



Power-to-Methane: A state-of-the-art review

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ABSTRACT

Power-to-Methane is a concept that converts electrical into chemical energy using CO₂ and H₂O. The concept brings the possibility of connecting the power grid to different sectors, where CH₄ is needed such as mobility and industry. In this review, a comprehensive overview of the state-of-the-art of Power-to-Methane is presented. The Power-to-Methane process chain is described in detail. Fundamentals of water electrolysis are highlighted and cell technologies are discussed and assessed. CO₂ sources are pointed out, CO₂ separation technologies are depicted and compared, and some separation projects worldwide are listed. Thermodynamics of methanation process is analyzed; catalysts and reactors used are described and evaluated. Finally, Power-to-Methane plants in operation and construction are addressed.

1. Introduction

The power capacity from renewable energy sources has seen a rapid growth. In the last 10 years, the average annual growth amounted to 15.9% [1], whereby the variable renewable energy sources (VRESs; mainly wind and solar) have afforded the largest shares. These tendencies are expected to continue in the future [2].

Power produced from VRESs cannot match electrical demand to 100%. With the growth in investments in VRESs, solutions to reduce the inherent issue of VRESs become increasingly necessary [3–7]. The attractive option will remain the energy storage [8–18].

There are different energy storage technologies that can be classified according to their work principles: (i) electrical (superconducting magnetic energy storage), (ii) mechanical (pumped storage, compressed air, flywheels), (iii) thermal (latent heat, sensible heat, thermochemical), and (iv) chemical (supercapacitors, batteries, power-to-gas, power-to-liquid) [19–22]. Besides the work principles, the storage technologies differ in further characteristics such as energy capacity, response time, self-discharge, efficiency and operating constraints, covering different fields of applications [23]. Accordingly, an energy storage mix will be needed.

In regions, where a natural gas infrastructure exists, the Power-to-Methane (PtM) concept is a promising option to absorb and exploit surplus renewable energy [20]. Fig. 1 shows the principle of the PtM concept and applications for it. A PtM plant basically consists of a water electrolyzer, a CO₂ separation unit, if CO₂ is not available as pure gas or

in suitable gas mixture, and a methanation module [24–26]. At times of surplus power, H₂ is produced by water splitting in the electrolyzer. The generated H₂ and CO₂ are then converted in the methanation unit to a gas mixture that mainly contains CH₄ and H₂O [27]. The product gas is then treated to a methane-rich gas, so-called synthetic natural gas (SNG) [28,29]. The SNG conditioning unit and balance-of-plant components are not depicted in the figure. The SNG produced can be used as fuel for mobility, in the residential sector, for power generation at times, when the power demand overbalances the power supply, and as raw material in industry.

The purpose of this review paper is to present an extensive updated state-of-the-art of PtM technology giving the reader a structured technical understanding of the technology. The paper is structured as follows. Water electrolysis is handled in Section 2. CO₂ for PtM is discussed in Section 3. Methanation is approached in Section 4. PtM plants in operation and construction are addressed in Section 5. Finally, conclusions are drawn in Section 6.

2. Water electrolysis

The conversion of electrical into chemical energy in form of H₂, water electrolysis, is the first part of the PtM process chain. Fig. 2 illustrates a typical scheme of water electrolysis systems. A system mainly consists of an electrolysis stack, an ion exchanger to obtain a high purity of the water fed into the stack, H₂ and O₂ separators, and a converter for power conditioning [30]. A stack contains a number of cells

Abbreviations: AEL, alkaline electrolysis; GHSV, gas hourly space velocity; PEMEL, polymer electrolyte membrane electrolysis; PtM, Power-to-Methane; SOEL, solid oxide electrolysis; VRES, variable renewable energy source

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Nomenclature

E_T	Thermal energy (J mol^{-1})
F	Faraday's constant (C mol^{-1})
m_{H_2}	Mass of hydrogen (g)
M_{H_2}	Molar mass of hydrogen (g mol^{-1})
Q	Electric charge (C)
T_K	Absolute temperature (K)
V	Voltage (V)
V_{Oh}	Ohmic voltage (V)

V_{OV}	Overvoltage (V)
V_r	Reversible cell voltage (V)
V_{act}	Real cell voltage (V)
V_{tn}	Thermoneutral cell voltage (V)
z	Electric charge (dimensionless)
ΔG_R	Gibbs energy (J mol^{-1})
ΔH_R	Reaction enthalpy (J mol^{-1})
ΔS_R	Reaction entropy ($\text{J mol}^{-1} \text{K}^{-1}$)

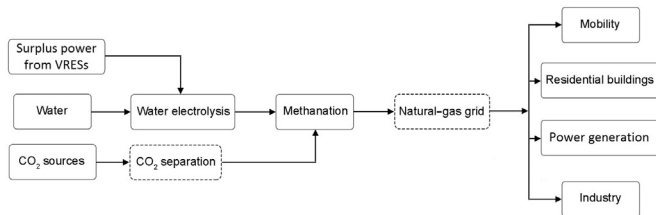


Fig. 1. Principle of the PtM concept and its applications.

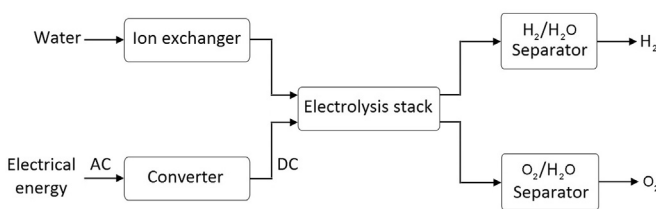


Fig. 2. Typical scheme of water electrolysis systems.

connected in series due to the low cell voltage. Each cell in turn consists of a cathode, an anode and an electrolyte in between. In general, three cell technologies named after their electrolytes can be distinguished: alkaline (AEL), polymer electrolyte membrane (PEMEL) and solid oxide (SOEL) [31]. The first two types are classified as low temperature electrolysis technologies since their typical operational temperature is lower than $100\text{ }^\circ\text{C}$ [32]. The third one is classified as high temperature electrolysis that is operated at temperatures up to $1000\text{ }^\circ\text{C}$. In this section, fundamentals of the water electrolysis are first illustrated. The three electrolysis technologies are then presented and compared.

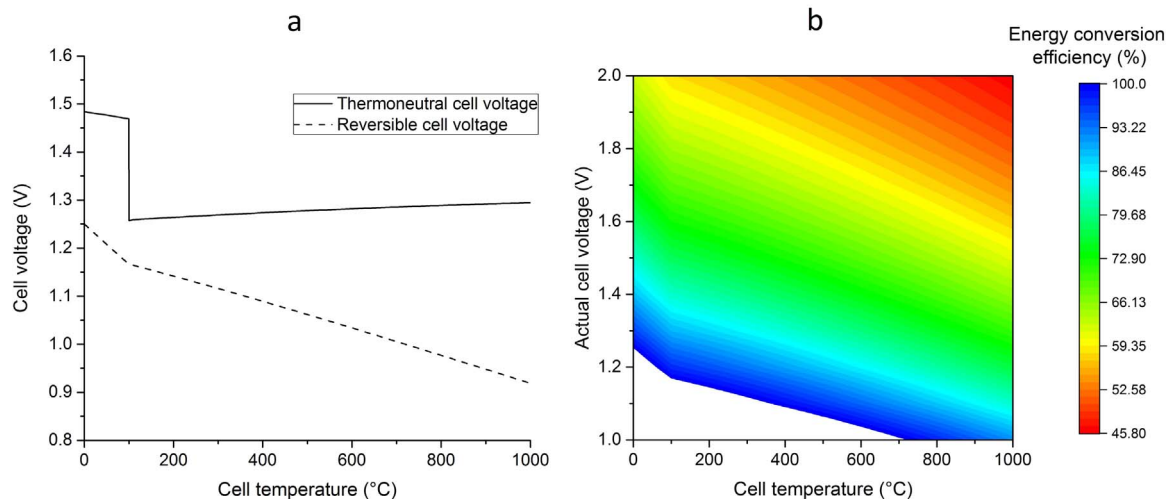


Fig. 3. a: thermoneutral and reversible cell voltages for water electrolysis as functions of temperature at 1 atm; b: energy conversion efficiency of water electrolysis as function of temperature and actual operating cell voltage at 1 atm.

2.1. Fundamentals

The reaction equation of the water electrolysis process can be written as follows:



According to the Faraday's law of electrolysis [33], the relationship between the mass of hydrogen (m_{H_2}) generated at a cathode and the electric charge (Q) passed through the cathode is as follows:

$$m_{\text{H}_2} = \frac{M_{\text{H}_2}Q}{zF} \quad (2)$$

where M_{H_2} is the molar mass of hydrogen, z the number of electrons involved in the electrochemical reaction (Eq. (1)), and F the Faraday's constant [34].

The cell voltage required to decompose water (thermoneutral cell voltage (V_{tn})) is proportional to the water decomposition enthalpy (ΔH_R):

$$V_{\text{tn}} = \frac{\Delta H_R}{zF} \quad (3)$$

According to the second law of thermodynamics and because the entropy change of the water electrolysis is positive [35], a part of the reaction enthalpy can be applied as thermal energy, which is the product of the entropy change of the water decomposition reaction (ΔS_R) and the absolute temperature (T_K):

$$E_T = T_K \Delta S_R \quad (4)$$

The difference between ΔH_R and $T\Delta S_R$ is the change in the Gibbs energy of the water decomposition reaction (ΔG_R). This is proportional to the minimum cell voltage (reversible cell voltage (V_r)) needed to split H_2O [36,37]:

$$V_r = \frac{\Delta G_R}{zF} \quad (5)$$

Fig. 3a displays V_{tn} and V_r as functions of temperature at 1 atm. The abrupt changes of V_{tn} and V_r at about 100 °C are due to the change in state of water from liquid to vapor. When $V < V_r$, where V is the voltage applied to water electrolysis cell, no water splitting can occur. When $V_r \leq V < V_{tn}$, water electrolysis is possible by adding heat. When $V_{tn} \leq V$, water electrolysis takes place at constant temperature ($V_{tn} = V$) or under heat dissipation ($V_{tn} < V$).

In practice, the voltage of an operating electrolysis cell is significantly higher than the reversible cell voltage due to different resistances in process [38]. The charge transfer resistances at anode/electrolyte and cathode/electrolyte interfaces and the resistivity of electrolyte cause the highest resistances [39]. The charge transfer resistances depend on the metal materials used as catalysts. According to Ref. [40], metal materials for hydrogen evolution reaction are divided into three classes: metals with high overpotential (Cd, Tl, Hg, Pb, Zn, Sn), metals with middle overpotential (Fe, Co, Ni, Cu, Au, Ag, W), and metals with low overpotential (Pt, Pd). The actual cell voltage (V_{act}) can be expressed as follows [40]:

$$V_{act} = V_r + V_{OV} + V_{Oh} \quad (6)$$

where V_{OV} is the overvoltage caused by the charge transfer resistances and V_{Oh} the ohmic voltage caused by the resistivity of electrolyte.

Fig. 3b shows the energy conversion efficiency of water electrolysis as function of actual operating cell voltage and temperature at 1 atm.

2.2. Cell types

2.2.1. AEL

In an AEL cell (Fig. 4), two electrodes (e.g. mild steel for the cathode and nickel for the anode) are immersed in an aqueous alkaline solution and separated by a membrane (e.g. Zirfon® Perl) [36]. Aqueous solutions of potassium or sodium hydroxide (KOH_{aq} or $NaOH_{aq}$) are typically used. KOH_{aq} offers higher electrical conductivity than $NaOH_{aq}$ at the same concentration; otherwise the corrosion resistance of steel and nickel is better in KOH_{aq} than in $NaOH_{aq}$ [41,42]. The concentration of KOH is usually in the range of 30–40 wt % in order to provide a high electrical conductivity [43]. In the last decade, studies were devoted to intensify the AEL process by adding activating compounds into electrolyte [44–48]. E.g. Stojic et al. [47] reported that they could reduce the power need for water electrolysis up to 10% by adding tris(ethylenediamine)cobalt(III) chloride complex or tris(trimethylenediamine) cobalt (III) chloride complex into KOH solution.

During the electrolysis process, hydroxide ions are oxidized at the anode to oxygen and water as follows [36]:



Driven by a power source, the electrons flow through an external circuit towards the cathode, where they react with water to hydrogen and hydroxide ions according to [40]:



Then, the hydroxide ions move across the membrane to the anode side driven by the concentration gradients.

2.2.2. PEMEL

In contrast to AEL, PEMEL enables hydrogen production from pure water. In a PEMEL cell (Fig. 5), water is introduced at the anode where it is split into protons and oxygen (Eq. (9)). The protons travel through the membrane to the cathode to form H_2 (Eq. (10)), while oxygen remains back with water [49]. The electrodes are pressed against a membrane (e.g. Nafion) characterized by ionic conductivity and electronic isolation, forming the so-called membrane-electrode-assembly [50]. This construction enables a short inter-electrode distance and absence of gas bubbles between the electrode and the membrane, thus minimizing ohmic voltage losses [49]. The catalyst layers on the electrodes are usually based on precious metals such as platinum and iridium [30]. The precious metal catalysts ensure high specific productivity [49].



2.2.3. SOEL

The reversible cell voltage for water electrolysis decreases with the increase of temperature. E.g. it amounts to 0.95 V at 900 °C. Theoretically, the water electrolysis at this temperature consumes 20% less electrical energy than that at 80 °C. On the other hand, overvoltages and ohmic voltage drop are also decreased at high temperatures. This benefits that elevated temperature provides make the SOEL a promising technology for water electrolysis. A further advantage that can result through the choice of SOEL for PtM is that the methanation reactor can provide the heat requirement for steam generation for SOEL.

The principle of the SOEL cell is displayed in Fig. 6. A cathode for the hydrogen evolution reaction and an anode for the oxygen evolution reaction are separated by a solid electrolyte [51]. H_2O is decomposed to H_2 and O^{2-} on the cathode (Eq. (11)). Then, O^{2-} is transported through the solid electrolyte to the anode where it is oxidized to O_2 (Eq. (12)) [52]. The conventional solid electrolyte is ZrO_2 doped with Y_2O_3 (yttria-stabilized zirconia, YSZ) that possesses an excellent conductivity and stability [53,54]. The most common cathode catalyst is nickel [55–58]. Lanthanum strontium manganite is regarded as the best catalyst candidate for the anode [59–61].



2.2.4. Comparison of the water electrolysis technologies

The AEL is seen as a mature technology, while the PEMEL in the early phase of commercialization and the SOEL in the development [62–64]. As in every sector, the costs and durability associate with the technology maturity. AEL is currently the cheapest and most reliable technology. However, PEMEL is thought to be the best choice for PtM plants in order to absorb intermittent energy amounts [27]. The SOEL must be demonstrated first. The traditional drawbacks of AEL are the corrosion and the limited operating pressure and load ranges. However, recently progresses have been

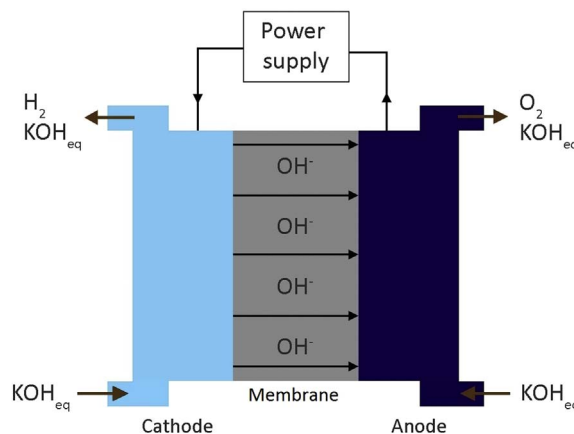


Fig. 4. Schematic representation of an AEL cell.

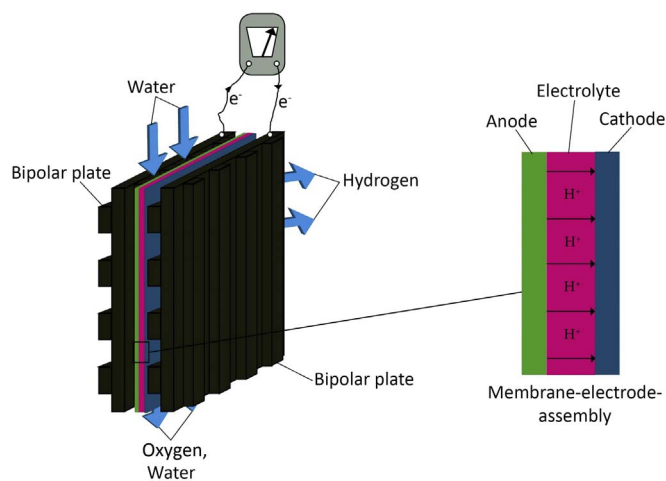


Fig. 5. Schematic representation of a PEMEL cell.

reported. New AEL designs would allow variable operation ranging from 5% to 100% of the nominal capacity and starting from cold within a few minutes [65]. Due to the electrolyte type used in PEMEL, this offers better operating flexibility and is capable of operating at pressures up to 100 bar [66]. On the other hand, the use of precious metals as catalysts intensive the hydrogen production (relatively high current density) [67]. However, the use of these materials has disadvantages such as high investment costs and low durability. The SOEL is operated at high temperature, which accelerates the kinetics and reduces the reversible cell voltage of the electrolysis process (Fig. 3a). The SOEL is therefore a promising technology, if the issues related to the durability of the ceramic materials at high temperature and long-term operation are solved [31]. The tightness of cells plays an important role in the performance. Sealing PEMEL stacks is easy by using materials such as synthetic rubber or fluoroelastomer [67]. Sealing AEL stacks is less easy because of the corrosive electrolyte; typically, metallic sealants are applied [68]. Sealing SOEL stacks is a significant challenge to be overcome due to the high operating temperature; currently, glass and glass ceramic sealants are the most used solutions [69]. In order to reduce the mechanical stress caused by thermal expansion on the sealant materials, electrolysis stacks are sometimes designed in tubular configuration [58]. However, planar stacks offer more uniform distribution of fluid species and are easier for mass production [70]. Table 1 provides quantitative data to the characteristics of the different water electrolysis technologies.

Table 1
Features of cell technologies.

Feature	AEL	PEMEL	SOEL
Maturity	Mature	Early phase of commercialization	Development
Temperature (°C)	40–90 [71]	20–100 [71]	600–1000 [40]
Pressure (bar)	< 30 [71]	< 100 [66]	–
Voltage (V)	1.8–2.4 [71]	1.8–2.2 [71]	0.95–1.3 [32]
Efficiency (%)	62–82 [71]	67–82 [71]	–
Current density (A cm ⁻²)	< 0.5 [72] 0.2–0.4 [65]	< 2 [32] 1.0–2.0 [65]	< 1 [32]
Cold start up time (min)	15 [32] 20 [65]	< 15 [32] 5 [65]	> 60 [32]
Degradation rate (mV h ⁻¹)	< 3 [71] 2 [73]	< 14 [71] 5 [73]	–
Life time (stack)	< 90,000 [32] < 75,000 [65]	< 62,000 [65]	–

3. CO₂ for Power-to-Methane

In the second conversion step of the PtM process chain, CH₄ is formed by the reaction of H₂ with CO₂. However, CO₂ is often not available as pure gas or in suitable gas mixtures for generating applicable PtM products. In this section, candidate CO₂ sources are presented, CO₂ separation technologies are depicted and compared, and some separation projects worldwide are listed.

3.1. CO₂ sources

In addition to supporting penetration of VRESs, PtM uses CO₂ as a raw material and not as a waste, thus, can contribute to the decrease of greenhouse gas emissions. CO₂ for PtM can be won from biomass plants, power generation plants, industrial processes and ambient air. Table 2 shows candidate processes, their exhaust gases can be used as CO₂ sources for PtM. Industrial CO₂ sources, in which the use of renewable H₂ would lead to avoid CO₂ emissions (e.g. ammonia process [74] and hydrogen production by reforming of hydrocarbons [52]), and in which heat or steam is generated by the combustion of fossil fuels as in power generation plants, are not considered. Biogas can directly be injected into the methanation reactor after removing the damaging trace components such as hydrogen sulfide [75]. The biogas upgrading and bioethanol production plants emit CO₂ gases that can be utilized in PtM without additional energy or cost effort [66,76]. The

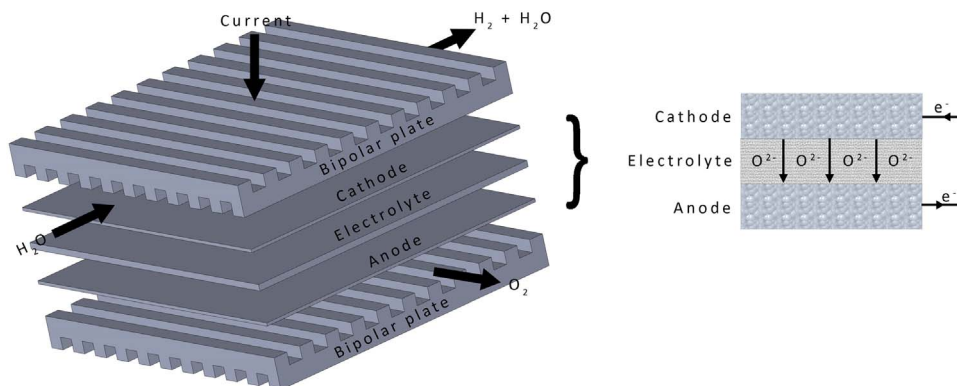


Fig. 6. Schematic representation of a SOEL cell.

Table 2
Candidate CO₂ sources for PtM.

Sector	CO ₂ sources	CO ₂ concentration in exhaust gas [vol%]
Biomass processes	Biomass fermentation	15–50 [88]
	Biogas upgrading	≈100 [88]
	Bioethanol production	≈100 [89]
Power generation plants	Natural gas combustion	3–5 [90]
	Petroleum combustion	3–8 [90]
	Coal combustion	10–15 [91]
Industrial processes	Cement production	14–33 [78]
	Iron and steel production	20–30 [78]
	Ethylene oxide production	≈100 [92]
Environment	Ambient air	≈0.04 [93]

power and industry sectors combined emit more than one third of the global CO₂ emissions [77]. Capturing CO₂ from these sectors is technically feasible, however, economically depends i.a. on the CO₂ partial pressure in exhaust gas [78]. The higher the CO₂ partial pressure, the more economical the separation process is. The most relevant CO₂ sources, which will remain indispensable in future, are these from cement manufacturing, iron and steel making, and chemical processes, in which CO₂ is generated as by-product as in the process of ethylene production [79]. In recent years, many studies [80–86] have investigated the separation of CO₂ from ambient air. Technically, this concept is also feasible [87]. Its advantage is that no CO₂ transportation to the site of the PtM plant is needed. However, due to the very low partial pressure of CO₂, the specific costs of the vision are very high.

3.2. CO₂ separation technologies

3.2.1. Absorption

As the name suggests, this technology is based on the absorption of CO₂ into a liquid. The principle of the process can be described as follows: a liquid is used to capture CO₂ from a gas mixture in a column (Fig. 7a); the absorbent loaded with CO₂ is transported to a different column, where CO₂ is released by heating and/or depressurization [94]. The regenerated absorbent is then sent back to the absorption column. There are several absorbents, which can be categorized into chemical and physical ones. In the first category, amines, aqua ammonia and sodium carbonate are usually used [95]. Alcohols, polyethyleneglycol and other oxygenated compounds have been used as physical absorbents [85].

3.2.2. Adsorption

Adsorption is considered as one of the promising CO₂ separation methods [91]. The adsorption technology uses a solid sorbent to bind CO₂ [96]. Fig. 7b shows the adsorption process in a simple version. Gas mixture is compressed and injected into a vessel, where CO₂ is adsorbed on the surface of the adsorbent. When the adsorbent has been fully loaded, the CO₂ is released by depressurization (and heating) [97]. The process is therefore discontinuous. Typical adsorbents are activated carbons, zeolites, amine functionalized adsorbents and metal organic frameworks [95,98–100].

3.2.3. Membrane

The membrane technology uses the advantage of the different sizes of gas compounds [90]. Three different flows can be defined in a membrane module (Fig. 7c): the feed (gas mixture), retentate (usually CO₂-poor gas) and permeate (usually CO₂-rich gas). The feed enters the module, and the permeate passes through the membrane and exits on the downstream side [78]. The driving force for the permeation is the

difference in partial pressure of the components between the feed side and the permeate side of the membrane [100]. There are many types of membranes which are suitable for CO₂ separation. They can be classified into organic (such as polyimides, polycarbonates and polyethylene oxides), inorganic (such as alumina, silica and zeolites) and mixed matrix membrane [101–104].

3.2.4. Cryogenic distillation

The process of cryogenic distillation splits CO₂ from a gas mixture by condensation [105]. Fig. 7d shows a simple drawing of the process. The gas mixture is compressed and in the heat exchanger cooled down. The cooled pressurized fluid mixture is then fed into the distillation column (tray or packed). CO₂-rich stream usually exits the column at the bottom.

3.2.5. Comparison of the CO₂ separation processes

The chemical absorption is the preferred method for capturing CO₂ from gas streams containing low to moderate partial pressures of CO₂ (3–20%) [95] and is seen as the most developed method [106]. Its main drawbacks are the corrosion by some absorbents and need of heat for absorbent regeneration [107,108]. However, the last issue can be solved through the use of the heat released from the methanation process. The physical absorption requires costly high pressure for the CO₂ separation and is not well suited for the separation of CO₂ from dilute sources [85]. However, the regeneration by heating or reduced pressure is less energy intensive than in the case of chemical absorbents. The physical absorbents are in addition non-corrosive. In contrast to absorption, in which the absorbed component enters into the bulk of the solvent and forms a solution, adsorbed molecules remain on the surface of the adsorbent in the adsorption process. Consequently, the adsorption process is characterized with relatively low efficiency [100]. On the other hand, the adsorbents are sensitive to high temperature. Their capacities decline fast with increasing temperature. Moreover, in the case of physical adsorption the selectivity between different gases (such as CO₂-N₂ mixtures) is low, which makes capture from sources containing low CO₂ concentrations impractical. The membrane technology is still far away to realize its potentialities for CO₂ separation, although there are significant developments, and it has been found many current commercial applications in industry (e.g. hydrotreaters in refineries and O₂/N₂ separation) [78]. Cryogenic distillation is widely used for the separation of other gases such as N₂ and O₂ [109,110]. However, it is very energy intensive in its operation [111]. Table 3 summarized (further) advantages and disadvantages of the discussed CO₂ separation processes.

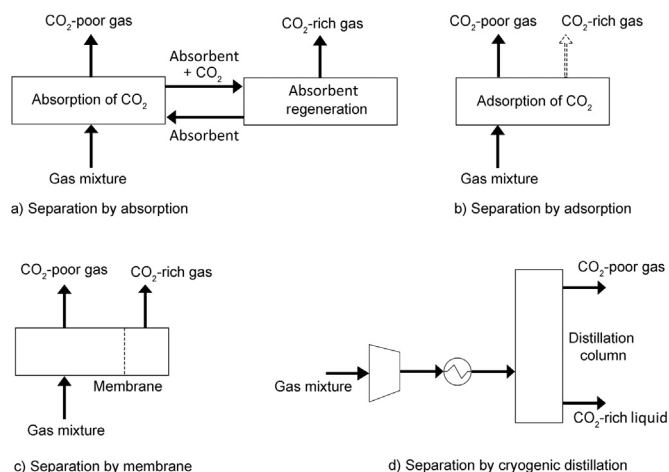


Fig. 7. Simple representation of CO₂ separation processes.

Table 3
Advantages and disadvantages of the aforementioned CO₂ separation processes [85,95,112–117].

Process	Advantages	Disadvantages
Chemical absorption:		
Amines	Mature.	Corrosion; amine degradation; high energy consumption.
Aqua ammonia	No equipment corrosion issues.	Equipment plugging due to solids formation upon CO ₂ capture; high ammonia vapor losses during stripping.
Sodium carbonate	Low equipment corrosion rate.	Slow absorption rate of CO ₂ .
Physical absorption	No equipment corrosion issues.	High operating pressure; not well suited for the separation of CO ₂ from dilute sources.
Adsorption:		
Activated carbons	Fast kinetics; high thermal stability; low costs.	Low CO ₂ capacity at low pressure.
Zeolites	Fast kinetics.	For complete regeneration, desorption must occur via the energy and time intensive temperature swing approach.
Amine functionalized adsorbents	Fast kinetics; adsorption capacity minimally impacted by CO ₂ partial pressure.	Degradation at temperatures around 100 °C; a temperature swing approach is needed for desorption.
Metal organic frameworks	High thermal stability; adjustable chemical functionality.	Low CO ₂ selectivity in CO ₂ –N ₂ gas streams; lack of experimental data on performance after multiple adsorption–desorption cycles.
Membrane	No regeneration step; low capital costs; compact design.	Gas stream must be compressed to 15–20 bar for efficient separation; high temperature of flue gas degrades organic membranes; single stage membrane systems are not capable of high CO ₂ capture efficiency.
Cryogenic distillation	No regeneration step; CO ₂ available at high pressure.	High energy consumption.

3.2.6. CO₂ separation projects

Table 4 lists a number of CO₂ separation projects that are currently planning, constructing and operating around the world.

4. CO₂ methanation

By the methanation process, H₂ and CO₂ are converted to CH₄ and H₂O. The process can be carried out chemically or biologically [119]. The second route is known in biogas production in which two main reaction paths can be distinguished: the acetoclastic methanogenesis and the hydrogenotrophic methanogenesis [120,121]. The last path results in the production of CH₄ from CO₂ and H₂ [121]. The biological methanation has positive characteristics such as operation at moderate temperatures (30–60 °C) and atmospheric pressure as well as a high tolerance against pollutant substances in the feed gas [122–124]. However, the process suffers from very slow kinetics, poor mass transfer, and low flexibility. In this paper, only the chemical methanation that is the most discussed technology will be considered. First, thermodynamics is described; then, catalysts are discussed; finally, reactors are evaluated.

4.1. Thermodynamics of the CO₂ methanation

The reaction equation of the chemical methanation (hereinafter called methanation) of CO₂ is expressed as follows [125]:



Table 4
CO₂ separation projects [118].

Project name	Location	Sector	Operation date	Separation process	Annual CO ₂ separated (million tonnes)
Sinopec Shengli Power Plant CCS Project	China	Power generation	2020's	Amine	1.0
Riley Ridge Gas Plant	United States	Natural gas processing	2020	Amine	2.5
Rotterdam Opslag en Afvang Demonstratieproject	Netherlands	Power generation	2019–20	Amine	1.1
Gorgon Carbon Dioxide Injection Project	Australia	Natural gas processing	2017	Amine	3.4–4.0
Petra Nova Carbon Capture Project	United States	Power generation	2017	Amine	1.4
Abu Dhabi CCS Project	United Arab Emirates	Iron and steel production	2016	Amine	1.0
Boundary Dam Carbon Capture and Storage Project	Canada	Power generation	2014	Amine	1.0
Petrobras Santos Basin Pre-Salt Oil Field CCS Project	Brazil	Natural gas processing	2013	Membrane	1.0
Snøhvit CO ₂ Storage Project	Norway	Natural gas processing	2008	Amine	0.7
Sleipner CO ₂ Storage Project	Norway	Natural gas processing	1996	Amine	1.0

During the synthesis, the carrier of chemical energy is converted, from H₂ with low chemical energy density to CH₄ with high chemical energy density. The efficiency of the conversion amounts to 83% relating to lower heating value at the Standard Conditions, whereby the remaining 17% is released as heat. On the other hand, the reaction of the methanation is exothermic and its change in moles is negative, therefore the synthesis is thermodynamically favored towards products at low temperature and high pressure.

By-products can be generated during the methanation. Mihet and Lazar [126] investigated the methanation on Ni/Al₂O₃, Ni-Pt/Al₂O₃, Ni-Pd/Al₂O₃ and Ni-Rh/Al₂O₃ catalysts experimentally. They reported that CO was formed in addition to CH₄ and H₂O. Frick et al. [127] reported that carbon and hydrocarbons are also generated but in small amounts. Fig. 8 shows the mole fractions of CH₄, H₂O and by-products in thermodynamic equilibrium depending on temperature at different pressures and initial molar composition of 80% H₂ and 20% CO₂. It can be deduced that the CH₄ yield increases with decreasing temperature and increasing pressure as stated above. The formation of CO as by-product is suppressed with decreasing temperature and increasing pressure, while that of hydrocarbons (C_nH_{2n} and C_nH_{2n+2} with 2 ≤ n ≤ 5) falls with decreasing temperature and pressure.

The formation of carbon leads to the fouling of catalyst surface and the blockage of catalyst pores [128]. Thermodynamically, carbon is formed at understoichiometric H₂-to-CO₂ ratios. Fig. 9 reveals this impact graphically and the impact of temperature. It can be seen, that the formation of carbon thermodynamically is suppressed with increasing temperature and H₂-to-CO₂ ratio.

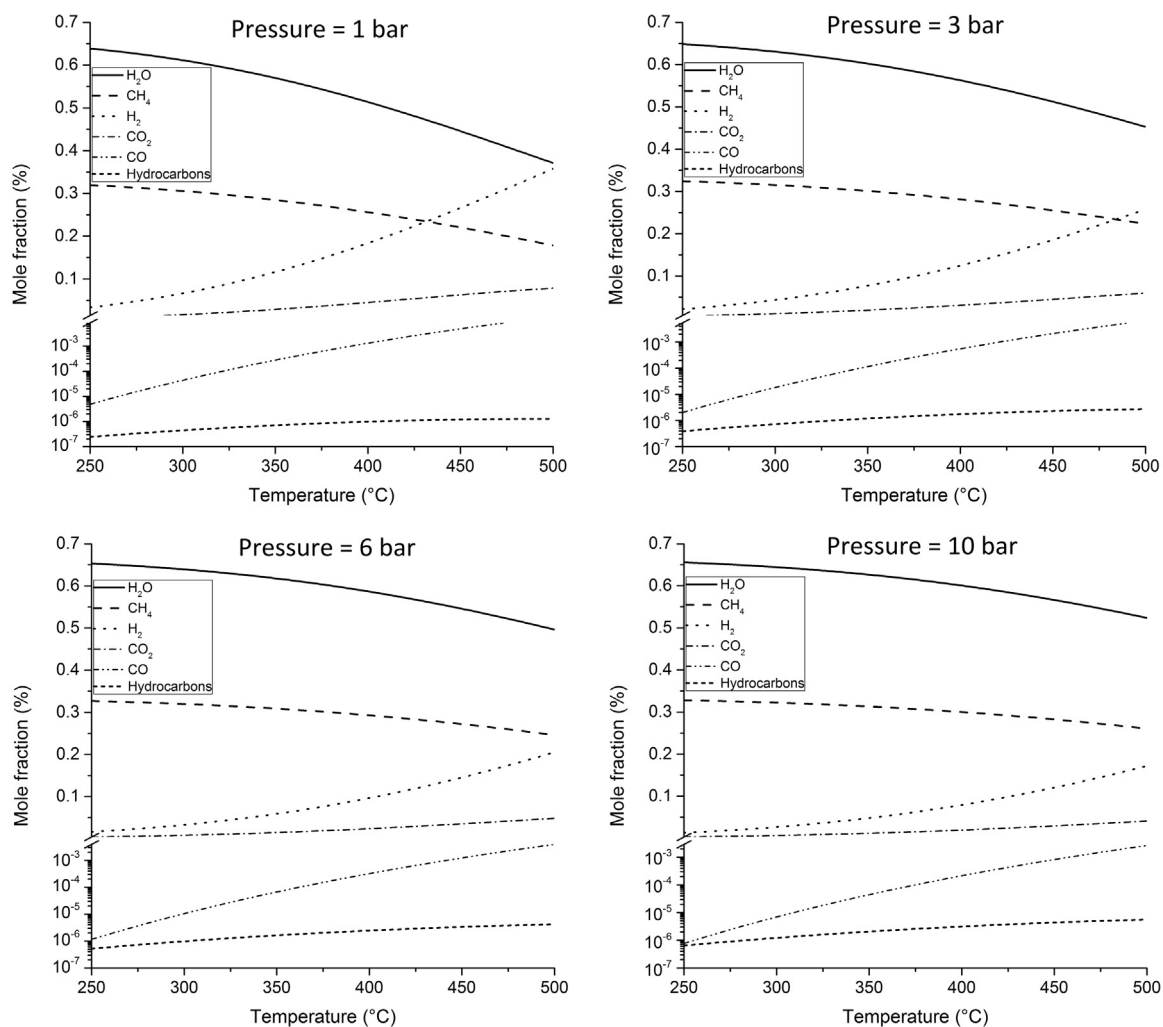


Fig. 8. Effect of temperature and pressure on mole fractions of H₂, CO₂, CH₄, H₂O and by-products in thermodynamic equilibrium at initial molar composition of 80% H₂ and 20% CO₂; hydrocarbons: C_nH_{2n} and C_nH_{2n+2} with 2 ≤ n ≤ 5.

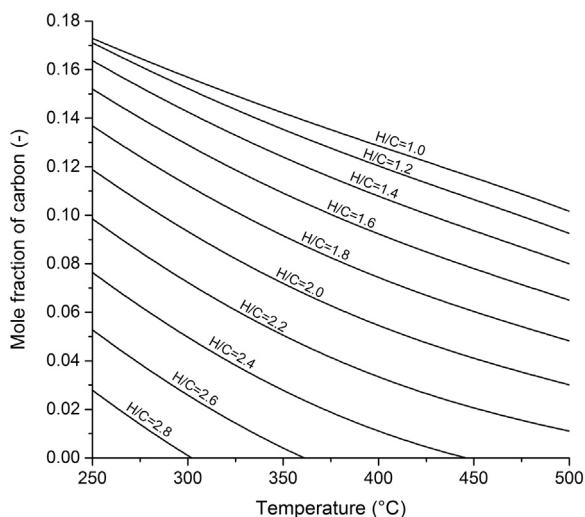


Fig. 9. Effect of temperature and initial H₂-to-CO₂ ratio (H/C) on the generation of carbon at 10 bar of thermodynamic point of view.

It can be concluded that the higher the pressure and the lower the temperature, the more favorable the methanation thermodynamically. However, high operation pressure is not economical, and low operating temperature requires a sufficiently high active catalyst, which is

currently one of the challenges for developing catalysts for methanation. A techno-economic compromise must be found.

4.2. Catalysts

The reduction of the fully oxidized carbon (+4) to methane (-4) is an eight-electron reaction. Consequently, the kinetic barrier is high and, thus, the reaction needs effective and efficient catalysts [129]. On the other hand, the catalyst must provide high thermal stability as well as good resistance to coke formation. Table 5 displays catalyst systems confirmed as active for the methanation reaction.

The catalyst system most used for the methanation reaction is Ni/Al₂O₃. Ni provides high activity and CH₄ selectivity, and is relatively

Table 5
Catalyst systems used for the CO₂ methanation.

Support	Metal	Refs.
Al ₂ O ₃	Ni; Pd; Rh; Ru/Mn/Cu, Ru/Mn/Fe	[130–136]
CeO ₂	Ru	[137]
CeO ₂ - ZrO ₂	Ni	[138]
La ₂ O ₃	Ni	[139]
MgO	Ni	[140]
SiO ₂	Co, Fe, Ni	[141–144]
TiO ₂	Ni, Ru	[140,145]
Zeolites	Ni	[146]
ZrO ₂	Ni	[147]

cheap. The main disadvantage of Ni is its high tendency to oxidize in oxidizing atmospheres like the other non-noble metals (Fe and Co) [27,148]. In addition, nickel carbonyl, which is very toxic to the human organism, can be formed [149–152]. Fe is very cheap [153]; however, it shows low CH₄ selectivity [154]. Co shows lower activity and is more expensive than Ni [154,155]. Consequently, the metal has not received so much attention [156]. Ru belonging to noble metals offers positive characteristics such as high activity, CH₄ selectivity (also at low temperatures) and high resistance to oxidizing atmospheres [157–160]. The main drawback is its high price that limits its application. Rh also offers high activity and high selectivity toward CH₄, but its price is also high. Pd is the least appropriate noble metal for the methanation.

The activity of a catalyst system is influenced by the support material [161,162]. Selecting the right material is thus an important factor for an efficient methanation. As mentioned above, Al₂O₃ is the most used support due to its ability to finely disperse metal species and its relatively low price. Recently, Ce–Zr binary oxide has been denoted as one of the most promising catalyst support for methanation because of its advantages, including unique redox property, excellent thermal stability, and resistance to sintering [163,164].

In order to enhance the performance of catalysts, promoters are added to modify the surface basicity (decreasing activation energy) and metal-carrier interface (better resistance to extreme conditions) as well as to improve the metal dispersion. E.g. when using Al₂O₃ or SiO₂ support with Ni or Ru metal, the addition of CeO₂ improves the activity and selectivity of the systems [165–167]. The better performance promoted by CeO₂ are attributed to its high capacity for metal dispersion and to its propensity to create oxygen vacancies. Further examples are given in Refs. [126,168–178].

Regarding the mechanism of methanation, this can be categorized into two types: mechanism with CO as intermediate [142,179–181] and that without forming CO as intermediate [138,182–187]. The first one consists of the reduction of CO₂ to CO followed by the conversion of CO into CH₄. The second one consists of the methanation through carbonates and formates, which are directly hydrogenated into CH₄.

4.3. Reactors

The methanation is a relatively high exothermic reaction. Fig. 10 demonstrates the average heat flow to reactor volume to be dissipated in methanation process as function of CO₂ conversion at different gas hourly space velocities (GHSV), initial molar composition of 80% H₂ and 20% CO₂ and 300 °C. However, it must be noted that heat dissipation gradients are formed inside reactors. Their variations depend on the catalyst activity. As a consequence, heat management is very important in reactor design. On the other hand, the methanation is thermodynamically limited at elevated temperature while it is kinetically limited at low temperature as discussed above. In summary, heat dissipation and temperature control are the key parameters in designing methanation reactors.

Various reactor types [27,131,146,152,154,158,159,188–193] have been adapted for the methanation. In this subsection, the most relevant ones, namely fixed-bed, monolith, microchannel, membrane and sorption-enhanced reactors (Fig. 11), are discussed.

The fixed-bed reactors are most used for the methanation [27]. They are characterized by the advantages that the contacting of the catalyst particles by the gas tends to be quite uniform, and long contact times are possible. They are designed adiabatic [194] or polytropic [190].

The adiabatic version is a cascaded process, in which multiple adiabatic reactors are used that operate in series and use heat exchangers between each reactor to the next downstream reactor to cool the process gas to the desired inlet temperature in order to obtain high CO₂ conversion [195]. In the reactors, the catalysts are packed in static beds, and the process reacting gas is then passed through the beds, where the reactions are induced as the gases contact the catalyst (Fig. 11a). The adiabatic reactors are relatively simple and cost-effective systems. Additionally, in the systems, the

methanation process can be carried out with high GHSV and steam can be produced with high temperatures in the intercoolers [196]. The main disadvantages of such reactors are the hot spots and the poor flexibility with respect to the load [197,198].

The polytropic design is a cooled tube-bundle system [199]. In this variant, a multitude of tubes of relatively small diameter are placed in parallel (Fig. 11b). While the number of parallel tubes is determined by the required production rate, the diameter of the tubes is chosen to match the required heat exchange area [200]. However, the diameter size is limited towards smaller sizes. In comparison to adiabatic reactors, the polytropic reactors exhibit lower temperature gradients that leads to an increased lifespan of the system, and a certain degree of flexibility [199]. However, the polytropic reactors are more expensive and relatively complex.

To optimize the fixed-bed systems in terms of the reactor number under the adiabatic version or the heat management under the polytropic version, different technical measures were undertaken. These are [152,194,196]:

- Recirculation of a part of the product gas to the educts or diluting the educts with water vapor.
- Partial feeding of educts at different stages along the reactor.
- Diluting the catalyst bed with inert particles.
- Designing the fixed-bed reactor as plate reactor.

The monolith reactors (Fig. 11c) have the advantages of high specific catalyst surface area, small pressure drop and short response time [201,202]. They have been widely used in exhaust gas cleaning [203]. Monolith reactors have also disadvantages: potential non-uniform gas distribution and thus lower effectiveness, and difficulty in installation of large industrial scale. The monoliths are made from ceramic or metallic materials. However, the ceramic type is brittle and cannot stand mechanical tensions. If the metallic type is chosen, its coating with the catalyst is a challenging issue (relatively short life-time).

The microchannel reactors (Fig. 11d) have the advantage of the improved hydrodynamics that suppresses the formation of hot spots and thereby the deactivation of catalysts [204–206]. In addition, their high catalyst-surface to reactor-volume ratio offers a relatively small reactor volume [207]. However, the microchannel reactors are single-use systems. In other words, if the catalyst is deactivated irreversibly, the whole reactor has to be replaced because the catalyst is fixed on the inner surface of the reactor. Moreover, their scaling-up is limited.

The membrane reactors combine reaction with separation or side feeding to increase the CO₂ conversion or improve the temperature

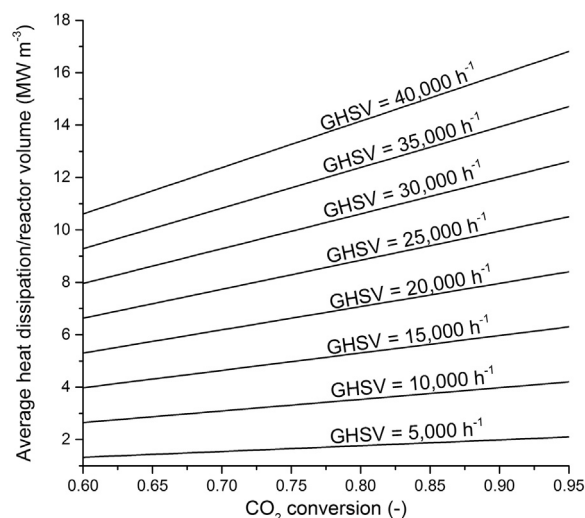


Fig. 10. Average heat flow to reactor volume to be dissipated in methanation process as function of CO₂ conversion at different GHSVs, initial molar composition of 80% H₂ and 20% CO₂ and 300 °C.

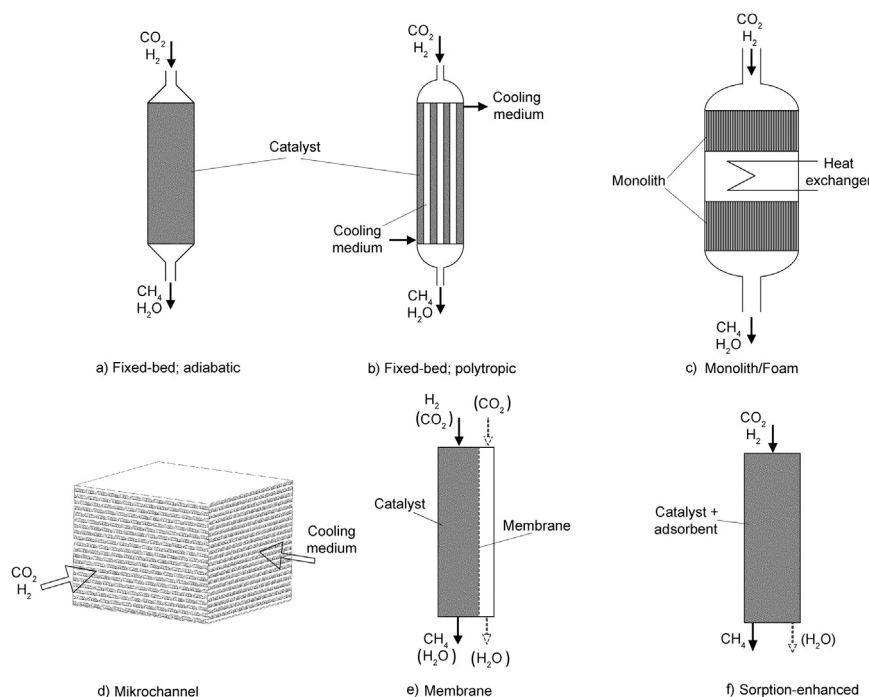


Fig. 11. Simple representation of methanation reactors.

control, respectively (Fig. 11e). Ohya et al. [189] experimentally tested a H₂O-permselective membrane to increase the CO₂ conversion, while Schlereth et al. [190] investigated the side feeding of CO₂ via a membrane to improve the temperature control. Removing H₂O during the process forces the equilibrium of the Methanation to the right side (according to Le Chatelier's principle that the conversion of reactants to products and the rate of forward reaction in an equilibrium-limited reaction can be increased by selectively removing some of the reaction products from the reaction zone), so that more of CH₄ is produced [35]. Furthermore, the product gas can be conditioned to SNG with significantly less effort. The addition of CO₂ into the reactor via a membrane leads to distributing the reaction heat along the reactor. The major disadvantage of these reactors concerns the cost of the membranes and their need to be replaced at regular intervals.

The sorption-enhanced reactor concept is already applied for several processes such as (reverse) water-gas shift and steam-reforming [208–212]. The reactor concept is also based on Le Chatelier's principle. The conversion is increased up to almost 100% by using a mixture of an adsorbent and a catalyst in the reactor. The adsorbent selectivity removes some of the reaction products from the reaction zone. The loaded adsorbent is then periodically regenerated in situ by using the principles of pressure- or thermal-swing adsorption, so that it can be re-used. For the methanation (Fig. 11f), Walspurger et al. [191] investigated the sorption-enhanced reactor concept. They used commercial nickel-based catalyst and zeolite 4 A adsorbent to capture H₂O. They demonstrated the methanation in their reactor between 250 and 350 °C, whereby they could achieve almost 100% CO₂-conversion. Further demonstration experiments can be found in Refs. [146,213]. Although the concept provides attractive advantages such as relatively high efficiency and no water condensation need after methanation; it is a complicated concept and could have short life-time due to the regeneration cycles.

Table 6 summarizes the benefits and drawbacks of the reactors discussed. Except the fixed-bed reactors, the other reactor concepts are at the development stage. Their technological and economic feasibility for the application in the PtM process must first be demonstrated. For the CO₂ methanation, fixed-bed reactors are offered on the market, e.g. from Outotec, EtoGas and MAN [154].

5. PtM plants

In the last three sections, the processes of the PtM process chain were discussed. They can be seen as developed. However, there is to date little experience with the entire PtM system. There are few plants worldwide that take power and CO₂-containing gas and produces CH₄-rich gas. In this section, two PtM plants in operation and one in construction are addressed.

5.1. ZSW 250-kW_{el} demonstration plant

The ZSW 250-kW_{el} demonstration plant (Fig. 12) went into operation at the end of 2012 [214]. It consists of a 250-kW_{el} alkaline high-pressure electrolyzer, a methanation unit and a process control system that ensures an optimal operation [215]. The methanation unit comprises a tube-bundle reactor and a plate reactor that can be operated alone or in combination. To avoid the formation of hot spots, the tube-bundle reactor is injected with the educt gas at different stages along the reactor and cooled with a molten

Table 6
Benefits and drawbacks of reactors used for methanation.

Reactor	Benefits	Drawbacks
Fixed-bed		
Adiabatic	Simple system, low capital costs.	Hot spots; unsuitable for unsteady operation.
Polytropic	Low capital costs.	Heat management.
Monolith	Relatively high specific catalyst-surface; small pressure drop; short response time.	Non-uniform gas distribution; scale-up limitation.
Ceramic monoliths		Brittle.
Metallic monoliths		Short life-time.
Microchannel	Good heat transfer	Single-use system; scale-up limitation.
Membrane		Membrane replacements and costs.
Partial feeding of an educt	Good temperature control.	
H ₂ O permeation	High CO ₂ conversion.	
Sorption-enhanced	Almost 100% CO ₂ conversion; relatively low operating pressure.	Discontinuous process; regeneration effort.



Fig. 12. ZSW 250-kWel demonstration plant (source: ZSW).

salt [216]. For the plate reactor, cooling of the main reaction zone takes place by the evaporation of water in the thermal plates [217]. For increasing the methane content in output, water vapor is removed between the reactors by a condenser or the output gas is upgraded by membrane unit separating H_2 . In the second case, only single-stage methanation is operated [217].

5.2. Audi e-gas plant

The Audi e-gas plant (Fig. 13) is an industrial PtM facility. It was commissioned in the fourth quarter of 2013 [218]. CO_2 is captured from biogas by amine absorption. H_2 is generated by three alkaline electrolyzers with a total capacity of 6 MW powered by an offshore wind park in the North Sea [219] and stored in a tank at approximately 10 bar before it is fed into the methanation reactor [220,221]. The intermediate storage of hydrogen allows a temporary decoupling of the unsteady operation of the electrolyzer from methanation reactor [217]. The methanation process takes place in a single tube-bundle reactor cooled with a molten salt. In order to avoid the formation of hot spots, the educts are fed at different stages along the reactor. The product gas is dried and fed as SNG into the natural gas grid in Werlte. It is prognosticated that the plant can be operated with surplus power for 4000 h per year. The heat released from the methanation reactor is used to regenerate the amine absorbent [217]. Performance data of the Audi e-gas plant are given in Table 7.

Table 7

Performance data of the Audi e-gas plant [222].

	Value
Specific energy of SNG on average	13.85 kW h
Annual electricity consumption (prognosis)	26–29 GWh a ⁻¹
Power to SNG efficiency (without using heat)	54%
Maximum H_2 output from electrolyzers	1300 N m ³ h ⁻¹
Maximum H_2 storage time	60 min
Maximum SNG output from plant	325 Nm ³ h ⁻¹
Annual operation time (prognosis)	4000 h a ⁻¹
Annual SNG production (prognosis)	1000 t a ⁻¹

5.3. HELMETH project

Within the HELMETH project, a highly efficient PtM-plant is realizing, and will input into operation in 2017 according to Ref. [223]. The concept developers aim to achieve an ambitious conversion-efficiency of more than 85% from renewable electricity to SNG [223]. The concept will be based on a SOEL system (Fig. 14) and a multi-stage methanation module, whereby the both conversion units will be thermally integrated. The heat released from the methanation module will be used to vaporize water feeding to the electrolyzer that will have a capacity of 15 kW and be operated at 800 °C and 15 bar [218]. The methanation module will consist of two fixed-bed reactors in series with intermediate water removal. The reactors will be operated at 300 °C and 30 bar with Ni-based catalyst [223]. The plant is



Fig. 13. Audi e-gas plant (source: EWE).

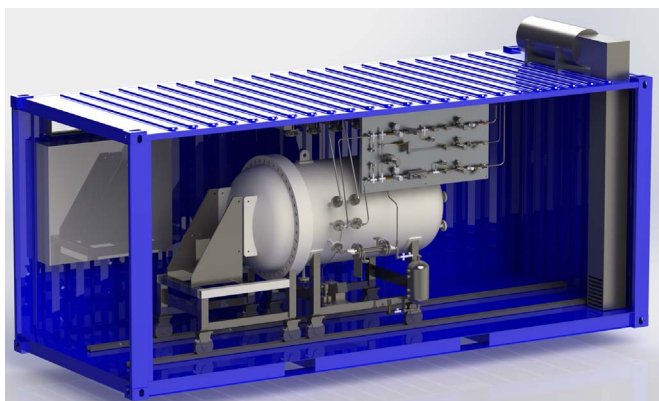


Fig. 14. SOEL system (source: Sunfire).

expected to managing partial loads down to 20% [224]. The project budget amounts to 3.8 million [225].

6. Conclusions

The world has seen a rapid growth in the development of renewable power generation, whereby the wind and solar sectors have contributed with the highest growths. Innately, the power profile generated from both energy sources and the human power demand profile cannot match together. For mitigating the mismatch, energy storage is the most useful solution.

There are a variety of energy storage technologies available on the market or under development. In regions, where a natural gas infrastructure exists, the PtM technology is seen as attractive option to absorb excess renewable energy. The methane-rich gas produced can be used for power generation at times, when the power demand overbalances the power supply, for heat generation and as fuel, having a holistic approach to the energy sector. In addition, it can be used as raw material in industry.

The PtM concept includes the main process steps: water electrolysis, CO₂ conditioning when this is not available as pure gas or in suitable gas mixtures, and methanation. There are three known electrolysis technologies, which are named after their electrolytes: AEL, PEMEL and SOEL. The AEL technology is characterized with relatively good technical and economical characteristics. However, the corrosion will remain its traditionally drawback. PEMEL exhibits an elevated power-to-hydrogen efficiency, relatively short response time and large dynamic range, being with its advantages more attractive for PtM. The PEMEL technology is however relatively expensive and has lower durability. The SOEL shows the most promising power-to-hydrogen efficiency level, but it is still in the development phase and considerable progresses are still required.

CO₂ can be won from biomass plants, power generation plants, industrial processes and ambient air. Often, CO₂ is not available as pure gas or in suitable gas mixtures. Therefore, CO₂ must be separated. A number of separation technologies could be employed. These include: absorption, adsorption, membrane and cryogenic distillation.

The methanation is the second and last conversion process of the PtM process chain. The process is favored with decreasing temperature and increasing pressure. On the other hand, the process can be accompanied by the formation of by-products such as CO, carbon and hydrocarbons. However, using a suitable catalyst the methanation can specifically be accelerated and, therefore, a high selectivity of the CO₂-to-CH₄ path can be achieved. Various metals have been tested for the catalysis of methanation reaction. It has been proven that many metals of group VIII B in the periodic table of elements can catalyze the methanation of CO₂. On the other hand, the activity of a catalyst is influenced by the support material. Selecting the right material is thus an important factor for an efficient methanation. Al₂O₃, SiO₂, ZrO₂, CeO₂, La₂O₃, MgO, and zeolites are confirmed as possible support materials. The formation of methane is a very exothermic process favored at low temperature, therefore heat

management and temperature control are the key parameters in designing methanation reactors. The most discussed reactors for the methanation are fixed-bed, monolith, microchannel, membrane and sorption-enhanced reactors, whereby the fixed-type can be seen as mature concept for the methanation.

PtM might play an important role in the future energy sector. The technology can utilize surplus power and recycle CO₂. The processes of the PtM process chain are widely developed. However, there is to date little experience with the whole system. Future research must also focus on the integration of PtM into the energy sector to address the real potential of this technology.

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