by three-phase methanation (Table 5). A biological methanation plant requires a reactor several orders of magnitude larger to convert a certain feed gas flow compared with an adiabatic fixed-bed reactor.

The maximum *GHSV* of 100 h^{-1} for the biological methanation in combination with a methane content of >90% is an optimistic value which, based on the published results, was not yet reached (see section 3.3, Table 3). The data in Table 3 indicate that a *GHSV* of <10 h^{-1} or even <1 h^{-1} is currently more realistic.

The maximum *GHSV* of adiabatic fixed-bed reactors of 2000–5000 h^{-1} assumed for technical plants was in agreement with data given in Refs. [28,69]. Usually, higher *GHSV* values can be achieved in laboratory tests compared with technical plants. For example, Tada et al. reported a *GHSV* for catalytic CO_2 methanation of 10,000 h^{-1} [118]. In technical fixed-bed reactors, the *GHSV* is lower for different reasons:

- Lower effectiveness factor because of larger particles
- The reactor is oversized to avoid frequent refilling due to catalyst deactivation
- Series of reactors and recirculation (equilibrium limitations at high temperatures)

The stark differences between the *GHSVs* of the methanation concepts are due to the following three aspects:

1. The most important aspect is the much higher process temperature, 300–550 °C for catalytic methanation versus 40–70 °C for biological methanation. Higher temperatures usually correlate to higher reaction rates.
2. The overall reaction rate is also influenced by mass transfer phenomena. In particular, the presence of a liquid phase (BM and 3PM) induces gas liquid mass transfer resistances. The gas liquid mass transfer is influenced by the volumetric mass transfer coefficient, $k_L a$, and the solubility ($1/H_{i,L}$) (Eq. (11))
3. The third aspect which needs to be considered is the backmixing of the gas (and liquid) phase. The backmixing in fixed-bed reactors is usually very low (PFR behaviour). The backmixing in the three-phase methanation is low for the gas phase and moderate for the liquid phase (homogeneous regime). In the biological methanation reactor, the backmixing depends on the specific reactor type. In the stirred reactor, the liquid and probably the gas phase can be assumed as perfectly mixed (CSTR behaviour).

The influence of these three aspects (temperature, gas liquid mass transfer, and backmixing) will be discussed for the three-phase methanation. Fig. 9 compares the calculated conversion and the calculated CH_4 content in the dried product gas for three cases:

Table 5
Comparison of biological and catalytic methanation processes.

Reactor type	BM (separate) isothermal CSTR	3PM isothermal slurry bubble column	Fixed-bed adiabatic
Phases involved	G, L (,S)	G, L, S	G, S
Stages	1	1–2	2–6
Backmixing	High	Moderate	Low
T in °C	20–70	300–350	300–550
p in bar	<10	≈20	>5
Stage of development	Lab scale/pilot	Lab scale/pilot	Commercial
GHSV in h^{-1}[a]	<< 100 (Table 3)	500–1000	2000–5000
Tolerance of impurities	High	Low–medium	Low
Process materials	Nutrients, buffer solution	Heat transfer liquid, catalyst	Catalyst
Heat utilisation	Poor	Good–very good	Very good

[a] *GHSV* which applies to a methane content in the product gas of >90% (dry basis).

1. Gas and liquid phases are perfectly mixed ("CSTR")
2. No backmixing in both phases ("PFR")
3. No backmixing in both phases and the gas liquid mass transfer resistance is low, because k_La is increased by a factor of 10 ("PFR + increased MT")

The calculations are based on a complex reactor model which is described in Ref. [58]. Detailed information can be found in the supplementary data.

As evident, temperature as well as backmixing have strong effects. An increase in temperature from 250 °C to 300 °C increases the CH_4 content from 13 % to 90 % (PFR case).

The effect of backmixing is relatively small for low conversions rates; however, at high conversions rates backmixing strongly influences the methane content in the product gas. At 300 °C, the methane content is 90% for the PFR case, but only 44% for the CSTR case. The strong influence of the backmixing at high conversion rates is a challenge for the biological methanation concepts. To increase the volumetric mass transfer coefficient k_La, the stirrer frequency needs to be increased (see section 3.3); however, this leads to increased backmixing. Reactor concepts achieving high volumetric mass transfer coefficients as well as a low backmixing have not yet been developed.

4.1.2. Tolerance of impurities

Depending on the CO_2 source, different impurities are present in the feed gas which may affect the methanation process. For a biogas plant with primary desulphurisation inside the digester, 50–200 ppmv of H_2S in the biogas can be expected for corn as a substrate [119]. The CO_2 feed from biogas plants using residues as substrate can have much higher sulphur loads. Additional impurities include O_2 [120] and siloxanes [119]. Details about impurities in Power-to-Gas plants can be found in Section 5.1.

Biological methanation is more robust against impurities than catalytic methanation. For biological methanation, process upset or infection from foreign organisms was not found to be an issue [34,115,121]. Minor disruptive components such as sulphur and oxygen were found to have no effect on the biological methanation. Furthermore, some of these components can be partly removed by biological methanation. However, the remaining sulphur components still have to be removed prior to gas grid injection.

Contrastingly, sulphur and sulphur-containing components are a known catalyst poison for the nickel catalysts used in catalytic methanation [67,122]. Thus, the feed gas for catalytic methanation process must be cleaned upstream of the methanation reactor (sulphur content << 1 ppm).

In the case of fixed-bed reactors, higher hydrocarbons are also an issue since they decompose at temperatures above ≈500 °C forming coke. The deposited coke leads to catalyst deactivation [123].

4.1.3. Process flexibility and minimum load

For methanation to be operated dynamically as part of a PtG chain, both the minimum load and the load change rate need to be considered. A more flexible methanation reactor significantly reduces the costs for upstream storage of hydrogen. Since hydrogen storage is a high cost factor, minimisation of this factor is crucial (see Section 5.3).

4.1.3.1. Load change rate. Based on the available literature, all three concepts can be operated dynamically. It was shown that the biology, the mass transfer, and/or the chemistry react very fast to load changes [28,59,115,124,125]. Hence, the load change behaviour of a methanation plant is dominated by the plant design and the peripheral equipment, respectively.

Fixed-bed methanation reactors are the most sensitive reactor concepts among those investigated with respect to dynamic or transient operation. Load changes induce temperature changes in the catalyst bed causing a runaway or a cooling down of the reaction [28,101]. It is reported that fast load changes can damage the methanation catalyst; however, measurements of KIT-EBI as well as ZSW Stuttgart [126] have not shown a negative effect of dynamic operation on the CO_2 methanation catalyst.

The liquid phase present in the biological and the three-phase methanation buffers the effect of load changes. Lefebvre et al. [59] have shown that the reactor time constant depended only on the final gas velocity and the volume of the plant, while the reactor temperature remained isothermal during all transient operations.

As a consequence, the limiting factor for load changes is related to the process control system and not to the process itself.

4.1.3.2. Minimum load (but no shutdown). In the following, the minimum load is discussed with respect to commercial application. The minimum loads measured in lab scale experiments are usually not transferable to commercial plants. One reason is that the peripheral equipment, such as compressors, has a limited operating range.

For biological methanation, it is reported that there is no

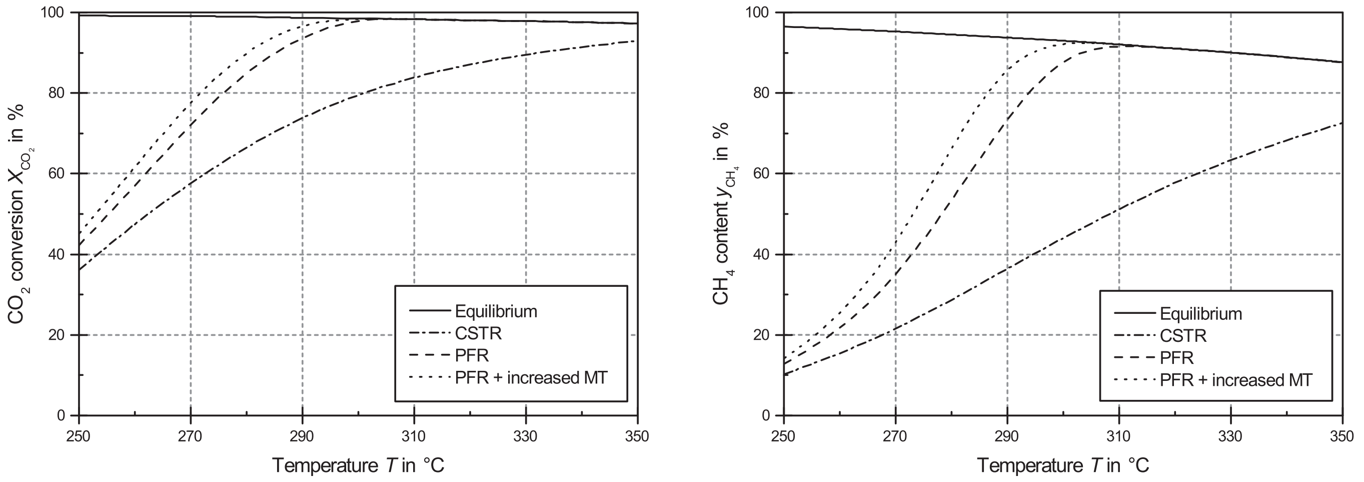

Fig. 9. Influence of temperature, backmixing, and gas liquid mass transfer in a three-phase methanation system; *left*: CO_2 conversion; *right*: CH_4 content in the product gas (dry basis); $H_2/CO_2 = 4$; $GHSV = 1200\ h^{-1}$; $\tau_{mod,CO2} = 84$ kg s mol^{-1}; 20 bar; MT = mass transfer.

minimum load based on biology [115]. However, the operation of the plant is not reasonable if the energy consumption of the stirrer exceeds the energy content of the produced SNG (approximation: minimum load > 10%).

The three-phase methanation can operate within a large load range. A minimum load of less than 10–20 % is necessary for homogeneous distribution of the catalyst in the heat transfer oil [28]. Minimum loads of less than 10% should also be possible. However, this needs to be evaluated in a demonstration scale process.

For adiabatic fixed-bed reactors, a minimum load of 40% is reported by Outotec GmbH [28,127]. However, lower minimum load rates could be possible with special reactor designs as well as with cooled fixed-bed reactors [28].

4.1.3.3. Shutdown. Krajete GmbH [115] reports that an immediate load change from 100 to 0 % can be realised with no negative effect on the biological methanation process. It was also demonstrated that a restart following a 560 h of stagnant operation was also possible without harmful consequences.

A shutdown of a catalytic methanation reactor is also possible. However, the reactor should be flushed with hydrogen or an inert gas before shutting down (see Section 3.2.2). Furthermore, the reactor temperature needs to be kept above 200 °C to avoid formation of nickel carbonyls and to enable a fast restart of the process. The high heat capacity of the three-phase methanation reactor caused by the liquid phase helps to store the heat after a shutdown [58].

4.1.4. Current state of development

Currently, biological methanation has only been investigated at the laboratory or pilot scale (e. g. PtG-Foulum-Project with 50 m^3/h H_2 as feed gas and a $GHSV < 10\ h^{-1}$ [34]). Three-phase methanation has only been tested at the laboratory scale (maximum 1 m^3/h H_2). Both are currently being tested at larger scales (see Section 5.4).

A challenge of the BM is the adequate and energy efficient mixing of a large scale biological reactor with respect to the hydrogen supply. Crucial parts of the upscaling of 3PM include the backmixing behaviour and the hydrodynamics in large scale reactors. In contrast, fixed-bed methanation is well established in commercial industry.

4.2. Energy efficiency

4.2.1. Power requirements

All of the catalytic methanation processes have a lower power requirement than the biological methanation. Most biological methanation reactors need a stirrer or some kind of agitation mechanism to effectively introduce H_2 into the liquid phase. According to MicroEnergy GmbH [115], approximately 10% of the energy for the produced SNG is needed for stirring ($\approx 1\ kWh/m^3$ SNG). Although, three-phase methanation is also subject to mass transfer limitations, the mass transfer in this case is better than that for the biological methanation. For three-phase methanation, the elevated temperature increases the solubility of the H_2 in the heat transfer oil, increases the mass transfer coefficient, as well as increases the phase boundary by reducing the viscosity and the surface tension. As a consequence, a stirrer is not required; instead, the dispersion of the gas throughout the reactor occurs using a gas sparger that is present at the bottom of the reactor [58].

4.2.2. Efficiency of Power-to-SNG and utilisation of waste heat

The methanation reaction is a highly exothermic reaction. To increase the efficiency of a PtG process chain, use of the heat of reaction is necessary.

The waste heat from the biological methanation can be used to heat a biogas digester (e. g. 420 kW for a 5 MW plant [115]). Further opportunities for utilisation of the waste heat from biological methanation are scarce due to the low temperature level (<70 °C), which yields few potential uses. In contrast, the cooling of the reactor causes an additional energy demand.

The higher temperature level (at least 300 °C) of the catalytic methanation yields more opportunities for integration/utilisation of the waste heat streams. Respectively, highly valuable steam and power could be produced [68] (for details see Section 5.2).

4.3. Conclusion

For the following reasons, the biological methanation is only an option for small plant sizes:

- Low temperature can simplify the process, however, few possibilities to use the waste heat
- Large specific reactor volumes required
- Simplified gas cleaning because of high tolerance of impurities

Isothermal catalytic methanation concepts (e. g. three-phase methanation, fluidized-bed reactors) seem to be best for average plant sizes. The process setup is relatively simple and the waste heat can be used.

The fixed-bed methanation is well suited for large scale methanation plants (>100 MW). The process setup is relatively complex [58], but highly valuable steam can be produced [68].

5. System analysis

5.1. Carbon sources

Power-to-Gas requires a carbon source such as CO or CO_2. There are already several articles on CO_2 sources from the CCS (Carbon Dioxide Capture and Storage) technology available [128–130]. In contrast to PtG, CCS requires large stationary point sources of CO_2 such as power plants and refineries as well as the iron, steel, and cement industries to have an impact on the climate [129].

CO_2 sources from industry (Table 6) are one of the largest stationary CO_2 sources in the world [128]. However, CO_2 from iron and steel industries as well as from the cement industry would require a CO_2 capture and some upgrading in order to remove methanation poisoning trace components such as sulphur.

The removal of CO_2 from these gases reduces the energy efficiency and increases the costs significantly. In contrast, PtG requires much smaller carbon sources. As evident in Table 7, even biogas plants, which are relatively small carbon sources, can help to store several MW of chemical energy via the PtG process chain. The use of all the CO_2 emitted from a power plant would require huge electrolysers. Power plants and other carbon sources with low CO_2 contents will not be discussed in the following section because of the large availability of CO_2 sources which are better suited for the PtG process. Furthermore, CO_2 sources will not be discussed if the direct addition of H_2 to the process avoids the CO_2 emission (e. g. ammonia synthesis [131] and hydrogen production for refineries via steam reforming).

5.1.1. Biogas

Biogas is an often discussed CO_2 source. The main components of biogas are CH_4 (50–70 %) and CO_2 (30–50 %), while H_2S, mercaptans, and siloxanes are trace components [119,132].

After removing the trace components, biogas (what is usually used for power generation) can be directly injected to the methanation reactor. Alternatively, the CO_2 from biogas upgrading plants ("biomethane plants") can be used. The main advantages of biogas

Table 6
Properties of different industrial large scale carbon sources [128].

CO_2 source	Average emissions per source (Mt/a)	CO_2 concentration in the flue gas (vol% dry)
Iron and steel	3.5	20–27
Cement	0.79	14–33
Hydrogen (e. g. for refineries)	–	15–20

Table 7
Typical volumetric flows and required power for electrolysis of different carbon sources.

CO_2 source		Biogas plant	Biomass gasification	Industrial processes	power plant
Typical feed gas in m^3/h (STP), dry	CO_2	500	2100	30,000	300,000
	CO	–	2500	–	–
	H_2	–	4000	–	–
	CH_4	500	1100	–	–
Additional H_2 from electrolysis in m^3/h		2000	11,900	120,000	1,200,000
Power demand for electrolysis in MW (5 kWh/m^3 H_2)		10	59.5	600	6000
Produced CH_4 (total) in m^3/h		1000	5700	30,000	300,000
Produced CH_4 (total) in MW		11	63	332	3320

as part of the PtG chain include low gas cleaning expenses and the possibility to utilise the heat from methanation and the oxygen from the electrolysis (see Section 5.2) [133,134].

Particularly in Germany [131,135,136], but also in some other countries there is already a significant potential of CO_2 from biogas plants. According to the European biogas association [137], 1.3 10^9 m^3 of biomethane were produced in 2013. Assuming a CO_2 content of 45% in the biogas, approximately 12 TWh/a of chemical energy could be stored in the form of methane. Moreover, there are almost 15,000 biogas plants in Europe which do not inject into the gas grid (from Refs. [137], primary source: European Biogas Association).

China [138–140] and the USA [141] also have numerous biogas plants. However, so far there is little interest in PtG in these two countries.

5.1.2. Biomass gasification

In the future, a Biomass-to-Gas (BtG) process combined with PtG could play an important role. This combination was already proposed by Gassner and Maréchal in 2008 [142]. The integration of hydrogen from surplus electricity into BtG offers many benefits [28,91,142,143]:

- Total carbon exploitation can be more than doubled (Fig. 10)
- Higher overall process efficiency
- O_2 from electrolysis can be used for gasification
- By adding hydrogen from electrolysis, the use of the water-gas shift reaction can be avoided

Furthermore, a large H_2 storage can be avoided. In times without the availability of surplus electricity, the methanation can be operated with synthesis gas only. This significantly increases the full load hours of the methanation reactor.

Since only a few biomass gasification plants exist, this process chain is not yet a feasible carbon source in most countries.

5.1.3. (Additional) high-purity CO_2 sources

Several processes in industry and fuel production yield relatively pure CO_2 streams. However, some of these sources depend on fossil fuels. Some examples of pure CO_2 sources include natural gas processing, coal-to-gas and coal-to-liquids, ethanol production, and ethylene oxide production [129,144,145]. According to [146], there were 14 ethylene oxide plants in Europe in 2003. Furthermore, some industrial complexes have relatively pure CO_2 streams. However, the availability of such pure CO_2 sources is very country-specific.

5.2. Efficiency and system integration

To assess the PtG process efficiency, the following system is examined. Current available electrolysis technologies (AEL and PEM) delivering H_2 at 25 bar with an electrical efficiency of 70% are considered. The methanation reactor is operated at 20 bar with an efficiency of 78% (maximum chemical efficiency). CO_2 is already compressed to 20 bar for the methanation reaction (otherwise 2% efficiency loss). The Sankey diagram of this considered system is shown in Fig. 11.

The Sankey diagram shows two improvement potentials for PtG. First, the efficiency of water electrolysis could be improved (see section 2.2). Also, heat from the methanation reactor could be utilised.

High temperature heat is produced during catalytic methanation. 165.1 or 206.3 kJ is produced during the methanation of 1 mol of CO_2 or CO, respectively (see Eq. (6) and Eq. (7)). In addition to the heat of reaction, the methanation gas with a temperature level of 300–700 °C (depending on the reactor concept) has to be cooled down prior to injection into the gas grid. Both of these energy sources can be utilised to improve the PtG process efficiency.

Heat from methanation can be utilised to improve the efficiency of the implemented CO_2 source system [68,133,143,147]. The methanation waste heat can also be used to produce steam for further use in a steam power cycle [148]. If a SOEC is implemented for H_2 production, the produced steam can be used as reactant for the electrolysis process [42,43].

Low temperature heat ($T < 100$ °C) from the electrolyser or methanation reactor (in particular for biological methanation) is more difficult to valorise. One option is to use this heat for district heating if the PtG facility is near inhabited areas [149].

From water electrolysis, 8 kg of O_2 are produced per kg of H_2 (2 m^3 O_2 per m^3 CH_4 for CO_2 methanation). So far, no O_2 valorisation has been implemented in the installed PtG facilities [28]. However, several options for O_2 valorisation exist [150]:

- Blast furnaces and electric arc furnaces in the steel industry
- Glass melting
- Oxycombustion in power plants
- Gasification processes
- Medical care

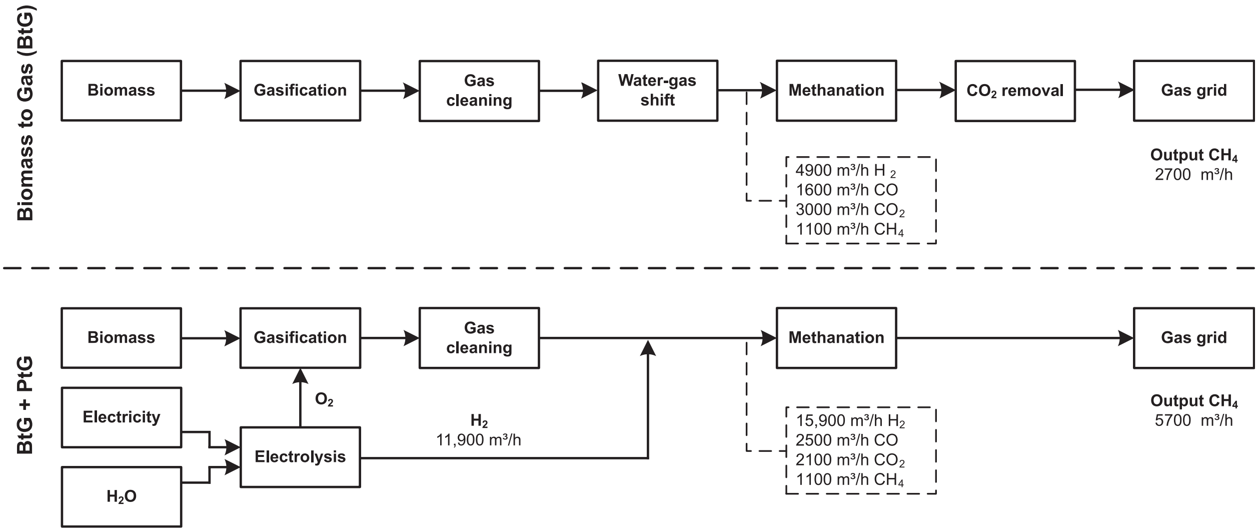

Fig. 10. Increase in CH_4-production for Biomass-to-Gas by integrating H_2 from wind and sun power.

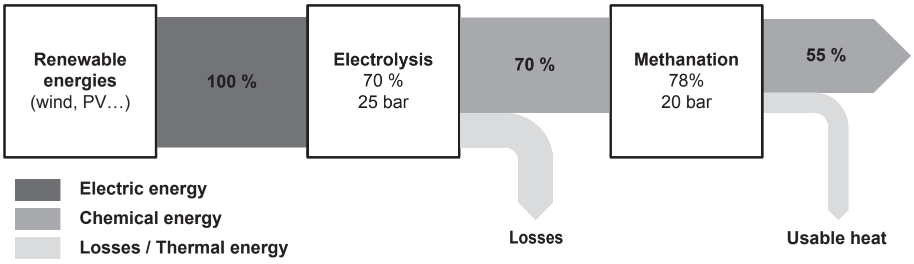

Fig. 11. Sankey diagram of the PtG process efficiency (heat integration is not taken into account).

Another option consists of the utilisation of O_2 for primary desulphurisation of biogas [127,133].

O_2 is usually transported in its liquid form. Since O_2 liquefaction would represent an additional cost for the PtG facility, it is foreseen that O_2 would be directly utilised at the electrolyser site [49]. Another issue to consider with O_2 valorisation is the intermittency of the electrolyser: O_2 will only be produced when the electrolyser is in operation.

5.3. *Economics of "Power-to-Gas"*

A couple of papers and studies deal with the overall role of PtG in the future energy system. In particular, the German energy transition (Energiewende) is examined extensively [12,151–153]. Besides the overall storage demand, overall costs, climate relevant issues, and integral and spatial PtG capacities in accordance with the expected shares of volatile renewable energy sources are evaluated. In this context, combinations of different storage technologies are also considered. For instance, Power-to-Heat and Power-to-Gas can be both relevant in a scenario with 85% renewables in the German electricity production [6]. In Refs. [28,154,155], the evaluation of various business models, market integration, and impact of different PtG applications is considered in detail. Depending on the assumptions, the results of the studies can differ significantly. In the following, the influence of the different assumptions on the SNG costs will be discussed.

5.3.1. *Capital expenditures (CAPEX)*

The following process steps have to be considered:

- Electrolysis
- Hydrogen storage and hydrogen compression (optional)
- Methanation

5.3.1.1. Electrolysis vs. catalytic methanation. The most significant contributor to the total CAPEX is the electrolysis ([28,33,115,127,148,149] and Table 8). However, the reported investment differs significantly. The investment for the electrolysis was already discussed in Section 2.2 and it is in the range of approximately 800–3000 €/kW (el.). Less literature is available about methanation investment. Outotec GmbH [28] reported investment costs of 400 €/kW SNG for a 5 MW plant and 130 €/kW SNG for a 110 MW plant (both data sets are for 2014 and 20 bar operating pressure). Gassner and Maréchal [156] investigated the Biomass-to-Gas process chain with a 14.8 MW CO methanation (15 bar) in 2009. The investment costs for the methanation were 175 €/kW SNG which is in agreement with data from Outotec GmbH.

Lehner et al. [149] compared three different articles/reports and identified a range of 300–500 €/kW. Ausfelder et al. [157] assume investment costs of 600 €/kW in 2050. Methanation costs of 1500 €/kW (currently) – 500 €/kW (2030) are given by E&E Consultant [49]. Finally, Ueckerdt et al. [153] assume 1000 €/kW SNG.

In conclusion, there is a strong uncertainty regarding the methanation investment costs. The data from Outotec GmbH seem to be most realistic because they are based on size-specific calculations from a plant engineering company. That would mean that most other studies use overestimated methanation costs.

Table 8
Investment for different parts of a Power-to-Gas plant (36 MW electrolysis, pressure in H_2 storage: 30–200 bar, methanation pressure: 20 bar) [127].

Investment in M€	Electrolysis	Compressor	H_2 storage	Methanation	Total
Case 1	28.8	1	8.3	0.7	38.8
Case 2	28.8	1	4.8	1.2	35.8

5.3.1.2. Hydrogen storage. Usually, the electrolysis can be operated more dynamically than the methanation reactor. As a consequence, hydrogen storage is necessary. A less dynamic methanation results in larger hydrogen storage. Furthermore, smaller hydrogen storage requires a larger methanation plant. Aicher et al. [127] investigated the influence of methanation dynamics on hydrogen storage investment (see Table 8). A wind farm in northern Germany was used as power source with an installed electrolysis capacity of 36 MW (el.). The following two cases are compared in Table 8:

- Case 1: The methanation operates in steady state mode and produces 311 m^3/h CH_4. The required hydrogen storage volume is 1700 m^3.
- Case 2: The methanation can be operated within a load range of 40–100 %. The total capacity of the methanation is 591 m^3/h CH_4; however, the annual methane production is similar to case 1. The hydrogen storage has a volume of 850 m^3.

As seen in Table 8, the hydrogen storage is the second most significant contributor to the investment of a PtG plant. In this example, the total investment of the PtG chain can be reduced by 8% by operating the methanation dynamically compared with a steady state operation (although the investment for the methanation increases).

5.3.2. Operational expenditures (OPEX) and resulting SNG costs

Important aspects influencing the OPEX are the electricity price and potential CO_2 costs as well as a possible heat and oxygen utilisation.

5.3.2.1. Utilisation of heat and oxygen as well as CO_2 costs. As described in Section 5.2, heat and oxygen can be used in other processes (e. g. biogas plant). Using oxygen from electrolysis for primary biogas desulphurisation, approximately 32,000 €/a can be expected for a 1000 m^3/h biogas plant [127]. Vandewalle et al. [155] investigated the effect of two different oxygen prices (10 and 70 €/t O_2) on the SNG costs assuming that all of the oxygen produced can be sold. In this case, oxygen utilisation could reduce the SNG costs by approximately 2 ct/kWh (5000 h/a operation). In Refs. [28], a reduction of the SNG costs by 1.3 ct/kWh is reported for O_2 utilization. The authors also report a small effect of heat utilization on the SNG costs. Similar results are reported in Ref. [49].

Little information is available on CO_2 costs. Usually, CO_2 is regarded as being freely available [49]. However, CO_2 costs of 100 €/t CO_2 could increase the SNG price by 2 ct/kWh SNG [157].

5.3.2.2. Biological vs. catalytic methanation. Furthermore, it is of interest to compare the costs for biological methanation with catalytic methanation. According to [28,115], for a small plant size (5 MW) the production costs for biological methanation are slightly higher than for catalytic methanation. For larger plant sizes (110 MW), the methanation production costs for biological methanation are nearly 2.5 times that of catalytic methanation. In contrast, higher costs for catalytic methanation compared with biological methanation are reported from E&E Consultant [49], however, it was shown above that the catalytic methanation costs assumed by E&E Consultant are probably too high.

5.3.2.3. Generation costs for SNG (all data in Eurocent/kWh SNG). In Refs. [28], the SNG costs are investigated. Some of the results are shown in Fig. 12. The coupling with a biomethane plant (5 MW SNG generation capacity), with a biomass gasification (30 MW SNG generation capacity), and with an ammonia plant (110 MW SNG generation capacity) is illustrated for different annual operation times. An increase in full load hours (FLH) from 1200 to 3000 FLH decreases the SNG costs by about 50%. A further increase has less of an effect on the SNG costs.

Buchholz et al. [148] accomplished a PtG design study with CO_2 from a lignite power plant. The annual operation time was estimated at between 800 and 1200 h/a. With SNG generation costs of about 60–90 ct/kWh, the produced SNG is much more expensive than natural gas. Nevertheless, the authors see economic benefits in the increased flexibility in operating of the lignite power plant.

A study from E&E Consultant [49] reports SNG costs from 16.5 to 39.2 ct/kWh for today and 7.2–10.2 ct/kWh for 2050 including heat and O_2 utilisation.

In Refs. [158], different options for renewable transportation are compared. Besides direct usage of electricity, numerous energy storage concepts such as DME, methanol, and methane production were analysed. The derived production costs of methane, methanol, and DME were comparable in a range of 6 (2050) to 8 (2020) ct/kWh for 5000 FLH per year.

Summarising, the generation costs for H_2 and for SNG strongly depend on the annual operational time and the electricity price. Compared with natural gas (approximately 2–3 ct/kWh), the costs are much higher (Table 9). For economic feasibility, relevant annual operational times and low electricity costs are obligatory [28,33,34,155]. However, these aspects are contradictory. For low full load hours, the CAPEX for the electrolysis is dominant, for larger full load hours, the electricity price is the most important parameter influencing the economics.

5.3.3. Conclusion

The microeconomic evaluation shows that SNG from PtG processes is not competitive with natural gas or even biomethane ($\approx$7 ct/kWh). For economic feasibility, different business cases such as mobility, balancing services, and CO_2 certificates have to be combined [28]. With respect to a macroeconomic consideration, it has to be taken into account that PtG can contribute to minimise the expansion of the electricity grid infrastructure [160] and to increase the share of renewable energy in the transport and the heating sectors. Therefore, PtG can play a major role in the realisation of the ambitious transition of the energy system.

5.4. Demonstration plants

An overview of Power-to-Gas demonstration plants is already available in literature [26,28,34]. Therefore, only some of the most important demonstration plants and projects aiming to produce SNG are described in this section.

The first PtG pilot plant was probably that which was built in Japan at the **Tohoku Institute of Technology** in 2003. The plant is relatively small, producing 1 m^3/h methane (electrical power at electrolyser < 10 kW). Seawater is used for electrolysis [8].

The **Audi e-gas plant** in Wertle, Germany is the biggest Power-to-Gas plant worldwide. Hydrogen is produced from three alkaline

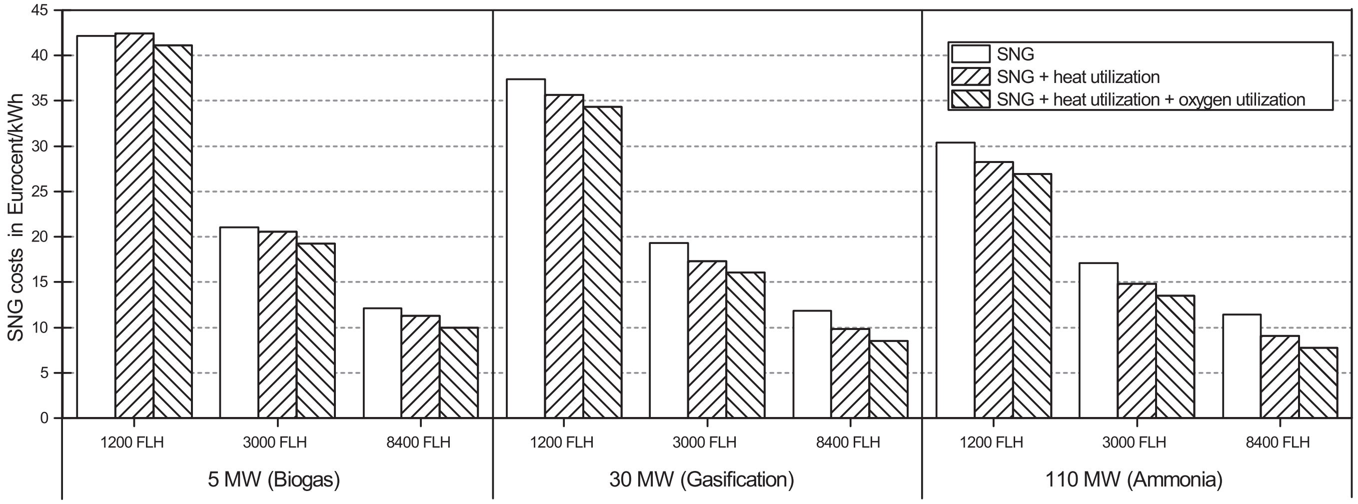

Fig. 12. SNG generation costs for the coupling of PtG with different CO_2 sources (electricity price 5 ct/kWh, heat price = 4 ct/kWh, oxygen price = 7 ct/m^3) [28].

Table 9
Overview of SNG generation costs produced via PtG (in most cases, the original papers show more data than given here; in this case, data for 1200 and 3000 FLH were chosen to compare the calculations).

Source	FLH	Assumptions	Year	SNG costs in Eurocent/kWh SNG
Buchholz et al. [148]	1200	1200 FLH 80 MW electrical power input Energy integration with lignite power plant	2012	60
Müller-Syring et al. [33]		0–9 ct/kWh electricity	2013	19–50
Schaaf et al. [28]		5 ct/kWh electricity 110 MW SNG output	2014	27–30
Vandewalle et al. [155]		0–5 ct/kWh electricity 10 €/t O_2	2015	10–16
Schaaf et al. [28]	3000	5 ct/kWh electricity 110 MW SNG output	2014	13.5–17
Brunner et al. [159]		0–3.3 ct/kWh electricity	2014	6.3–21
Vandewalle et al. [155]		0–5 ct/kWh electricity 10 €/t O_2	2015	4–8
E&E Consultant [49]	–	Heat and O_2 utilisation	2014	16.5–39.2
E&E Consultant [49]		Heat and O_2 utilisation	2050	7.2–10.2
Aufelder et al. [157]		6 ct/kWh electricity Installed electrolysis power: 60 GW	2050	21.8

electrolysers with a total electrical power of 6 MW [161]. The CO_2 is provided by a biogas plant [162]. Operation began in 2013. Cooled, fixed-bed methanation reactors are used.

The combination of Power-to-Gas with biomass gasification is demonstrated in the **KIC-Project „DemoSNG“** [91]. The volumetric feed gas flow for the methanation is 10 m^3/h (STP) and the plant is currently under commissioning (as of June 2015). A novel methanation concept based on a honeycomb reactor is used.

The **BioCatProject** aims to use the biological methanation developed by Electrochaea as part of the Power-to-Gas process chain. An alkaline electrolyser with an electrical power input of 1 MW will provide the hydrogen. The plant, which is located in Denmark, is currently under construction [163].

6. Summary

Power-to-Gas (PtG) might play an important role in the future energy system. However, technical and economic barriers have to be solved before PtG can be commercially successful.

Electrolysis:

- Improvement in efficiency (during transient operation) and cost reduction are required
- Currently, alkaline electrolysis is the cheapest and most reliable technology
- In the near future, PEM electrolysis could be the better choice for PtG plants because of the better performance with respect to transient operation
- Solid oxide electrolysis is in the development phase, however, the technology has a high potential for coupling with exothermic reactions at steady-state operation

Catalytic methanation:

- Almost 30 groups working on methanation technologies (mostly fixed-bed and structured reactors; additionally fluidized-bed reactors and three-phase methanation)
- Few results are published about the dynamic operation of methanation reactors
- Recent results indicate that the dynamic operation is not significantly reducing the catalyst stability
- The control of the reactor temperature of adiabatic reactors is difficult; consequently cooled fixed-bed reactors are under investigation to handle the above mentioned issue
- The application of three-phase reactors leads to isothermal conditions during dynamic operation

Biological methanation:

- Biological methanation can be carried out in biogas digesters (addition of H_2 to biogas digesters) or in separate reactors
- The poor H_2 mass transfer is the limiting aspect regarding the process performance
- Mostly CSTR reactors are used which have the advantage of a high volumetric mass transfer coefficient k_La, however, the backmixing in the gas and liquid phase makes it difficult to achieve high methane contents

Comparison of biological and catalytic methanation:

- Biological methanation has a higher tolerance of impurities
- Catalytic methanation requires much smaller reactor sizes for the same feed gas flow (orders of magnitude smaller)
- Use of catalytic methanation leads to higher efficiencies because (I) no stirrer is required and (II) the waste heat can be utilised

Process chain:

- Biogas and biomass gasification could become important CO_2 sources for PtG
- The hydrogen production costs dominate the whole process costs
- Hydrogen storage can be another significant cost factor
- The dynamic behaviour of the methanation determines the size of the H_2 storage
- Heat utilisation from methanation is required to increase the PtG efficiency

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Symbols and abbreviations

Abbreviations and indices

*	Equilibrium
0	Standard conditions
3PM	Three-phase methanation
AEL	Alkaline electrolysis
BM	Biological methanation
BtG	Biomass-to-Gas
CAPEX	Capital expenditures
CCS	Carbon Dioxide Capture and Storage
CSTR	Continuous Stirred-Tank Reactor
DME	Dimethyl ether
DVGW	Deutscher Verein des Gas-und Wasserfaches
eff	Effective
el.	Electrical
FLH	*Full load hours*
G	Gas phase
GDF	Gaz de France
i	Component i
in	Inlet
KIT	Karlsruhe Institute of Technology
L	Liquid
MT	Mass Transfer
OPEX	Operational expenditures
out	Outlet
PFR	Plug Flow Reactor
PEM	Polymer electrolyte membrane
PtG	Power-to-Gas
PtL	Power-to-Liquid
PV	Photovoltaics
R	Reactor
S	Solid
SNG	Substitute Natural Gas
SOEC	Solid Oxide Electrolysis
STP	Standard Temperature and Pressure: 0 °C, 101,325 Pa
TU	Technische Universität
ZSW	Zentrum für Sonnenenergie-und Wasserstoff-Forschung Baden-Württemberg

Symbols

c	Concentration (mol/m^3)
E_V	Equilibrium cell voltage (V)
F	Faraday constant (96,485 C/mol)
F_n	Molar stream (mol/h)
F_V	Volumetric stream (STP) (m^3/h)
$GHSV$	Gas Hourly Space Velocity (Eq. (5)) (h^{-1})
ΔG_r^0	Standard Gibbs free energy (kJ/mol)
$H_{i,L}$	Mass based Henry's law coefficient $\left(p_i \cdot \left(\frac{n_i}{m_i+m_L}\right)^{-1}\right)$ (bar kg/mol)
H_S	Higher heating value (kWh/m^3)
${}^VH_{i,L}$	Volume based Henry's law coefficient $\left(p_i \cdot \left(\frac{n_i}{V_i+V_L}\right)^{-1}\right)$ (bar l/mol)
ΔH_r^0	Standard enthalpy of reaction (kJ/mol)
k_La	Volumetric mass transfer coefficient (s^{-1})
MFR	Methane Formation Rate (Eq. (10)) (h^{-1})
m	Mass (kg)
n	Number of moles, number of transferred electrons (mol, -)
p	Pressure (bar)
$r_{i,eff}$	Effective reaction rate $\left(\frac{1}{V_R}\frac{dn_i}{dt}\right)$ (mol s^{-1} m^{-3})
T	Temperature (K, °C)
V	Volume (m^3)
X_i	Conversion of component i (-)
y_i	Mole fraction (gas phase) (-)
ρ	Density (kg/m^3)
$\tau_{mod,CO2}$	Modified residence time (mass of catalyst divided by the molar stream of CO_2) (kg· s/mol)

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.renene.2015.07.066.

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