

Power-to-methane, coupling CO₂ capture with fuel production: An overview

D. Hidalgo^{*}, J.M. Martín-Marroquín

CARTIF Technology Center, Parque Tecnológico de Boecillo, 205, 47151, Boecillo, Valladolid, Spain

ARTICLE INFO

Keywords:

Biological CO₂ methanation
Chemical CO₂ methanation
Catalytic CO₂ methanation
Carbon capture
Energy storage
Power-to-Gas

ABSTRACT

This paper provides a revision of the latest studies on the topic methanation, a multi-stage process where water is first converted into hydrogen in an electrolyzer, which subsequently reacts with carbon dioxide to produce methane. The present and future of the most common water electrolysis technologies is addressed. Critical issues to take into consideration when selecting a carbon dioxide source are evaluated. Chemical and biological approaches, together with photocatalytic configurations are discussed, analyzing pros and cons in all the cases. This paper also highlights the extensive work being done in the development of catalysts capable of selectively converting carbon dioxide into methane, as well as the different reactor configurations that can be used with this aim in any of the available methanation modalities. Relevant power-to-methane plants in Europe have been identified and assessed regarding their location, year of commissioning, capacity, technology for electrolysis and methanation type. Finally, cost issues are analyzed, highlighting economic perspectives of the power-to-methane technologies for the next decades. This document reviews all the key elements associated with the methanation process, revealing which aspects can pave the way for the large-scale implementation of this power generation model. In this sense, the gradual cost reduction of the equipment involved and the continuous increase in the efficiency of the processes are revealed as crucial aspects that can lead to a general implementation of the methanation concept on the way to a low carbon economy.

1. Introduction

The demand for natural gas is expected to increase in the coming decades since its use for electricity generation, heating and as a chemical raw material is on the rise [1]. In contrast, known fossil fuel reserves are expected to last only another 60 years, or even less [2,3]. This situation makes it necessary to establish a sustainable, alternative source of methane, the main component of natural gas, not based on fossil elements. This is the only way to meet the growing demand for this chemical raw material and fuel, while reducing the environmental impact associated with its use. It is estimated that the combustion of natural gas represents nowadays 20% by weight of global CO₂ emissions [4]. Of course, there are elements that can, in the future, satisfy the energy demand covered today by methane, such as the hydrogen generated during the electrolysis of water. But methane coming from methanation processes has the advantage of being a direct substitute for fossil methane (same composition, same calorific value, same needs for

transportation, management and use), which makes it to be in a privileged place to become its direct substitute. On the other hand, it should not be forgotten that the methanation process can also become a CO₂ capture process, which would contribute to solving another of today's great environmental problems, the global warming.

Sustainable production of synthetic natural gas (SNG) is a core part of the Power-to-Gas (PtG) concept. In literature, the SNG concept can refer to a fuel gas (usually methane) produced from fossil fuels such as lignite or coal, from biofuels or by using electricity with power-to-gas systems. In this paper, we will only refer to the last modality. PtG is an option to store in a combustible gas the chemical energy produced by conversion of electrical energy [5]. An electrolyzer using electrical energy divides water into its two components: hydrogen on one side, and oxygen on the other. Hydrogen can be used directly, since it is a combustible gas, or be fed into a downstream methane generation process via the Sabatier reaction (i.e., methanation). This process of converting CO₂ into methane is among the most promising and interesting

Abbreviations: PtG, Power-to-Gas; PtM, Power-to-Methane; SNG, Synthetic Natural Gas; VRES, Variable Renewable Energy Sources; AEC, Alkaline Electrolysis Cell; PEMEC, Proton Exchange Membrane Electrolysis Cells; SOEC, Solid Oxide Electrolysis Cells.

^{*} Corresponding author.

E-mail address: dolhid@cartif.es (D. Hidalgo).

<https://doi.org/10.1016/j.rser.2020.110057>

Received 27 January 2020; Received in revised form 5 June 2020; Accepted 30 June 2020

Available online 20 July 2020

1364-0321/© 2020 Elsevier Ltd. All rights reserved.

technologies for transforming electrical energy into renewable chemical energy [6]. In doing so, it is possible to overcome the considerable difficulties associated with large-scale storage, transport and use of hydrogen. It is also a new way to store renewable energy such as wind and photovoltaic, to transform biogas effectively to biomethane and to convert CO₂ to chemical feedstock and fuel [7,8]. In addition, methane has several advantages over hydrogen, as it easily liquefies, can be stored and transported more safely, and is widely used in energy intensive applications as the main component of natural gas [9]. CO₂ methanation is exothermic with high equilibrium conversion between 25 °C and 400 °C [10].

Fig. 1 gives a schematic overview of possible PtG pathways focusing on methane production, but also shows how this concept is integrated in the global objective of carbon capture and utilization, taking CO₂ as a carbon source in the synthesis of highly competitive alternative fuels and chemicals. The synthesis of CH₄ from CO₂ is the less energetically demanding reaction pathway, although it is also possible (and in some cases, also economically profitable) to extend the hydrocarbon chain to either paraffins or olefins. These can either be stored as an energy carrier instead of CH₄, or directly used as a chemical feedstock or as liquid fuels [10]. The production of electricity-based fuel for mobility, industry or households can be the main driver of the implementation of methanation processes. On a broader scope, the integration at all levels of variable renewable energy sources (VRES) is also a key driver for the implementation of PtG pathways in general, and methanation processes in particular, into different economic sectors [8]. Seasonal energy storage, by converting VRES into chemical energy transporters easily storable, is one of the main advantages. In parallel, an additional flexible load is provided to the energy system what can favor sector coupling.

This paper aims to give a brief overview on methanation, updating, analyzing and completing previous reviews and providing the reader with a structured technical description of the process in general, including technologies, projects and costs. The document highlights the fact that PtM processes could play an important role in the future energy system. This article compares the available electrolysis and methanation technologies against the stringent requirements of the PtG chain, such as the requirement for high flexibility and high efficiency throughout the system. The three most developed water electrolysis technologies to date are analyzed: alkaline electrolysis, PEM electrolysis and solid oxide electrolysis. Alkaline electrolysis is currently the most widely implemented technology; however, the other two systems may be more suitable in the future for the PtM process chain. As stated in the document, several different concepts can be followed for the methanation reaction.

For catalytic methanation, the key to the efficiency is focusing on the search for new catalysts. Another approach is biochemical conversion, where the focus to increase efficiency seems to be on facilitating mass transfer processes inside the reactors. A third option is photocatalytic methanation, with interested characteristics for its implementation on an industrial scale. Finally, all critical economic aspects of the PtG process are discussed, such as the availability of CO₂ sources or the cost of equipment. This document shows a picture of the current status of the methanation process, highlighting the opportunities that are arising and the barriers that still need to be overcome to achieve the standardization of processes and, thus, their widespread implementation.

2. Process inputs

2.1. Hydrogen from water electrolysis

Core inputs for the methanation process are hydrogen and carbon dioxide. In the absence of an abundant source of hydrogen, for example, that generated in some industrial processes [11], water electrolysis is the first part of the power-to-methane process chain. Three water electrolysis technologies are the most popular, although at different degree of development: Alkaline Electrolysis Cells (AEC), Proton Exchange Membrane Electrolysis Cells (PEMEC) and Solid Oxide Electrolysis Cells (SOEC). Table 1 shows their main characteristics. AEC is the predominant and widely used water electrolysis technology for large-scale industrial applications [13]. AEC systems are commercially available and show durability and a comparatively low capital cost because no noble metals are used and the stack components are mature [14]. However, low operating pressure, load ranges, corrosion and low density affect the hydrogen production costs and system size in a negative way. Nowadays the research trends in AEC systems are focused on increasing the working pressures and the operating density, as well as the modification of the system design for achieving dynamic operation (varying power input and frequent starts/stops) and to allow operation with intermittent renewable sources [15]. General Electric was the first introducing PEMEC system in the 1960s to overcome the drawbacks associated with the performance of AECs [16]. These systems are based on the concept of 'solid polymer electrolyte', promising materials for electrochemical device applications, as water electrolysis [17]. The technology is not as mature as AEC and is normally used for demo-scale applications [18]. The main advantage of PEMEC systems is the efficiency of the cells together with their flexible operation. This characteristic makes PEMEC the best option for PtM plants to absorb amounts of intermittent energy

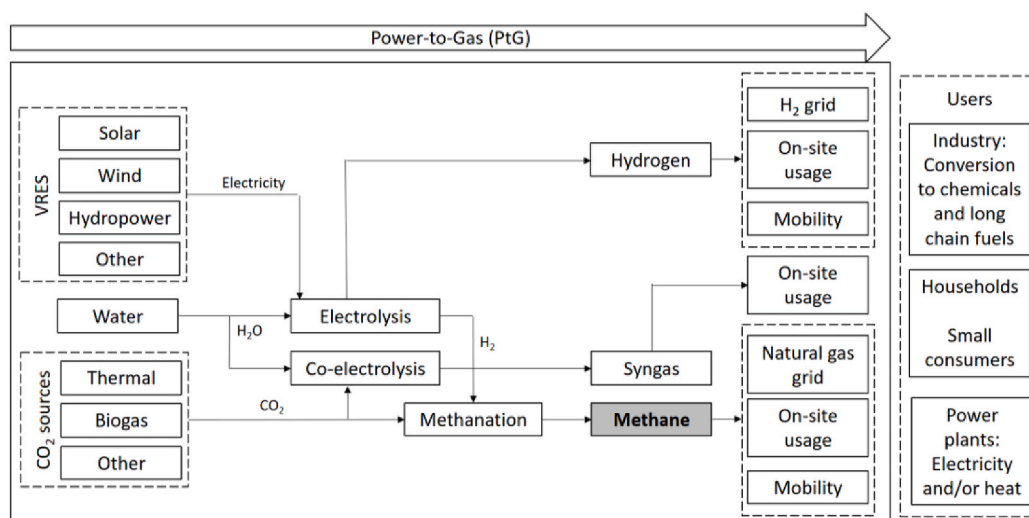
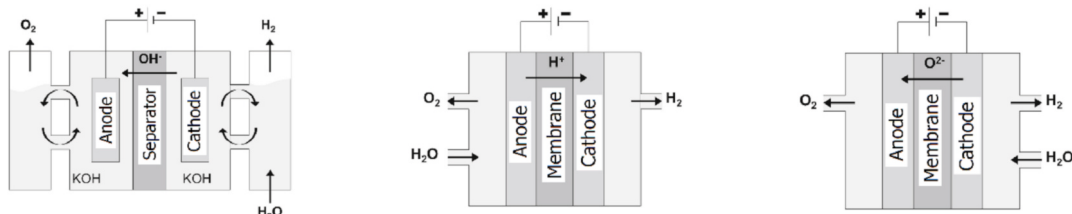


Fig. 1. Overview of Power-to-Gas concept.

Table 1

Main characteristics of three electrolysis cell technologies: AEC, PEMEC and SOEC. Adapted from Ref. [12].

	AEC	PEMEC	SOEC
Set-up			
Electrolyte	Aq. Potassium hydroxide	Polymer membrane	Yttria stabilised Zirconia
Cathode	Ni, Ni–Mo alloys	Pt, Pt–Pd	Ni/YSZ
Anode	Ni, Ni–Co alloys	RuO ₂ , IrO ₂	LSMb/YSZ
Operating T ^a	60–80 °C	50–80 °C	650–1000 °C
Operating P	<30 bar	<200 bar	<25 bar
Production (m ³ H ₂ h ^{−1})	<760	<40	<40
Gas purity	>99.5%	99.99%	99.9%
Maturity	Mature	Commercial	Demonstration
Capital Cost (€ kW ^{−1})	1000–1200	1860–2320	>2000

[19]. PEMECs are also able to supply highly compressed and pure hydrogen and are characterized by a high power density. On the other side, their disadvantages include the high price of the materials, the operational complexity associated to the high pressure, and a shorter lifespan than the AEC [20]. Therefore, costs reduction efforts are aimed at using less expensive materials to low capital costs [21]. SOEC is the most recent development in electrolysis technology. The system has been demonstrated on a laboratory scale with promising results [22]. SOEC uses solid ion-conducting ceramics as an electrolyte, which allows operation at high temperatures. Positive aspects include the interesting possibility to operate in reverse mode as a fuel cell or in co-electrolysis way producing synthesis gas from carbon dioxide and water, apart from low material cost and high electrical efficiency [23]. As the system works at high temperatures, a challenge to face is the fast degradation of the components. Therefore, current research to finally reach the market focuses on developing new materials and reducing the operating temperature [24].

2.2. Carbon dioxide from residual streams

The future of bioenergy depends mainly on the supply and demand of the different countries that are partly triggered by climate policies. In this sense, the combination of bioenergy production with carbon capture and sequestration is a practice that is expected to spread in the EU in the coming years, supported by environmental and energy policies. The role of bioenergy in general, and methanation in particular, in decarbonization strategies is an aspect broadly discussed nowadays [25]. CO₂ is the second core input for the methanation process. This compound is very abundant in residual streams, and even in the air. The CO₂ for methanation processes can be obtained from power generation facilities (fuel combustion), waste treatment facilities, biomass plants, cement plants, industrial processes, as steel-making plants, and ambient air [26]. The energy and industry sectors together produce more than one third of global CO₂ emissions [27]. Capturing CO₂ from these sectors is technically feasible, however, economically, it depends on the production conditions of the exhaust gases (mainly, partial pressure) [28]. The biogas generated in anaerobic digestion facilities of slurry or waste can be injected, after cleaning to eliminate harmful trace components such as hydrogen sulfide, into a methanation reactor [29,30]. The biogas upgrading plants generate a good quality CO₂ that can be used in methanation without additional cost [31,32]. Other relevant CO₂ sources are iron and steel manufacturing, chemical processes and cement production, in which CO₂ is frequently generated as a byproduct [33–35]. Another key source of CO₂ is ambient air. A great advantage of

this source is that CO₂ transport to the site of the methanation plant is not required, however, due to the very low partial pressure of CO₂ in the air, separation costs are usually high [36,37].

Another issue to take into consideration is that CO₂ in most common sources usually appears blended with other elements (hydrocarbons, CO, H₂S, NH₃, N₂, etc., the specific composition of the mixture will depend on the origin of this CO₂ source), being a component of a gas mixture, so a separation process is needed. The optimum CO₂-separation process differs from the point of view of emission scale, pressure or concentration. Five technologies are the most frequently used in CO₂ separation, some of them at pilot or demonstration level and others commercially available: chemical and physical absorption (scrubbing), pressure swing adsorption (PSA), water absorption, and separation with membranes (gas-gas membranes and membrane contactors or gas-liquid membranes) [38]. In biogas upgrading, for example, water scrubbing has traditionally been the most popular upgrading technology with 40% share years ago, followed by chemical scrubbing and PSA with 20% share each. However, nowadays, membrane separation competes for the first place with water absorption. Use of membranes has increased to make this one of the market leading technologies in CO₂ separation in this sector since 2014/2015 [39]. In more traditional sectors, as power or cement sectors, the absorption (usually chemical) is the preferred method for capturing CO₂ from gas streams since this method is considered well established and developed [40]. Amines are the most popular chemicals for CO₂ capture here, since their moderate interaction allows effective “catch and release” [38]. However, this kind of organic solvent also has a number of disadvantages: the amine solutions are corrosive, have a high vapor pressure, and, very important from the economic point of view, need high energy for recovery (regeneration) [41]. It is expected that these “more traditional sectors” move in a near future also to more competitive CO₂ separation technologies. Advanced membrane-based capture systems have been found the most promising option in terms of overall techno-economic metrics across a range of CO₂ removal levels and other design parameters. However, these techno-economic advantages depend on the availability of advanced membranes with high CO₂ permeability (>2000 GPU) and a good selectivity (>30) in large-scale industrial applications, such as large-scale power plants [42].

3. Methanation process options

3.1. Chemical (catalytic) methanation

Nowadays, heterogeneous catalytic methanation is the most

common way to achieve CO₂ methanation. In this approach, the process is carried out through two successive stages. The first one is the electrolytic division of water into molecular O₂ and H₂ using electricity proceeding from a renewable source. Then, CO₂ is converted to CH₄ by using H₂ as a reducing agent. In this type of chemical methanation, solid-phase metal catalysts, such as Co, Rh, Ru and Ni, supported on metal oxides, such as ZrO₂ or Al₂O₃ are commonly used to achieve the reduction of CO₂ to CH₄ [43]. Ni is the catalyst selected in most of the methanation plants due to its low cost, good CH₄ selectivity and high activity. Common operating pressures are between 1 and 100 bar, with temperatures ranging from 200 to 550 °C [44]. In any catalytic reaction, the potential interest of a catalyst is always defined by the selectivity of the product, together with the stability and activity of the selected material [10]. Once the CO₂ is obtained, its high stability can complicate the later conversion. The C=O bond is chemically stable and has a dissociation energy of approx. 750 kJ mol⁻¹, which requires catalytically active materials for CO₂ reduction, apart from an equivalent high energy input. This high energy demand appears as a constrain in the performance of the technologies available for hydrogenation of CO₂ to CH₄ at large scale. With respect to product selectivity, a variety of routes has been developed for the selective use of CO₂ towards CH₄ [45,46]. Alternatively, the conversion of CO₂ can be directed towards the formation of the mixture (CO + H₂), i.e. syngas. The implementation of two-step cascade processes is an interesting attempt taking into account the viability of posterior industrial options, for example, fermentation technologies for syngas, Fischer-Tropsch pathways or the production of alcohols or methane [47].

Evaluating and revealing the possible mechanistic routes allows the optimization of CO₂ transformation rates by the minimization of kinetic or thermodynamic barriers associated to intermediate reactions, and by permitting an improvement in the general selectivity of the product [10]. For example, the reduction of the fully oxidized carbon (from CO₂) to hydrocarbons (CH₄ and others) is a reaction highly limited by the transfer of the electrons. The idea behind this statement is that there are several possible routes for the transformation of CO₂ into CH₄ (and other hydrocarbons) and with a deep understanding of these chemical mechanisms, it is possible to select the most favorable option in terms of thermodynamics and kinetic requirements. When CO₂ is reduced to CH₄ in the presence of H₂, the latter easily dissociates over the metal phase that must be well dispersed. It is on the support itself where the hydrogenation of the carbon intermediates involved in the process takes place. Mechanically, it has been recognized that the reduction of the CO₂ molecule depends significantly on the catalyst selected, the operating conditions the type of support, and the CO₂ to H₂ ratios [46]. Kattel et al. [48] have proposed possible ways for the conversion of CO₂ to CH₄ on metal/oxide catalysts. The proposed pathways reflect a similarity with the synthesis of alcohols during hydrocarbon production, which can be a key point where acting in the production of new selective catalysts. The pathways followed by the reaction that involve the conversion, in a first phase, of CO₂ to CO, followed by a stage of methanation of intermediates (CO*) previously adsorbed, have been extensively investigated, especially by researchers dealing with Ni/Al₂O₃ catalysts [49–51]. The level of stability of the intermediate CO* defines whether the molecule will undergo further reduction or just desorb. It has been suggested that the reduction of CO* follows two different routes: (i) the dissociation of CO* in oxygen and carbon species that are then hydrogenated to water and CH₄, respectively, and; (ii) H₂-promoted transformation of the CO* to COH* or HCO*. Although there is a common formation of CO* as an intermediate, lower activation energies and a higher CH₄ selectivity have been reported when the atmosphere changes from CO to CO₂ [52].

The search for suitable catalysts for the methanation process has essentially been focused on alloy-based or metal catalysts embedded on metal oxides. Despite the dependence of CO₂ activation and the mechanistic pathways on the type of support used [53], it has been found that catalytic activity in metal oxide systems evaluated individually, as Al₂O₃, ZnO, CeO₂, MnOx, and ZrO₂, is limited [54,55] due to the absence

of H₂ dissociation sites. On the contrary, the selectivity of the product is markedly defined by the selected metal, and the reaction is preferably driven to CH₄ or long chain hydrocarbons based on the emerging catalytic fingerprints of the incorporated metal element [10]. Catalysts based on Ni, Ru, Co, Pd, Rh and Pt selectively support the formation of CH₄ under specific operating conditions. Research efforts have focused simultaneously on improving the selectivity, stability and activity of these systems [56–60]. For the production of methane at moderate or even atmospheric pressures, most of the works assessing the direct route of CO₂ to CH₄ in the presence of H₂ have been carried out at relatively high temperatures (>300 °C), which supposes a great inconvenience to achieve relevant reaction rates [61]. CO₂ methanation is highly exothermic but requires the incorporation of catalysts showing high activity at low temperature ranges in which unwanted endothermic reactions are suppressed. Table 2 summarizes the behavior of the most common catalysts used in the production of methane by chemical methanation.

Catalysts systems incorporating Ni are the most broadly studied due to their high effectiveness and moderate cost [10]. It has been proven that the slow adsorption of CO₂, results in a greater H₂:CO surface ratio, and consequently favors the selective production of CH₄ over other compounds, such as long-chain hydrocarbons [62]. However, this Ni-rich catalysts show an activity lower than Pd or Ru-based systems, and present other disadvantages, as a quite intense activity decrease due to carbon deposition and Ni poisoning and sintering when operating at elevated temperatures [26,63]. For these reasons, a research objective in this field is the design of new Ni-based catalysts, complemented with a support of high surface area, for example, SiO₂, TiO₂, CeO₂ or Al₂O₃ with a twofold aim: to favor improved support-metal interactions, and to avoid the deactivation of the active centers of Ni [46,64]. Comparing experimentally and theoretically researched reference materials in recent decades, the catalysts based on Ru and Rh revealed a remarkable selectivity of CH₄ and catalytic activities, even close to room temperature [65]. Ruthenium reactivity is related to its boundary activity, and it is considered to depend on the oxidation state of Ru during the reaction, the catalysis temperature, the size of the particle, and the composition of the reactive mixture [54,66]. Ru/TiO₂ is broadly well-known as one of the most interesting catalytic formulations that achieves complete selectivity of CH₄ under temperatures below 200 °C and atmospheric pressure [67]. At 473 and 523 K, this formulation with TiO₂ achieves improved activities compared to MgO, Al₂O₃, SiO₂ and ZrO₂ [68]. Pd and Pt have appeared on the scene as promising catalysts for CO₂ methanation and their study is on the rise, although today there are still no results that improve those of other more mature catalysts. Pt-based catalysts reveal promising conversion levels at the cost of lower profitability [69]. In comparison, Pd shows an insignificant conversion at moderate temperatures (below 300 °C) and a preferential pathway to CO formation over CH₄ at these temperature intervals [69]. Despite its excellent hydrogenation performance and good development perspectives, the high cost of noble metals limits their large-scale industrial application [70]. Finally, the development of Co-based catalysts has appeared in recent years as a promising and profitable way to produce CH₄ with high selectivity and, above all, high activity [71–73]. Cobalt-based catalysts have traditionally been considered candidates in methanation processes aimed at obtaining long carbon chains from syngas [74]. However, when the reaction feed was changed to a mixture of CO₂ and H₂, it was shown that traditional Co-based catalysts favored the formation of CH₄ as a consequence of the low CO₂ adsorption rates on the catalyst surface due to of their thermodynamic and chemical stability [75].

Also the support plays a key role in the stability, selectivity and activity of the catalytic system. In 1979, Vannice and Garten [76] already showed that the specific activity of Pd/Al₂O₃ could be improved up to 70-fold compared to large crystallites of unsupported Pd and 35-fold compared to Pd/SiO₂ catalysts. These observations underline the importance of the incorporation and selection of a specific support and

Table 2Metal-based catalysts used in CO₂ to CH₄ conversion. Adapted from Ref. [10].

Base metal	Metal (%)	Catalyst	H ₂ /CO ₂	T ^a (°C) ^a	Selectivity (%) ^b	LHSV ^c (Lg ⁻¹ h ⁻¹)
Ni	1	Ni-MCM-41	4	500 (50%)	83	19.7
	15	Ni/RHA-Al ₂ O ₃	4	500	90	30
	10	Ni/TiO ₂	4	400	95	10,000 h ⁻¹
	10	Ni/Al ₂ O ₃	4	350	98	10,000 h ⁻¹
	15	Ordered mesoporous nickel alumina	5	350	94	91
	23	Ni/CaO-Al ₂ O ₃	4	335	100	10,000 h ⁻¹
	10	Co-Impregnated Ni-1 wt% MgO/SiO ₂	4	325	98	15
	12	Ni/ZrO ₂ -Al ₂ O ₃	3.5	325	100	8.1
	10	Ni/Al ₂ O ₃	4	300	100	20
	10	Ni@MOF-5	4	300	100	2000 h ⁻¹
	10	Ni/CeO ₂	4.6	300 (73%)	100	22
	10	NiO-MgO-Al ₂ O ₃	4	290	96	15
	10	Ni/CeO ₂ (hard template synthesis method)	4	285	100	45
	20	Ni/mesoporous nanocrystalline g- c	3.5	275	100	9
	10	Ni/CeO ₂	4	270	100	10,000 h ⁻¹
	10	Ni/CeO ₂	4	270	100	20
	10	Ni/ZrO ₂	4	260	100	20
	10	Ni/Sm ₂ O ₃	4	260	100	20
	10	Ni/Y ₂ O ₃	4	240	100	20
Pd	6.2	Pd/SiO ₂	4	450 (41%)	10.4	3300 h ⁻¹
	6.2	Pd-Mg/SiO ₂	4	450	95	3300 h ⁻¹
	6.2	Pd-Ni/SiO ₂	4	450 (51%)	89	3300 h ⁻¹
Co	3	Co/SiO ₂	4	277 (14%)	42	1640 h ⁻¹
	10	Co/ZrO ₂	4	400 (93%)	99.9 (3 MPa)	3.6
	10	Co/SiO ₂	4	400 (80%)	97.8 (3 MPa)	3.6
	10	Co/Al ₂ O ₃	4	400 (78%)	96.5 (3 MPa)	3.6
	10	Co/SiC	4	400 (78%)	96.4 (3 MPa)	3.6
	20	Co/Al ₂ O ₃	4	300	- (1.5 MPa)	5000 h ⁻¹
	20	Co4N/Al ₂ O ₃	4	230	98 (1.5 MPa)	5000 h ⁻¹
Ru	-	Ce _{0.96} Ru _{0.04} O ₂	4	450 (55%)	99	10,000 h ⁻¹
	0.80	Highly dispersed Ru NP/TiO ₂	4	140	100	4.18
	0.75	Ru NP/TiO ₂ ("wet" impregnation)	4	200	100	4.18
	5	Ru/TiO ₂ (rutile) reduced at 400 °C	4	295	100	75
	5	Ru/TiO ₂ (anatase) reduced at 400 °C	4	335	100	75
	0.89	Single-atom Ru/CeO ₂	4	295	100	120
	2.56	Ru nanoclusters/CeO ₂	4	270	100	120

^a Information compared with the reference on the temperature appropriate to achieve 60% CO₂ conversion unless other value is stated.^b Selectivity at an operating pressure of 0.1 MPa unless other value is stated.^c Liquid hour space velocities.

were subsequently confirmed with the evaluation of Pd and Rh-based systems. In this case, activities follow the following trend depending on the support used: TiO₂>Al₂O₃>SiO₂ [77]. Nowadays, support selection (e.g. zeolites, perovskites, Al₂O₃, La₂O₃, SiO₂, TiO₂, CeO₂, ZrO₂, among others), as well as the surface areas and the corresponding crystalline structures have proven to be the determining elements in the dispersion and morphology of the active phase and have a dominant influence on the final results of the catalytic reaction [78,79]. It has also been shown that calcination temperatures, as well as products used for impregnation and metal loading, define the characteristics of the precursor species generated [80]. It has been established that metal-support interfaces play a key role in the governance of the chemical and electronic properties of the resulting catalytic systems, which dominates surface chemistry and directly impact the transfer of charge and the transport of mass in the reactive molecule activation [81].

3.2. Biological methanation

Biological (hydrogen) methanation, also called biocatalytic methanation, is a highly promising approach to move the type of energy from electricity to natural gas. Biological methanation is carried out through two successive steps that coincide with those explained in the case of chemical methanation. The difference lies in the fact that, in biological methanation, CH₄ producing microorganisms are applied as biocatalysts. In a typical plant for the production of biogas by anaerobic digestion, the first step in the whole process is the hydrolysis of an organic substrate to simple monomers (monosaccharides and amino acids). Next, these monomers are converted into fatty acids

(acidogenesis), acetate, carbon dioxide and hydrogen (acetogenesis). Finally, methane is produced by aceticlastic methanogenesis (acetate depletion) and hydrogenotrophic methanogenesis (reduction of CO₂ with H₂) [82]. The production of methane directly from CO₂ and H₂ is carried out by microorganisms (archaea), which grow obtaining energy by metabolizing these two compounds anaerobically. Within the biological methanation, autotrophic hydrogenotrophic methanogens act as autocatalyst and transform the reactive gases of molecular carbon dioxide and hydrogen into water and methane [83]. Class I methanogens (*Methanococcales*, *Methanopyrales*, and *Methanobacteriales*), as well as most class II methanogens (*Methanocellales*, *Methanomicrobiales*, and *Methanosarcinales*) are hydrogenotrophs. Methanogens can be active at temperatures between 0 and 122 °C and pressures between 1 and 10 bar [84], although the most common working conditions for these systems are 20–70 °C and atmospheric pressure [19]. Autotrophic hydrogenotrophic methanogens form the most abundant group of methanogens, therefore, it is expected that the methanation process can be carried out in all existing biogas plants [85]. While catalytic-chemical methanation is already a commercial technology, the technical applications of biological methanation are currently being developed on a pilot scale [5,8,19]. Biological methanation has a reaction rate lower than chemical methanation because it works at a lower temperature and has a lower volumetric mass transfer coefficient [19]. On the other hand, the biological process has a high tolerance to impurities of the incoming gas (as NO_x, H₂S, NH₃, or particles) [86]. The advantages of this mode of methanation arise also from its synergies with the traditional anaerobic digestion process. After the reduction of carbon dioxide through the injection of hydrogen in the process, the biogas has a much higher

calorific value due to the conversion of CO_2 into CH_4 . Therefore, the process could reduce the costs of refining biogas to the quality of natural gas [87].

Two different configurations can be used for biological methanation: in-situ and ex-situ [88] (Fig. 2). In-situ microbiological biogas upgrading is carried out by addition of H_2 directly into the anaerobic digester. In this case, the internally produce CO_2 is the carbon source used for CH_4 production [89]. The other option is the introduction of carbon dioxide and hydrogen in a stoichiometric ratio of 1:4 into an external reactor operating in parallel with the anaerobic digester. Due to the additional injection of hydrogen into the reactor, biological applications of in-situ methanation usually lead to an important increase in H_2 partial pressure. There are different opinions on the real effect of this high pressure on the chemical reactions taking place in the reactor. While some authors found that the increase in the partial pressure of molecular hydrogen causes the inhibition of the acetogenesis step [90], other authors did not find any biological alteration under this increase if it occurs slowly to prevent the accumulation of intermediates [91] and if CO_2 is continuously available in the system, either by on-site production or by external addition [92]. Furthermore, the addition of H_2 produces an increase in the pH value that must be counteracted to avoid the system inhibition [85]. A good strategy in this case to control pH levels is the addition to the reactor of a pH-acidic wastewater stream (e.g. potato starch wastewater). Another key operational parameter is temperature. Several authors reported a rise on the methanation rate by increasing the temperature of the system from the mesophilic to the thermophilic state [91,93]. It is interesting to observe, how this increase in temperature levels affects the responsiveness of the whole system. The solubility of gases (in this case, carbon dioxide and molecular hydrogen) in water, clearly depends on the temperature, and the solubility of the gases always decreases with a higher temperature of the liquid phase, thus theoretically hindering the gas-liquid mass transfer. However, it seems that the effect of a lower solubility is, somehow, compensated by the lower concentration in the liquid of dissolved gases. The reason is the greater biological activity, which again increases the mass transfer between gas and liquid phases, favoring, at the same time, the reaction rate [90]. Increasing the operating pressure of the reactors could be another way to elevate the conversion efficiency of methanation systems since it positively affect the solubility of H_2 and CO_2 in the liquid phase, and reduce the size of bubble gases increasing reactive area for microorganisms [19].

The expansion of a traditional anaerobic digestion reactor to perform

in-situ CO_2 methanation requires less additional investment than building a new reactor to perform ex-situ methanation [94]. Technically, the in-situ methanation faces a major challenge: the amount of H_2 injected must be continuously adapted to the production of carbon dioxide in the anaerobic digester, which leads to high-cost associated with gas automation and measurement equipment. The productivity of in-situ systems, in terms of methane production, is very low compared to the productivity of ex-situ facilities, up to 1000 times lower according to a study conducted by Lecker et al. [83]. The reaction between carbon dioxide and hydrogen in an ex-situ reactor is not limited by the availability of these two gases, as occurs in an in-situ reactor where the injection of H_2 must be controlled to adapt at any time to the amount of CO_2 available in the biogas formed [95]. Biological methanation, when compared with catalytic methanation, is more tolerant to the presence of impurities in the feed gas. Sulphur-containing components are a well-known poison for nickel catalyst [96] and hydrocarbons can decompose at temperatures above 500°C leading to catalyst deactivation [97]. However, the microbiota of the biological reactors can adapt to the presence of impurities, without this greatly influencing their overall performance [83].

3.3. Photocatalytic methanation

This section focuses on the CO_2 methanation reaction assisted by solar or artificial light (Fig. 3). In solar methanation, light energy is introduced into the methanation process by using photocatalytic water splitting to produce H_2 . This step is common with the other methanation modalities discussed in this paper. In the second step, the methanation reaction enables CO_2 transformation via light-driven photo-electrochemical reactions. In photothermal or plasmon-driven process, photons generate high catalysis temperatures, thereby promoting the CO_2 methanation reaction. A second option is the biophotocatalytic process, where microorganisms (CO_2 -metabolizing archaea), alone or combined with inorganic material, catalyze CO_2 methanation. Finally, photoredox methanation (heterogeneous or homogeneous) that occurs because the catalyst is excited by solar light and become more reactive. Photothermal catalysis includes, as a first step, the electronic excitation of the catalyst through the absorption of light. Depending on the energy of the incident photon and the type and properties of catalyst used (such as thermal and electronic conductivity, size and shape of the catalyst/support systems), plasmonic electronic excitations can be generated, which implies a collective excitation of the electrons in the conduction

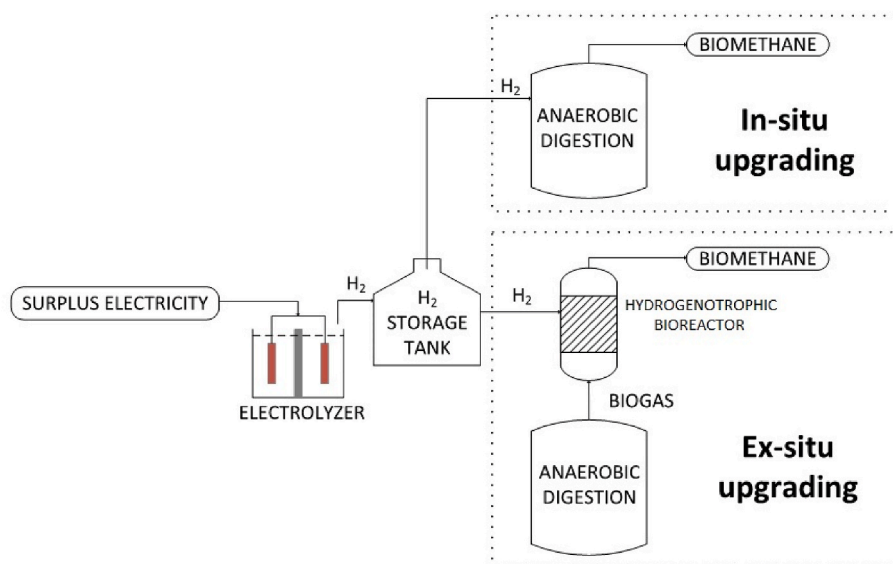


Fig. 2. Biological methanation configurations. Adapted from Ref. [88].

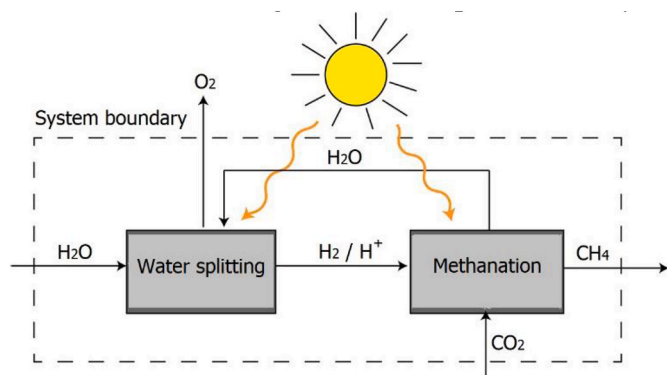


Fig. 3. Solar CO₂ methanation. Adapted from Ref. [9].

band [98]. After electronic excitation, the captured energy is converted to heat. When designing a photothermal catalyst, the first condition is to ensure that the heat is generated at the active catalytic points driving the reaction. That is why many catalysts use a support material to improve catalytic stability and activity, being the conductivities of each component, both electrical and thermal, important [99]. In addition, although they can be a barrier to heat transfer from the support, the phase limits present an opportunity for thermal energy carriers to be dispersed back into the active catalyst material, which can maximize the photothermal effect by fixing heat more effectively [100]. Plasmonic nanometals, additionally to their properties as photothermal catalysts, can start chemical reactions on the surface through the “injection of hot electrons”, where the energy of identified surface plasmons excites charge carriers on the external area of the metal [101]. The nanoscale metal catalysts used for heterogeneous catalytic methanation (e.g. Fe, Ni, Au, Ru, Pd and Rh) can also act as photothermal catalysts, as a consequence of their interesting absorption characteristics [102]. These catalysts can be supported in different materials, including TiO₂, Al₂O₃, Nb₂O₅, ZnO, or Si, among others, to improve stability and dispersion.

The type of support material selected can influence the absorption of light by the system catalyst-support. Traditional supports, such as Al₂O₃ or TiO₂, show high CO₂ adsorption capacities and high specific surface areas, which favors catalysis process. But these supports cannot be considered optimal for the collection of light since their reflection losses are high and their broadband absorption is moderate [9]. Recently, other light absorbing support materials have been studied with promising results, such as those Si-based, able to considerably enhance CO₂ methanation rates [103]. Irradiation of a photothermal CO₂ methanation catalyst could favor the behavior of this process at industrial scale. The photothermal effect would be useful to increase the temperature of a reaction system, avoiding the use of heat exchangers as a heating jacket or other systems [104]. The added benefit is the possibility of producing high local temperatures in areas very close to the catalyst, which serves to reduce distances for heat transfer when comparing to conventional heating methods, and allows faster starting times and greater loading flexibility. The effective reaction rate can be also improved by the introduction of light into a methanation reactor due to a faster activation of the catalyst. This could increase the process yield for a given reactor size or allow smaller systems to achieve the same process performance [105]. In the biophotocatalytic methanation, methane-producing microbiota (the same microorganisms than those involved in the biological methanation) or hybrid systems composed of microorganisms coupled with inorganic materials transform CO₂ into CH₄ in presence of light and water. As the reaction of CO₂ with H₂ is an exergonic process, microorganisms use it as an energy source, which is eventually stored in molecules such as ATP [9]. Since this form of CO₂ metabolism does not require photosynthesis, the generation of dihydrogen using light can be related to the formation of CH₄ using bioreactors inoculated with methanogens [106]. This method of methanation usually requires

advanced bioreactor engineering for the process to work efficiently [107]. As in the more conventional biological methanation, the low solubility of H₂ in aqueous medium and the low transport rate of involved gases, H₂ and CO₂, are the main drawbacks. Many different designs of bioreactors have been suggested in literature to get over this mass transfer problem [10,19,108]. The latest trends advocate the incorporation of inorganic components in biological reactors [105,109]. Recently, hybrid systems formed by an electrolysis cell with active microorganisms (methanogens) in the cathode compartment have been developed. These cells include a photoactive cathode coated with platinum to feed the microorganisms with H₂ and a photoactive anode of n-TiO₂ for water oxidation, providing the electrons for the production of H₂ [110]. Another hybrid cell design for hydrogen production proposes cathodes that support immobilized hydrogenases with photoactive anodes [111].

There is abundant current research on the use of microorganisms, natural or genetically modified, for the selective production of methane and other hydrocarbons [108,112]. The selective and effective transformation of carbon dioxide to methane by these microorganisms (despite the presence of impurities in the gas stream, including nitrogen oxides, hydrogen sulfide, particles or ammonia, to give some examples) makes these biological approaches very attractive [19,86]. However, it is not yet known whether inorganic components, which have a fundamental role in hybrid bioinorganic photocatalytic systems, are affected or not by the presence of impurities from the feed gas. Another challenge that arises is the scaling of these bioreactors. These systems face issues to solve very different from those presented by more conventional, homogeneous and heterogeneous, catalytic processes. That is why extensive research is still needed to make viable photobiocatalytic methanation on an industrial scale. Photoredox methanation is based on the difficulties that a catalyst in an electronically excited state has to be reduced and oxidized [113]. The photoexcited catalyst allows CO₂ to be reduced to CH₄ by redox reactions caused by light. A distinction can be made between heterogeneous and homogeneous photoredox catalysis. In the first case, it includes the utilization of several molecular components: a photosensitive molecule acting as a light absorbing agent, usually a metal complex, and a photocatalyst that is another metal complex that receives the absorbed energy and produces the reduction of CO₂. Iron [114], copper [115] and cobalt [116] metal centers are the catalytic complexes most frequently used to perform this process. Instead of the photocatalyst, there may be a sacrificial electron donor acting as an intermediary by receiving the absorbed energy and transferring its electrons to the photocatalyst, to carry out the reduction of the carbon dioxide. In heterogeneous photoredox methanation, semiconductor materials are used to produce excited electronic states that allow to generate heterogeneous redox reactions [113]. In this process, a photon with high energy excites an electron from the valence band of a semiconductor to its conduction band to initiate the oxidation of H₂O to O₂ and H⁺, while the CO₂ reduction reaction is activated by a photoexcited electron. Researchers are nowadays focusing their work on the study of photoelectrochemical cells (PEC) and composites in order to develop a material photocatalytically active and, simultaneously, able to absorb light [117–120]. Heterogeneous photoredox catalyst composites often include in their composition metals (Re, Cu, Ru, Au or Pt) linked to semiconductors (P-Si, GaN, GaP, GaAs, or TiO₂) [121]. While heterogeneous photoredox systems allow the direct conversion of CO₂ and H₂O to CH₄ in a convenient way, homogeneous systems require costly sacrificial electron donors that restrict their implementation at large-scale. More research is necessary to identify homogeneous catalysts capable of producing methane in a competitive way. Several characteristics of the photoredox methanation make it an advantageous process for its implementation on an industrial scale. Photoredox systems can favor the economic viability of full-scale CO₂ methanation by avoiding the previous production of hydrogen and thus the need for storage. Furthermore, photoredox systems operate under moderate pressure and temperature conditions, which gives advantages over

traditional heterogeneous catalytic methanation processes that are carried out at high temperature and high pressure.

4. Methanation facilities in Europe

This section intends to give a general overview on PtM plants in Europe, differing those with biological methanation implemented from those based on chemical-catalytic processes (Table 3). Plant power, when appearing, refers to the electrical capacity of the electrolyzer. Out of the 73 methane plants analyzed, 30 (41%) opted for biological methanation while 37 (51%) opted for chemical methanation. There are 6 plants in which there is no record of the type of technology used. As for the location of the facilities, the majority is situated in Central Europe, predominantly in Germany (37 plants, 51%), Denmark (13 plants, 18%), Switzerland (7 plants, 10%) and the Netherlands (4 plants, 6%). As for the installed capacity (electric power of the electrolyzers), Denmark reaches the highest amount with about 28 MWel. Germany is in the second place with 13 MWel (considering only those facilities of known capacity). It is noteworthy that the Netherlands plans to increase its capacity up to 12 MWel in 2020 and Hungary plans a 10 MWel project by 2022. The installed capacity in PtM plants has been continuously increasing during the period analyzed, from small installations in the first years, to large plants planned for the next decades. A great advance is observed between 2012 and 2015 when the number and size of the facilities grew exponentially. This exponential trend should continue supported by the energy policies that are expected in the coming years, with the European Union pursuing a proactive climate policy and integrating a significant amount of renewable technologies into the established energy system [122].

With regard to the technology used for the electrolyzer, half of the plants analyzed for which information is available use PEMEC electrolyzers, closely followed by those using AEC technology and only a few projects are testing SOEC systems. According to Schmidt et al. [12] although nowadays AEC systems predominate in most PtG facilities, most experts believe that between 2020 and 2030 PEMEC systems will become the most widespread technology for electrolysis powered by renewable generators. Although the cost of PEMEC has been reduced in recent years, it is considered that it will be only in 2030 that the costs of these systems together with a greater operational flexibility will result in a commercial advantage. On the other hand, the SOEC systems are under development but experts also expect this technology to reach the cost and service life of the AEC and PEMEC systems by 2030. Referring the reactor type, most European plants dealing with chemical methanation use fixed-bed reactors, followed by fluidized bed and three-phase systems. In the case of biological methanation, microbiota is usually confined in a liquid fermentation, both in a stirred tank (CSTR) or trickle bed reactors [5,19]. All these systems have proved to provide an interesting efficiency and scalability [10,83].

5. Process costs

Investment costs for methanation, no matter chemical or biological, are expected to decrease progressively in the next decades. According to several authors [5,12,19,123], the average investment costs for AEC electrolyzers will be reduced from, approximately, 1300 € kWel⁻¹ in 2017 to less than 500 € kWel⁻¹ in 2050, while specific costs for PEM electrolyzers will probably fall from, approximately, 1900 € kWel⁻¹ in 2017 to 500 € kWel⁻¹ in 2050. The result will be a cost decrease for both systems of approximately 75%, although the certainty of these forecasts may depend on future EU energy policies. The main reasons for the reduction in costs are expected to be the increase in automation and production capabilities, in addition to greater technological development for PtG application electrolyzers [124]. With regard to cost forecasts for the methanation stage, there is greater uncertainty. Golling et al. [125] (Fig. 4) estimated, in the case of chemical methanation, a reduction in the costs required for the process from an average of 800 €

kWel⁻¹ in 2017 to an average of 400 to 130 € kWel⁻¹ in 2050, which represents a variable cost decrease in the range of 50–84% depending on the technology used. In the case of biological methanation, these authors estimate a cost fall of 75%, from approximately 1200 € kWel⁻¹ in 2017 to 300 € kWel⁻¹ in 2030 in terms of energy consumption. All cost figures are related to the electrical power input of the system. According to these authors, the decrease in costs here would be related to an economy of scale, and greater technological development.

Gorre et al. [126], included in their cost analysis not only those cost associated with electrolysis and methanation components, but also with initial power source (wind, PV and market mix) and intermediate hydrogen storage. In this scenario, they assume a 10 MWel alkaline electrolyzer and medium pressure hydrogen storage (up to 30 bar) as a base for comparison. For hydrogen storage, the size and the necessary peripheral equipment is very variable and this will have an impact on its cost, which ultimately depends on the design and operating conditions of the system [127]. Chemical-catalytic methanation carried out in fixed bed reactor is chosen for the analysis. The study reveals that methane production costs may be reduced up to 17%, depending the situation, if the methanation capacity and the hydrogen storage size are optimized, being this cost reduction associated to reduce capital expenditures. The drawback of this optimization is the potential inability to use excess electricity since the equipment design is very tight. Generally, electrolysis is revealed as the most significant contributor to the global investment cost in PtM projects, followed by hydrogen storage. Some authors [19,128] recommend to operate with a dynamic load range of 40–100% in the methanation reactor, what is indicative of an oversize. This allows to work with smaller hydrogen storage volumes, what usually drives to process economy (even when the investment for methanation increases). When comparing costs of biological methanation versus catalytic, it is observed that for small plants (5 MW or less) the production costs for catalytic methanation are somewhat lower than for biological methanation, but when the costs for electrolysis are considered, the difference is negligible. However, for larger plants (more than 100 MW), the methane production costs for the biological option are approximately 2.5 times higher than those for catalytic methanation. In all the cases considered, hydrogen production remains the most important element in the overall costs of methane production [129].

6. Trends and perspectives

6.1. Techno-economic analysis

As highlighted in previous sections, the methanation processes are being subjected nowadays to exhaustive research since, despite the promising prospects of PtM, the technology does not come without challenges. Although there are already full-scale facilities operating, there is still room for improvement, and that is why more research is needed to promote the deployment of the PtM model in a generalized way. Economically, methane from PtM processes needs to reach a price similar to the natural gas derived from fossils in order to be competitive and occupy a relevant position on the energy scene. This is why this model requires low-price electricity sources, low specific CAPEX and a high number of operating hours (to reduce CAPEX's contribution to cost). Furthermore, from an environmental point of view, it is necessary to have a source of electricity with a low CO₂ footprint to lead to a net reduction in CO₂, representing a better environmental alternative than fossil gas. That is why the success of PtM model will be always associated with the use of biogenic CO₂ and energy from renewable sources. It should not be forgotten either that PtM is an enabling process that can provide other products and services simultaneously apart from methane, such as heat and oxygen, thus increasing the interest of the process.

Regarding the environmental performance, only the contribution of “clean” renewable electricity to the electrolysis step can generate real environmental benefits for PtM compared to conventional gas production. In particular, more than 90% of the environmental loads of the life

Table 3

Overview of Power-to-Methane plants in Europe. Adapted from Ref. [5,8].

Plant name	Location	Commi-sioning	Power (MW _{el})	Methanation type	Type of electrolyzer
Biological methanation in a trickle-bed reactor CH ₄	Donau/Tulln, AT	2016	n.a.	Biological	n.a.
MicrobEnergy GmbH	Dietikon, CH	2019	n.a.	Biological	n.a.
SolarFuel-Alpha 5th site	Rapperswil, CH	2015	0.025	Chemical	AEC
Store&Go-Project, Hybrid plant Aarmatt	Zuchwil/Solothurn, CH	2018	0.35	Biological	PEMEC
ESI Platform	n.a., CH	2016	0.1	Chemical	PEMEC
RENERG2	Villigen, CH	2015	0.1	Chemical	n.a.
COSYMA	Zürich/Werdhölzli, CH	2017	n.a.	Chemical	n.a.
Swisspower Hybridkraftwerk	n.a., CH	2018	2	Biological	n.a.
BioPower2Gas	Allendorf (Eder), DE	2015	0.3	Biological	PEMEC
BioPower2Gas-phase 2	Allendorf (Eder), DE	2016	n.a.	Biological	PEMEC
Exytron Zero-Emission-Wohnpark	Alzey, DE	2016	0.063	Chemical	AEC
Klimafreundliches Wohnen	Augsburg, DE	2019	n.a.	Chemical	n.a.
Methanation at Eichhof, SolarFuel-Alpha 4th site	Bad Hersfeld, DE	2012	0.025	Chemical	PEMEC
Direct methanation from biogas	Bad Hersfeld, DE	2017	0.05	Chemical	n.a.
GICON-Großtechnikum	Cottbus, DE	2015	n.a.	Biological	n.a.
Biocatalytic methanation	Cottbus, DE	2013	n.a.	Biological	n.a.
Forschungsanlage TU Clausthal	Clausthal-Zellerfeld, DE	2017	n.a.	Chemical	n.a.
PtG-Emden	Emden, DE	2015	0.312	Biological	n.a.
WindGas Falkenhagen	Falkenhagen, DE	2015	2	Biological	AEC
SSE	Freiburg, DE	2011	0.006	Chemical	n.a.
Biologische Methanisierung in Rieseltbtreaktoren	Garching, DE	2016	n.a.	Biological	n.a.
Smart Grid Labor	Hamburg, DE	2015	n.a.	Biological	n.a.
Einsatz der biologischen Methanisierung [...]	Hohenheim, DE	2016	n.a.	Biological	n.a.
ORBIT 2nd site	Ibbenbüren, DE	2020	0.001	Biological	n.a.
HELMETH	Karlsruhe, DE	2015	0.008	Chemical	n.a.
Research facility of the DVGW research centre at the EBI	Karlsruhe, DE	2014	n.a.	Chemical	n.a.
Lab-scale reactor in Fraunhofer IWES	Kassel, DE	2016	n.a.	n.a.	n.a.
bioCONNECT	Lemgo, DE	2016	n.a.	n.a.	PEMEC
SolarFuel-Alpha 3rd site	Morbach, DE	2011	0.025	Chemical	n.a.
CO2RRECT	Niederaußem, DE	2013	0.1	Chemical	n.a.
INFINITY I	Pfaffenhofen a. d. Ilm, DE	2020	1	Biological	PEMEC
Energiepark Pirmasens-Winzeln	Pirmasens, DE	2015	2.5	Biological	AEC
Research facility at the technical centre of the PFI	Pirmasens, DE	2013	n.a.	Biological	AEC
ORBIT 1st site	Regensburg, DE	2018	n.a.	Biological	n.a.
EXYTRON Demonstrationsanlage	Rostock, DE	2015	0.021	Chemical	n.a.
PtG am Eucolino	Schwandorf, DE	2013	0.108	Biological	n.a.
Mikrobielle Methanisierung	Schwandorf, DE	2015	0.275	Biological	PEMEC
Biogasbooster	Straubing, DE	2015	n.a.	Biological	n.a.
SolarFuel-Alpha 1st site	Stuttgart, DE	2009	0.025	Chemical	n.a.
REG-Technikum	Stuttgart, DE	2012	0.25	Chemical	n.a.
MicroPyros GmbH	Weilheim-Schongau, DE	2018	0.25	Biological	n.a.
SolarFuel-Alpha 2nd site	Werlte, DE	2010	0.025	Chemical	n.a.
Audi e-Gas-Anlage Werlte	Werlte, DE	2013	6	Chemical	AEC
Integrated High-Temperature	n.a., DE	2017	0.015	Chemical	SOEC
PtG 250	n.a., DE	2012	0.25	Chemical	AEC
Amprion, OGE	Northern NI/NRW, DE	2030	50–100	n.a.	n.a.
El-Opgraderet Biogas	Foulum, DK	2013	0.04	Chemical	n.a.
P2G-Foulum Project	Foulum, DK	2013	0.025	Biological	n.a.
MeGa-stoRE 2	Heden, DK	2018	0.25	Chemical	AEC
BioCat Project	Kopenhagen/Avedore, DK	2016	1	Biological	AEC
MeGa-stoRE 1	Lemvig, DK	2013	n.a.	Chemical	AEC
SYMBIO	Lyngby, DK	2014	n.a.	Biological	n.a.
BioCat Roslev ApS	Roslev, DK	>2020	8	Biological	n.a.
SYNFUEL	Lyngby, DK	2019	n.a.	Chemical	SOEC
Towards the Methane Society, Phase 1	Midtjylland Region, DK	2011	n.a.	Chemical	n.a.
Biogas upgrading	n.a., DK	2016	0.05	Chemical	SOEC
MeGa-stoRE Com 1	n.a., DK	2035	10	Chemical	n.a.
MeGa-stoRE Com 2	n.a., DK	2050	10	Chemical	n.a.
Greenlab Skive	n.a., DK	2020	n.a.	Chemical	AEC
RENOVAGS Project	Jerez de la Frontera, ES	2015	0.015	Chemical	AEC
Fixed bed bioreactor for biocatalytic methanation of H ₂ and CO ₂	Helsinki, FIN	2016	n.a.	Biological	n.a.
Jupiter 1000	Fos-sur-Mer, FR	2018	1	n.a.	AEC./PEMEC
MINERVE	Minerve, FR	2017	n.a.	Chemical	SOEC
HyCAUNAS Project	Saint-Florentin, FR	n.a.	2	Biological	n.a.
CymruH2Wales project	Baglan near Swansea, GB	2008	0.049	n.a.	n.a.
Electrochaea GmbH	n.a., HU	2023	10	Biological	n.a.
Ingrid-STORE&GO	n.a., IT	2016	1	Chemical	PEMEC
Energy Valley Delfzijl	Delfzijl, NL	2020	12	n.a.	n.a.
P2G Project	Rozenburg, NL	2013	0.008	Chemical	AEC
W2P2G	Wijster, NL	2014	0.4	Chemical	n.a.
Power-to-Flex	n.a., NL-DE	2018	n.a.	Biological	AEC
CO2-SNG	n.a., PL	2018	n.a.	Chemical	n.a.
DemoSNG (1st site)	Stockholm, SE	2014	0.006	Chemical	PEMEC
n.a.: no available					

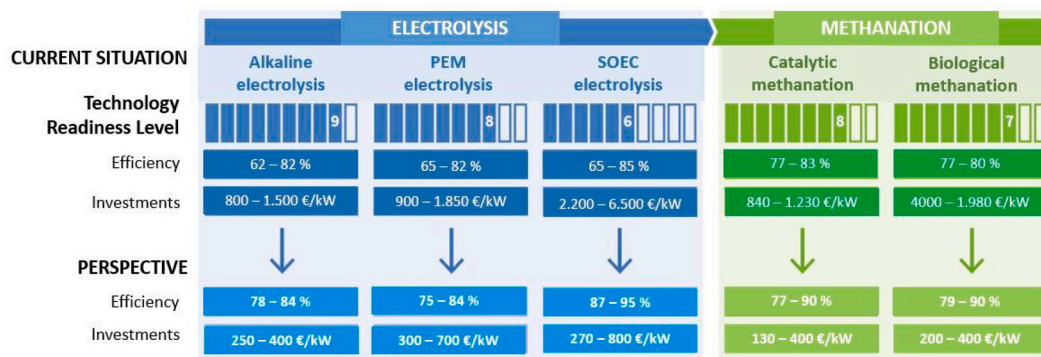


Fig. 4. Power to methane: state of the art and perspectives. Adapted from Ref. [125].

cycle are dominated by the supply of electricity to electrolysis for the production of hydrogen, so that any research that provides energy savings in this phase will result in an environmental improvement of the global system performance. This is why research efforts focused on improving SOEC systems as well as on the developments of novel AEC and PEMEC designs, with higher efficiency and less cost, will have a direct impact also on the promotion of the PtM model. Another aspect of interest when dealing with PtM processes is how they fit into the CO₂ biorefinery concept. PtM processes can be also considered as the first step in the production of chemicals and fuels. Producing fuels for transportation, for example, would be another important application of PtM in a near future. Traditional refineries are also expected to focus their attention on PtM process in the way of lowering the carbon footprint of their products.

6.2. Policy analysis

The EU has the ambition of being climate neutral in 2050, and this objective is the core of the European Green Deal. Prioritize energy efficiency and develop a power sector based largely on renewable sources is one of its main principles. Key elements to achieve this goal are promoting renewable energy sources at all levels, including biomass, carbon capture and storage, and energy efficiency. Solar and wind energy are identified as crucial technologies for the early stages of this transformation, although their great variability in space and time is a significant disadvantage. Therefore, there is a need for other alternatives that could be complementary to compensate its fluctuations and provide flexibility to the system. Power-to-gas and, more specifically, power-to-methane, emerges here as an option to meet this need, as has been demonstrated throughout this paper. As already mentioned in previous sections, the advantages of PtM are multiple. It allows, for example, converting energy into a product that can be used to reduce CO₂ emissions in other sectors; it also uses the existing natural gas infrastructure and is suitable for large-scale and long-term storage, giving high flexibility to the energy system. When considered as a storage option, CH₄ has a high energy density (>1000 kWh m⁻³, compared to hydrogen also generated in PtG processes, which has only 270 kWh m⁻³). To these advantages we must add the fact that there are already more than 1000 TWh of storage capacity in operation. Taking into consideration all these positive elements, and with a near future characterized by EU policies promoting low CO₂ emission scenarios, the future of PtM processes seems to be promising, with CO₂ methanation playing a key role in the new energy model.

According to the elements analyzed in this document, and taking into account the current political EU context where processes sustainability is a critical aspect, several key parameters can speed up or delay the implementation of the PtM model. CO₂ reduction target will be the first one. It is foreseen that PtM will play a more important role as objective on CO₂ net emissions becomes stricter. Also the lack of development or

social acceptance for alternative carbon capture and storage options (for example, underground storage) can be a catalyst in the PtM promotion. PtM development will be closely associated to VRES implementation. Since it is foreseen an important development of solar and wind parks in the next years, this could lead to high electricity surplus to deal with. This will require flexibility in the energy system and, under these conditions, PtM could play an important role. The reduction in the costs of technology and the increase in the efficiency of the methanation processes will create the perception of less economic and technological risk, which may attract political support for PtM. Finally, some regulatory measures to promote the technology might be necessary in the first stages of this new policy to attract the interest of private investors. Some specific regulatory measures, such as a direct subsidy to the PtM technology or an indirect tax on fossil fuels, could greatly accelerate the deployment of methanation facilities.

6.3. Practical implications of this study

Based on the findings of this study, it is clear that the optimization of parameters such as the selectivity, activity, and stability of the methanation systems, represents a key aspect towards their eventual large-scale commercial implementation. The availability of quality CO₂ and H₂ sources also remains a handicap in the economic viability of these technologies. Overall, the energy demand and the costs associated with the production of H₂ represents the main limitation for an economically sustainable implementation of the methanation processes. In the current state of technological development, thermochemical methanation has the highest probability of being applied on a full scale, since it offers the better yields of methane production in addition to the highest reaction rates. Another advantage of these systems is that they are mostly compatible with industrial plants in operation, compared to photocatalytic or electrocatalytic systems. Despite these advantages of chemical methanation, it is still necessary to investigate new developments to design cost-effective catalytic systems. Biological systems can also be made compatible with already operative anaerobic digesters, but biological methanation, although is a promising pathway for future energy storage, still faces important challenges in its current degree of development. These systems have a lower reaction rate and lower volumetric mass transfer coefficient than chemical methanation. It has been shown that the gas-liquid mass transfer is the factor with the largest influence on this methanation performance. However, the biological process has a high tolerance to impurities of the incoming gas what allows to work with less strict previous stages of gas cleaning.

The use of CO₂ driven by solar energy is a perfect solution to reduce operation costs and offers an interesting scalability potential compared to other systems. Although photocatalytic methanation is still far from being a practical consideration, important knowledge has been accumulated up to know to understand its key factors. Further efforts are expected in the near future in the advancement of electrolytic systems

for the generation of H_2 from water, and the development of reactors and appropriate operating conditions that allow progress in the practical implementation of large-scale methanation processes. The implementation of the PtM concept is developing rapidly in Europe. This review identifies 73 demonstration projects in operation or planning. The leading country in this development is Germany, followed at a distance from Denmark, Switzerland and the Netherlands in that order, with PEM and alkaline electrolyzers being the most frequently used in all the facilities. The increasing development of the technology with respect to cost is notable. It is estimated that investment costs for electrolysis and methanation technologies will fall from more than 1000 € kW_{el}^{-1} nowadays to around 500 € kW_{el}^{-1} in the future. This cost reduction is a clear indicative that the market implementation of the PtM concept is underway.

7. Conclusion

In this work, recent investigations and future trends on the use of CO_2 for its sustainable conversion to methane have been described. The possibility to close carbon cycles through the production of CH_4 by means of electrochemical, thermochemical, photochemical and biological processes catalytically assisted, has revealed hopeful results that can provide a solution to growing environmental problems and an alternative fuel source for a defossilised future. Furthermore, the evolution of the European energy context in the coming years, as well as the expected technological improvements will contribute to the general reduction of costs associated to the PtM concept. This paper has tried to summarize the main and most recent research works carried out in the PtM field, extracting essential information that will allow the reader to analyze and compare the existing technological approaches with the focus on the viability and feasibility of each approach in the next years, as a way to stimulate continuous progress in the field.

Author statement

Dolores Hidalgo: Conceptualization; Formal analysis; Funding acquisition; Writing - original draft; Jesús M. Martín-Marroquín: Methodology; Validation; Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by CYTED (Ref. 918PTE0539) and by the Spanish Ministry of Science, Innovation and Universities (Ref. PCI2018-092948) in the frame of the BIOMETRANS project.

References

- [1] Aziz MBA, Kassim KA, Bakar WAW, Mato A. Fossil free fuels: trends in renewable energy; boca ratón. CRC Press; 2019.
- [2] Newell R, Raimi D, Aldana G. Global energy outlook 2019: the next generation of energy. 2019.
- [3] IEA. World energy outlook 2019. Paris: IEA; 2019. <https://www.iea.org/reports/world-energy-outlook-2019>.
- [4] IEA. Global energy & CO2 status report. Paris: IEA; 2019. 2019, <https://www.iea.org/reports/global-energy-and-co2-status-report-2019>.
- [5] Thema M, Bauer F, Sterner M. Power-to-Gas: electrolysis and methanation status review. *Renew Sustain Energy Rev* 2019;112:775–87.
- [6] Sun Y, Lin Z, Peng SH, Sage V, Sun Z. A critical perspective on CO_2 conversions into chemicals and fuels. *J Nanosci Nanotechnol* 2019;19(6):3097–109.
- [7] Yan X, Sun W, Fan L, Duchesne PN, Wang W, Kübel C, Wood TE. Nickel@Siloxene catalytic nanosheets for high-performance CO_2 methanation. *Nat Commun* 2019;10:1–11.
- [8] Wulf C, Linße J, Zapp P. Review of power-to-gas projects in Europe. *Energy Procedia* 2018;155:367–78.
- [9] Ulmer U, Dingle T, Duchesne PN, Morris RH, Tavasoli A, Wood T, Ozin GA. Fundamentals and applications of photocatalytic CO_2 methanation. *Nat Commun* 2019;10(1):1–12.
- [10] Marques F, Kim DH. From CO_2 methanation to ambitious long-chain hydrocarbons: alternative fuels paving the path to sustainability. *Chem Soc Rev* 2019;48(1):205–59.
- [11] Nikolaidis P, Poullikkas A. A comparative overview of hydrogen production processes. *Renew Sustain Energy Rev* 2017;67:597–611.
- [12] Schmidt O, Gambhir A, Staffell I, Hawkes A, Nelson J, Few S. Future cost and performance of water electrolysis: an expert elicitation study. *Int J Hydrogen Energy* 2017;42(52):30470–92.
- [13] Zhang X, Chan SH, Ho HK, Tan S-C, Li M, Li G, et al. Towards a smart energy network: the roles of fuel/electrolysis cells and technological perspectives. *Int J Hydrogen Energy* 2015;40:6866–919.
- [14] Lehner M, Tichler R, Steinmüller H, Kopper M. Power-to-Gas: technology and business models. Springer Briefs in Energy. 2014.
- [15] Luo Y, Wu X, Shi Y, Ghoniem AF, Cai N. Exergy efficiency analysis of a power-to-methane system coupling water electrolysis and Sabatier reaction. *ECS Transactions* 2017;78(1):2965–73.
- [16] Mo J, Dehoff RR, Peter WH, Toops TJ, Green JB, Zhang FY. Additive manufacturing of liquid/gas diffusion layers for low-cost and high-efficiency hydrogen production. *Int J Hydrogen Energy* 2016;41(4):3128–35.
- [17] Li Y, Sun Z, Liu D, Gao Y, Wang Y, Bu HT, Ding S. Composite solid polymer electrolyte incorporating MnO_2 nanosheets with reinforced mechanical properties and electrochemical stability for lithium metal battery. *J Mater Chem* 2020.
- [18] Elsoe K, Kraglund MR, Hjelm J, Jacobsen T, Grahl-Madsen L, Mogensen MB. Challenges and possibilities of EIS on PEMEC. In 6th European PEFC and electrolyzer forum. 2017 [European Fuel Cell Forum].
- [19] Götz M, Lefebvre J, Mörs F, Koch AM, Graf F, Bajohr S. Renewable Power-to-Gas: a technological and economic review. *Renew Energy* 2016;85:1371–90.
- [20] Yang G. Development of water electrolyzers with additive manufacturing for efficient and low-cost energy conversion and storage. Doctoral Thesis. University of Tennessee. 2018.
- [21] Yang G, Yu S, Kang Z, Dohrmann Y, Bender G, Pivovar BS, Zhang FY. A novel PEMEC with 3D printed non-conductive bipolar plate for low-cost hydrogen production from water electrolysis. *Energy Convers Manag* 2019;182:108–16.
- [22] Lang M, Raab S, Lemcke MS, Bohn C, Pysik M. Long term behavior of solid oxide electrolyzer (SOEC) stacks. *ECS Transactions* 2019;91(1):2713–25.
- [23] Ali S, Schaeperl R, Sørensen K, Nielsen MP. A comparative study of SOEC and Co-SOEC for a combined power-to-gas system. In 14th Conference on Sustainable Development of Energy 2019. Water and Environment Systems.
- [24] Jiang SP. Challenges in the development of reversible solid oxide cell technologies: a mini review. *Asia Pac J Chem Eng* 2016;11(3):386–91.
- [25] Mantulet G, Bidaud A, Mima S. The role of biomass gasification and methanisation in the decarbonisation strategies. *Energy* 2020;193:116737.
- [26] Ghaib K, Ben-Fares FZ. Power-to-Methane: a state-of-the-art review. *Renew Sustain Energy Rev* 2018;81:433–46.
- [27] Gerres T, Avila JPC, Llamas PL, San Román TG. A review of cross-sector decarbonisation potentials in the European energy intensive industry. *J Clean Prod* 2019;210:585–601.
- [28] Cau G, Tola V, Ferrara F, Porcu A, Pettinau A. CO_2 -free coal-fired power generation by partial oxy-fuel and post-combustion CO_2 capture: techno-economic analysis. *Fuel* 2018;214:423–35.
- [29] Dannesboe C, Hansen JB, Johannsen I. Removal of sulfur contaminants from biogas to enable direct catalytic methanation. *Biomass Convers Bior* 2019:1–12.
- [30] Witte J, Calbry-Muzyka A, Wieseler T, Hottinger P, Biollaz SM, Schildhauer TJ. Demonstrating direct methanation of real biogas in a fluidised bed reactor. *Appl Energy* 2019;240:359–71.
- [31] Batlle-Vilanova P, Rovira-Alsina L, Puig S, Balaguer MD, Icaran P, Monsalvo VM, Colprim J. Biogas upgrading, CO_2 valorisation and economic revaluation of bioelectrochemical systems through anodic chlorine production in the framework of wastewater treatment plants. *Sci Total Environ* 2019;690:352–60.
- [32] Castellani B, Rinaldi S, Bonamente E, Nicolini A, Rossi F, Cotana F. Carbon and energy footprint of the hydrate-based biogas upgrading process integrated with CO_2 valorization. *Sci Total Environ* 2018;615:404–11.
- [33] Cui D, Deng Z, Liu Z. China's non-fossil fuel CO_2 emissions from industrial processes. *Appl Energy* 2019;254:113537.
- [34] Plaza MG, Pevida C. Current status of CO_2 capture from coal facilities. In: New trends in coal conversion. Woodhead Publishing; 2019. p. 31–58.
- [35] Scrivener KL, John VM, Gartner EM. Eco-efficient cements: potential economically viable solutions for a low- CO_2 cement-based materials industry. *Cement Concr Res* 2018;114:2–26.
- [36] Krekel D, Samsun RC, Peters R, Stolten D. The separation of CO_2 from ambient air—A techno-economic assessment. *Appl Energy* 2018;218:361–81.
- [37] Bajamundi CJE, Koponen J, Ruuskanen V, Elfving J, Kosonen A, Kauppinen J, Ahola J. Capturing CO_2 from air: technical performance and process control improvement. *J CO2 Util* 2019;30:232–9.
- [38] Nakao SI, Yogo K, Goto K, Kai T, Yamada H. Advanced CO_2 capture technologies: absorption, adsorption, and membrane separation methods. Springer. 2019.
- [39] Hidalgo D, Sanz-Bedate S, Martín-Marroquín JM, Castro J, Antolín G. Selective separation of CH_4 and CO_2 using membrane contactors. *Renew Energy* 2020;150:935–42. In press.
- [40] Bhowan AS, Freeman BC. Analysis and status of post-combustion carbon dioxide capture technologies. *Environ Sci Technol* 2011;45:8624–32.

- [41] Babamohammadi S, Shamiri A, Aroua MK. A review of CO₂ capture by absorption in ionic liquid-based solvents. *Rev Chem Eng* 2015;31(4):383–412.
- [42] Zhai H, Mantripragada HC, Rubina ES. A technical and economic assessment of advanced carbon capture technologies. 14th International Conference on Greenhouse Gas Control Technologies. GHGT-14. Melbourne: Australia; October 2018. p. 21–5.
- [43] Al-Fatesh A, Singh SK, Kanade GS, Atia H, Fakeeha AH, Ibrahim AA. Labhasetwar NK. Rh promoted and ZrO₂/Al₂O₃ supported Ni/Co based catalysts: high activity for CO₂ reforming, steam–CO₂ reforming and oxy–CO₂ reforming of CH₄. *Int J Hydrogen Energy* 2018;43(27):12069–80.
- [44] Bremer J, Sundmacher K. Operation range extension via hot-spot control for catalytic CO₂ methanation reactors. *React Chem Eng* 2019;4(6):1019–37.
- [45] Gong J. The interplay between structure and product selectivity of CO₂ hydrogenation. *Angew Chem Int Ed* 2019. Wiley Online Library.
- [46] Muroyama H, Tsuda Y, Asakoshi T, Masitah H, Okanishi T, Matsui T, Eguchi K. Carbon dioxide methanation over Ni catalysts supported on various metal oxides. *J Catal* 2016;343:178–84.
- [47] Hernández S, Farkhondehfar MA, Sastre F, Makkee M, Saracco G, Russo N. Syngas production from electrochemical reduction of CO₂: current status and prospective implementation. *Green Chem* 2017;19(10):2326–46.
- [48] Kattel S, Liu P. Chen. Tuning selectivity of CO₂ hydrogenation reactions at the metal/oxide interface. *J Am Chem Soc* 2017;139(29):9739–54.
- [49] Artetxe M, Alvarez J, Nahil MA, Olazar M, Williams PT. Steam reforming of different biomass tar model compounds over Ni/Al₂O₃ catalysts. *Energy Convers Manag* 2017;136:119–26.
- [50] Zhang Z, Tian Y, Zhang L, Hu S, Xiang J, Wang Y, Hu X. Impacts of nickel loading on properties, catalytic behaviors of Ni/geAl₂O₃ catalysts and the reaction intermediates formed in methanation of CO₂. *Int J Hydrogen Energy* 2019;44(9291). e9306.
- [51] Biset-Peiró M, Guileria J, Zhang T, Arbiol J, Andreu T. On the role of ceria in Ni–Al₂O₃ catalyst for CO₂ plasma methanation. *Appl Catal Gen* 2019;575:223–9.
- [52] Choe SJ, Kang HJ, Kim SJ, Park SB, Park DH, Huh DS. Adsorbed carbon formation and carbon hydrogenation for CO₂ methanation on the Ni (111) surface: ASED-MO study. *Bull Kor Chem Soc* 2005;26(11):1682–8.
- [53] Zhao B, Pan YX, Liu CJ. The promotion effect of CeO₂ on CO₂ adsorption and hydrogenation over Ga₂O₃. *Catal Today* 2012;194(1):60–4.
- [54] Dreyer JA, Li P, Zhang L, Beh GK, Zhang R, Sit PHL, Teoh WY. Influence of the oxide support reducibility on the CO₂ methanation over Ru-based catalysts. *Appl Catal B Environ* 2017;219:715–26.
- [55] Li W, Nie X, Jiang X, Zhang A, Ding F, Liu M. Song C. ZrO₂ support imparts superior activity and stability of Co catalysts for CO₂ methanation. *Appl Catal B: Environmental* 2018;220:397–408.
- [56] Fatah NAA, Jalil AA, Salleh NFM, Hamid MYS, Hassan ZH, Nawawi MGM. Elucidation of cobalt disturbance on Ni/Al₂O₃ in dissociating hydrogen towards improved CO₂ methanation and optimization by response surface methodology (RSM). *Int J Hydrogen Energy* 2019;45(36):18562–73.
- [57] Jia X, Zhang X, Rui N, Hu X, Liu CJ. Structural effect of Ni/ZrO₂ catalyst on CO₂ methanation with enhanced activity. *Appl Catal B Environ* 2019;244:159–69.
- [58] Teh LP, Triwahyono S, Jalil AA, Setiabudi HD, Aziz MAA. Catalytic CO methanation over mesoporous ZSMs with different metal promoters. *Bull Chem React Eng Catal* 2019;14(1):228–37.
- [59] Delmelle R, Duarte RB, Franken T, Burnat D, Holzer L, Borgschulte A, Heel A. Development of improved nickel catalysts for sorption enhanced CO₂ methanation. *Int J Hydrogen Energy* 2016;41(44):20185–91.
- [60] Stangeland K, Kalai D, Li H, Yu Z. CO₂ methanation: the effect of catalysts and reaction conditions. *Energy Procedia* 2017;105:2022–7.
- [61] Su X, Xu J, Liang B, Duan H, Hou B, Huang Y. Catalytic carbon dioxide hydrogenation to methane: a review of recent studies. *J Energy Chem* 2016;25(4):553–65.
- [62] Frusteri F, Frusteri L, Costa F, Mezzapica A, Cannilla C, Bonura G. Methane production by sequential supercritical gasification of aqueous organic compounds and selective CO₂ methanation. *Appl Catal Gen* 2017;545:24–32.
- [63] Zhou J, Ma H, Jin F, Zhang H, Ying W. Mn and Mg dual promoters modified Ni/α-Al₂O₃ catalysts for high temperature syngas methanation. *Fuel Process Technol* 2018;172:225–32.
- [64] Le TA, Kim MS, Lee SH, Kim TW, Park ED. CO and CO₂ methanation over supported Ni catalysts. *Catal Today*; 293:89–96.
- [65] Panagiotopoulou P, Kondarides DI, Verykios XE. Selective methanation of CO over supported Ru catalysts. *Appl Catal B Environ* 2009;88(3–4):470–8.
- [66] Falbo L, Visconti CG, Lietti L, Szanyi J. The effect of CO on CO₂ methanation over Ru/Al₂O₃ catalysts: a combined steady-state reactivity and transient DRIFT spectroscopy study. *Appl Catal B: Environmental* 2019;117791.
- [67] Thampi KR, Kiwi J, Graetzel M. Methanation and photo-methanation of carbon dioxide at room temperature and atmospheric pressure. *Nature* 1987;327:506–8.
- [68] Chen S, Abdel-Mageed AM, Li D, Bannmann J, Cisneros S, Biskupek J, Behm RJ. Morphology-engineered highly active and stable Ru/TiO₂ catalysts for selective CO methanation. *Angew Chem Int Ed* 2019;58(31):10732–6.
- [69] Wang H, Pei Y, Qiao M, Zong B. Advances in methanation catalysis. In: Spivey J, Han YF, editors. *Catalysis*, vol. 29. Royal Society of Chemistry; 2017. p. 1–28.
- [70] Song F, Zhong Q, Yu Y, Shi M, Wu Y, Hu J, Song Y. Obtaining well-dispersed Ni/Al₂O₃ catalyst for CO₂ methanation with a microwave-assisted method. *Int J Hydrogen Energy* 2017;42(7):4174–83.
- [71] Le TA, Kim MS, Lee SH, Park ED. CO and CO₂ Methanation over supported Cobalt catalysts. *Top Catal* 2017;60(9–11):714–20.
- [72] Ilsemann J, Straß-Eifert A, Friedland J, Kiewidt L, Thöming J, Bäumer M, Güttel R. Cobalt@ silica core-shell catalysts for hydrogenation of CO/CO₂ mixtures to methane. *ChemCatChem* 2019;11(19):4884–93.
- [73] Kuznecova I, Gusca J. Property based ranking of CO and CO₂ methanation catalysts. *Energy Procedia* 2017;128:255–60.
- [74] Gong D, Li S, Guo S, Tang H, Wang H, Liu Y. Lanthanum and cerium co-modified Ni/SiO₂ catalyst for CO methanation from syngas. *Appl Surf Sci* 2018;434:351–64.
- [75] Dorner RW, Hardy DR, Williams FW, Davis BH, Willauer HD. Influence of gas feed composition and pressure on the catalytic conversion of CO₂ to hydrocarbons using a traditional Cobalt-based Fischer-Tropsch catalyst. *Energy Fuels* 2009;23(8):4190–5.
- [76] Vannice MA, Garten RL. Supported palladium catalysts for methanation. *Ind Eng Chem Prod Res Dev* 1979;18(3):186–91.
- [77] Henderson MA, Worley SD. An infrared study of the hydrogenation of carbon dioxide on supported rhodium catalysts. *J Phys Chem* 1985;89(8):1417–23.
- [78] Świrk K, Grzybek T, Motak M. Tri-reforming as a process of CO₂ utilization and a novel concept of energy storage in chemical products. *E3S Web of Conferences* 2017;14:2038. EDP Sciences.
- [79] Denkwitz Y, Makosch M, Geserick J, Hörmann U, Selve S, Kaiser U, Behm RJ. Influence of the crystalline phase and surface area of the TiO₂ support on the CO oxidation activity of mesoporous Au/TiO₂ catalysts. *Appl Catal B Environ* 2009;91(1–2):470–80.
- [80] Tao M, Meng X, Lv Y, Bian Z, Xin Z. Effect of impregnation solvent on Ni dispersion and catalytic properties of Ni/SBA-15 for CO methanation reaction. *Fuel* 2016;165:289–97.
- [81] Guo Y, Mei S, Yuan K, Wang DJ, Liu HC, Yan CH, Zhang YW. Low-temperature CO₂ methanation over CeO₂-supported Ru single atoms, nanoclusters, and nanoparticles competitively tuned by strong metal–support interactions and H-spillover effect. *ACS Catal* 2018;8(7):6203–15.
- [82] Kovalovszki A, Alvarado-Morales M, Angelidaki I. Bioaugmentation modeling in anaerobic digestion: the dynamics of methanogenesis. In: *Biogas science*. Torino: Italy; 2018.
- [83] Lecker B, Illi L, Lemmer A, Oechsner H. Biological hydrogen methanation-a review. *Bioresour Technol* 2017;245:1220–8.
- [84] Taubner RS, Schleper C, Firneis M, Rittmann S. Assessing the ecophysiology of methanogens in the context of recent astrobiological and planetological studies. *Life* 2015;5(4):1652–86.
- [85] Bassani I. Hydrogen assisted biological biogas upgrading. Doctoral Thesis. Kgs. Lyngby. DTU Environment: Technical University of Denmark; 2017.
- [86] Seifert AH, Rittmann S, Herwig C. Analysis of process related factors to increase volumetric productivity and quality of biomethane with *Methanothermobacter marburgensis*. *Appl Energy* 2014;132:155–62.
- [87] Ferella F, Cucchiella F, D'Adamo I, Gallucci K. A techno-economic assessment of biogas upgrading in a developed market. *J Clean Prod* 2019;210:945–57.
- [88] Kamel AM. Biological hydrogen methanation. MSc thesis. University of Valladolid. 2019.
- [89] Rittmann SKM. A critical assessment of microbiological biogas to biomethane upgrading systems. In: Guebitz G, Bauer A, Bochnermann G, Gronauer A, Weiss S, editors. *Biogas science and technology. Advances in biochemical engineering/biotechnology*, vol. 151. Cham: Springer; 2015. p. 117–35.
- [90] Benjaminsson G, Benjaminsson J, Rudberg RB. Power-to-Gas: a technical review. Svenskt gastekniskt center. http://sgc.camero.se/ckfinder/userfiles/files/SGC28_4_eng.pdf. [Accessed 12 January 2020].
- [91] Luo G, Angelidaki I. Co-digestion of manure and whey for in situ biogas upgrading by the addition of H₂: process performance and microbial insights. *Appl Microbiol Biotechnol* 2013;97(3):1373–81.
- [92] Cazier EA, Trabaly E, Steyer JP, Escudé R. Biomass hydrolysis inhibition at high hydrogen partial pressure in solid-state anaerobic digestion. *Bioresour Technol* 2015;190:106–13.
- [93] Guiot SR, Cimpoia R, Carayon G. Potential of wastewater-treating anaerobic granules for biomethanation of synthesis gas. *Environ Sci Technol* 2011;45(5). 2006–2012.
- [94] Vo TT, Wall DM, Ring D, Rajendran K, Murphy JD. Techno-economic analysis of biogas upgrading via amine scrubber, carbon capture and ex-situ methanation. *Appl Energy* 2018;212:1191–202.
- [95] Voelklein MA, Rusmanis D, Murphy JD. Biological methanation: strategies for in-situ and ex-situ upgrading in anaerobic digestion. *Appl Energy* 2019;235:1061–71.
- [96] Neuberg S, Pennemann H, Shanmugam V, Thiermann R, Zapf R, Gac W, Kolb G. CO₂ methanation in microstructured reactors–catalyst development and process design. *Chem Eng Technol* 2019;42(10). 2076–2084.
- [97] Neubert M, Treiber P, Krier C, Hackel M, Hellriegel T, Dillig M, Karl J. Influence of hydrocarbons and thiophene on catalytic fixed bed methanation. *Fuel* 2017;207:253–61.
- [98] Ghoussoub M, Xia M, Duchesne PN, Segal D, Ozin G. Principles of photothermal gas-phase heterogeneous CO₂ catalysis. *Energy Environ Sci* 2019;2:1122–42.
- [99] Robatjazi H, Zhao H, Swearer DF, Hogan NJ, Zhou L, Alabastri A, Halas NJ. Plasmon-induced selective carbon dioxide conversion on earth-abundant aluminum-cuprous oxide antenna-reactor nanoparticles. *Nat Commun* 2017;8(1):1–9.
- [100] Jones S, Andrén D, Karpinski P, Käll M. Photothermal heating of plasmonic nanoantennas: influence on trapped particle dynamics and colloid distribution. *ACS Photonics* 2018;5(7):2878–87.

- [101] Liu T, Besteiro LV, Liedl T, Correa-Duarte MA, Wang Z, Govorov AO. Chiral plasmonic nanocrystals for generation of hot electrons: toward polarization-sensitive photochemistry. *Nano Lett* 2019;19(2):1395–407.
- [102] Zhu L, Gao M, Peh CKN, Ho GW. Solar-driven photothermal nanostructured materials designs and prerequisites for evaporation and catalysis applications. *Mater Horiz* 2018;5(3):323–43.
- [103] Putra IR, Li JY, Chen CY. 18.78% hierarchical black silicon solar cells achieved with the balance of light-trapping and interfacial contact. *Appl Surf Sci* 2019;478:725–32.
- [104] Li X, Everitt HO, Liu J. Confirming nonthermal plasmonic effects enhance CO₂ methanation on Rh/TiO₂ catalysts. *Nano Res* 2019;12(8):1906–11.
- [105] Sreedhar I, Varun Y, Singh SA, Venugopal A, Reddy BM. Developmental trends in CO₂ methanation using various catalysts. *Catal Sci Technol* 2019;9(17):4478–504.
- [106] Welte C, Deppenmeier U. Bioenergetics and anaerobic respiratory chains of acetate-utilizing methanogens. *Biochim Biophys Acta* 1837;2014:1130–47.
- [107] Zabranska J, Pokorna D. Bioconversion of carbon dioxide to methane using hydrogen and hydrogenotrophic methanogens. *Biotechnol Adv* 2018;36:707–20.
- [108] Liao JC, Mi L, Pontrelli S, Luo S. Fuelling the future: microbial engineering for the production of sustainable biofuels. *Nat Rev Microbiol* 2016;14:288–304.
- [109] Baca M, Singh S, Gebinoga M, Weise F, Schlingloff G, Schober A. Microbial electrochemical systems with future perspectives using advanced nanomaterials and microfluidics. *Advanced Energy Materials* 2016;6(23):1600690.
- [110] Nichols M. Hybrid approaches to bio-materials and bio-inorganic electrochemical carbon dioxide reduction. Doctoral dissertation. Berkeley: University of California; 2017.
- [111] Sokol KP, Robinson WE, Warnan J, Kornienko N, Nowaczyk MM, Ruff A, Reisner E. Bias-free photoelectrochemical water splitting with photosystem II on a dye-sensitized photoanode wired to hydrogenase. *Nat Energy* 2018;3(11):944–51.
- [112] Ullrich T, Lemmer A. Performance enhancement of biological methanation with trickle bed reactors by liquid flow modulation. *GCB Bioenergy* 2019;11(1):63–71.
- [113] Subudhi S, Rath D, Parida KM. A mechanistic approach towards the photocatalytic organic transformations over functionalised metal organic frameworks: a review. *Catalysis Science & Technology* 2018;8(3):679–96.
- [114] Rao H, Schmidt LC, Bonin J, Robert M. Visible-light-driven methane formation from CO₂ with a molecular iron catalyst. *Nature* 2017;548:74–7.
- [115] Weng Z, Jiang J, Wu Y, Wu Z, Guo X, Materna KL, Wang H. Electrochemical CO₂ reduction to hydrocarbons on a heterogeneous molecular Cu catalyst in aqueous solution. *J Am Chem Soc* 2016;138:8076–9.
- [116] Shen J, Kortlever R, Kas R, Birdja YY, Diaz-Morales O, Kwon Y, Koper MT. Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin. *Nat Commun* 2015;6:1–8.
- [117] Deng X, Li R, Wu S, Wang L, Hu J, Ma J, Wang L. Metal-organic framework coating enhances the performance of Cu₂O in photoelectrochemical CO₂ reduction. *J Am Chem Soc* 2019;141(27):10924–9.
- [118] Wang Y, Xu Y, Liu Q, Sun J, Ji S, Wang ZJ. Enhanced low-temperature activity for CO₂ methanation over NiMgAl/SiC composite catalysts. *J Chem Technol Biotechnol* 2019;94(12):3780–6.
- [119] Long R, Li Y, Liu Y, Chen S, Zheng X, Gao C, Jiang J. Isolation of Cu atoms in Pd lattice: forming highly selective sites for photocatalytic conversion of CO₂ to CH₄. *J Am Chem Soc* 2017;139:4486–92.
- [120] Wu J, Huang Y, Ye W, Li Y. CO₂ reduction: from the electrochemical to photochemical approach. *Adv Sci* 2017;4(1). 1700194.
- [121] Rongé J, Bosserez T, Martel D, Nervi C, Boarino L, Taulelle F, Martens JA. Monolithic cells for solar fuels. *Chem Soc Rev* 2014;43(23):7963–81.
- [122] Tagliapietra S, Zachmann G, Edenhofer O, Glachant JM, Linares P, Loeschel A. The European Union energy transition: key priorities for the next five years. *Energy Pol* 2019;132:950–4.
- [123] Glenk G, Reichelstein S. Economics of converting renewable power to hydrogen. *Nat Energy* 2019;4:216–22.
- [124] Iaquaniello G, Setini S, Salladini A, De Falco M. CO₂ valorization through direct methanation of flue gas and renewable hydrogen: a technical and economic assessment. *Int J Hydrogen Energy* 2018;43(36):17069–81.
- [125] Golling C, Heuke R, Seidl H, Uhlig J. Roadmap power-to-gas 2017. Berlin, https://www.powertogas.info/fileadmin/dena/Dokumente/Pdf/9215_Broschuere_Baustein_einer_Integrierten_Energiewende_Roadmap_Power_to_Gas.pdf. [Accessed 21 January 2020].
- [126] Gorre J, Ruoss F, Karjunen H, Schaffert J, Tynjälä T. Cost benefits of optimizing hydrogen storage and methanation capacities for Power-to-Gas plants in dynamic operation. *Appl Energy* 2020;257:113967.
- [127] Abe JO, Ajenifuja E, Popoola OM. Hydrogen energy, economy and storage: review and recommendation. *Int J Hydrogen Energy* 2019;44(29):15072–86.
- [128] Aicher T, Iglesias-Gonzales M, Götz M. Arbeitspaket 5: betrachtungen des Gesamtsystems im Hinblick auf Dynamik und Prozessintegration. *Energ Wasser Prax* 2014:51–5. https://www.researchgate.net/publication/272488412_Arbeitspaket_5_Betrachtungen_des_Gesamtsystems_im_Hinblick_auf_Dynamik_und_Prozessintegration. [Accessed 21 January 2020].
- [129] Götz M, Koch AM, Graf F. State of the art and perspectives of CO₂ methanation process concepts for power-to-gas applications. In International Gas Union Research Conference. Copenhagen, https://www.researchgate.net/profile/Manuel_Goetz/publication/273139805_State_of_the_Art_and_Perspectives_of_CO2_Methanation_Process_Concepts_for_Power-to-Gas_Applications/links/5523ef9d0cf2c815e073eba8.pdf. [Accessed 21 January 2020].