



Ex-situ biological CO₂ methanation using trickle bed reactor: review and recent advances

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Abstract Power-to-methane technology is a promising solution to facilitate the use of excess variable renewable energy for biomethane production. In this approach, hydrogen produced via electrolysis is used to upgrade raw biogas, which can be subsequently used as fuel or stored in the gas grid. *Ex-situ* biomethanation is an emerging technology that could potentially replace conventional energy-intensive biogas upgrading methods and allow CO₂ utilization for biomethane production. This work provides a comprehensive overview on the current status of *ex-situ* biomethanation with particular attention to trickle bed reactor. The review includes description of *ex-situ* biomethanation and summarizes previous works on this topic. The key elements related to operational conditions, efficiency, and microbiology of *ex-situ* biomethanation using trickle bed reactor are described here. Additionally, the review highlights the technical and economic issues

that have to be addressed for future development and large-scale implementation of *ex-situ* biomethanation.

Keywords Biogas · Methane · *Ex-situ* biomethanation · Power-to-methane · Renewable energy

1 Introduction

Biogas is a mixture of methane (CH₄), carbon dioxide (CO₂) and small quantities of other gases produced during anaerobic digestion (AD) of organic matter in an oxygen-free environment (IEA 2020). Due to the presence of CH₄ in biogas, it possesses energetical properties that can be converted into electricity/heat or can be used as platform chemical for e.g., protein manufacturing (Jones et al. 2020). The content of CH₄ in biogas depends on the organic matter characteristic and can range from 55 to 80% (Barragán-Escandón et al. 2020). However, the CO₂ in biogas occupies a significant part of its volume (from 20 up to 45%) representing no energetical use (calorific value = 0.0 MJ/m³). Due to that, the calorific value of biogas ranges between 20 and 30 MJ/m³. Upgrading biogas to biomethane increases the energetical value of biogas, that can be approximated to the calorific value of pure CH₄ (37.7 MJ/m³) (Gasunie 1980). Therefore, it is of interest to increase the share of CH₄ in the produced biogas.

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Currently, most of the full-scale biogas upgrading plants are based on the physicochemical CO₂ removal. Commercially, the chemical/water scrubbing, membrane separation, pressure swing adsorption (PSA) are widely utilized in Europe for CO₂ removal in biogas plants (Pettersson and Wellinger 2009). These upgrading methods are robust, reliable, and capable to treat high gas loadings. However, these methods are expensive and consume energy due to high pressures (e.g., PSA), chemicals addition (e.g., chemical scrubbing) or use of expensive equipment such as membranes.

The methods for CO₂ reuse in biogas production recently gained much more interest. These methods treat the CO₂ as a potential resource for CH₄ production. The CH₄ produced from CO₂ can increase the share of CH₄ leaving the AD that can be e.g., readily injected into the existing gas grid and is a good platform for novel low carbon products (Burkhardt et al. 2015; Savvas et al. 2017a; Ashraf et al. 2020). One of the methods to produce CH₄ from CO₂ is biomethanation (BM) through the hydrogenotrophic methanogenesis catalyzed by methanogenic archaea (Guneratnam et al. 2017). In comparison to the physicochemical methanation (Sabatier process), BM does not require high temperatures (35–70 °C) and can be performed at ambient pressure, which reduce the maintenance cost of biogas upgrading. Additionally, BM has a higher resistance to the contaminants (e.g., H₂S and NH₃) than the physicochemical process (Rachbauer et al. 2016). However, to perform the hydrogenotrophic methanogenesis the second substrate in form of hydrogen (H₂) is required to produce CH₄.

The sourcing of H₂ for BM is one of the concerns regarding the sustainability of this process. Therefore, the source of H₂ is typically related to the renewable energy sources (hydro, wind and solar power). These sources generate and increase the share of variable renewable electricity (VRE) in the electricity network. The buffer capacity to cover peaks from renewable energy production (esp. wind and solar power) is low, while its further development for higher energy storage capacity is still too expensive (Alitalo et al. 2015). Therefore, it has been proposed that the peaks of produced energy can be used for H₂ production through water electrolysis avoiding energy squandering and enabling the grid balancing (Alfaro et al. 2018). From Norwegian perspective, where ca. 95% of

electricity originates from hydropower, there is a significant correlation between the rain precipitation and electricity costs. Therefore, the use of excess energy for H₂ production can potentially contribute to balance the grid that is mostly dependent on hydro power. In this context, BM opens new prospects in power-to-methane technology due to more efficient utilization of renewable energy. Although the BM offers economical and technical advantages, this method faces several challenges.

1.1 In-situ and ex-situ biomethanation

The fundamental challenge of BM is regarded to the low gas–liquid mass transfer rate of H₂ ($k_{1,a}$), which hinders H₂ uptake by methanogenic archaea for CO₂ conversion (Kougias et al. 2017). Therefore, the different concepts of H₂ injections were developed in the BM context such as *in-situ*, *ex-situ* and hybrid (combination of *in-situ* and *ex-situ*) (Angelidaki et al. 2018). The mostly studied in the last years is *in-situ* BM where the H₂ is injected directly to the AD (Fig. 1a). This approach is regarded as low-cost since it avoids the additional infrastructure for biogas treatment by utilizing the AD reactor as the upgrading unit (Wahid et al. 2019). By this approach the CH₄ concentrations around 99% could be achieved using continuous-stirred tank reactor (CSTR) (Wang et al. 2013). However, the operation of *in-situ* BM requires a rigorous monitoring and control of operational parameters. The direct injection of H₂ to the AD causes the depletion in buffer capacity of CO₂ that may cause the pH increase over 8.5 leading to the process disruptions and methanogenesis inhibition (Luo and Angelidaki 2012). Moreover, exogenous H₂ supply leads to an increase in H₂ partial pressure, which has a negative effect on particular anaerobic bacteria engaged in AD, possibly leading to process imbalance such as VFAs accumulation; hence, H₂ in the liquid phase should be extensively utilized (Rusmanis et al. 2019). Previous studies, on the other hand, demonstrated that H₂ was poorly soluble during *in-situ* BM, necessitating the use of advanced diffusion devices or extensive reactor stirring to generate small gas bubbles that can increase the contact area between gas and liquid (Bassani 2017; Voelklein et al. 2019).

To secure the stability of AD the *ex-situ* BM gained more attention in the recent years. The *ex-situ* BM occurs in a separate unit where H₂ and biogas/CO₂ are

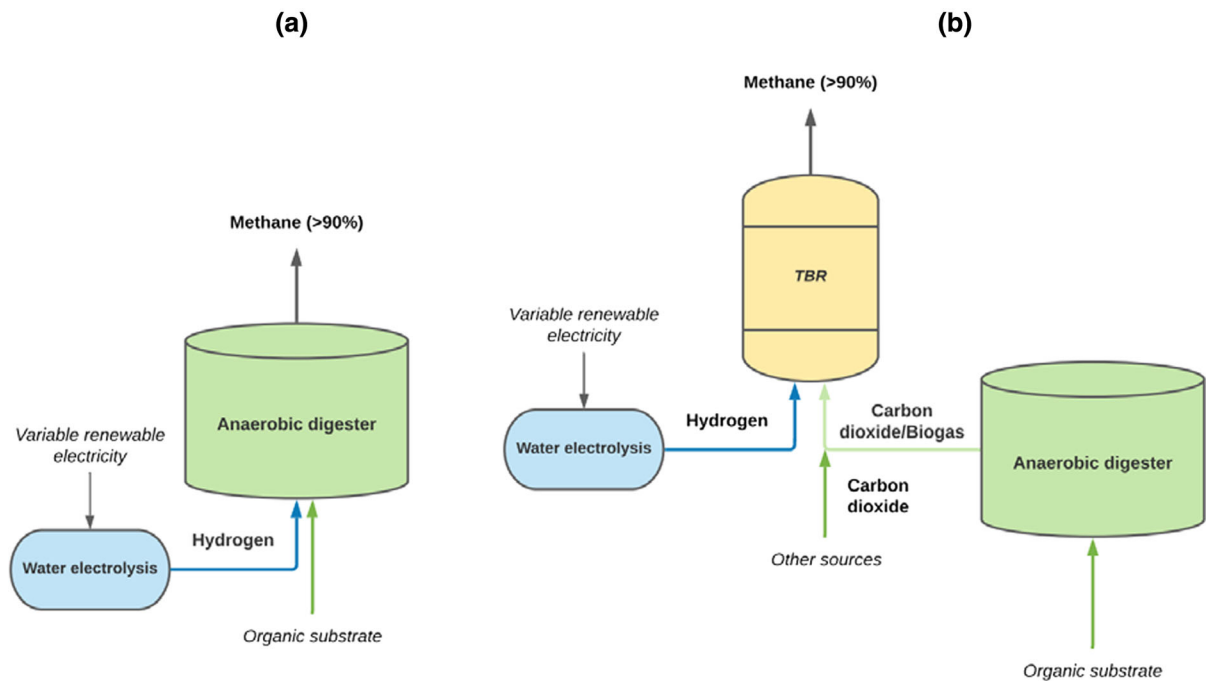


Fig. 1 *In-situ* **a** and *ex-situ* **b** biomethanation concept

supplied as gaseous substrates, typically tailored to accommodate the hydrogenotrophic methanogens (Fig. 1b). This concept gives also more flexibility where the waste CO_2 can be sourced from other processes. Due to that, compared to *in-situ* BM, the *ex-situ* BM usually gives a higher volumetric CH_4 production rates with shorter gas retention time (Voelklein et al. 2019; Wahid et al. 2019). Additionally, the advantages such as biomass independent process and simpler biochemical process can be mentioned (Angelidaki et al. 2018).

The studies on *ex-situ* BM were performed in different reactor configurations such as CSTR, fixed bed, bubble column and trickle bed reactor (TBR). The previously reported results frequently indicate high effluent CH_4 concentrations e.g., around 96% by using up-flow configurations with submerged filter or about 95% when employing CSTR (Luo and Angelidaki 2012; Bassani et al. 2017). However, the construction and maintenance of the additional *ex-situ* unit imposes additional costs while due to the poor H_2 solubility the diffusion system and large volume of upgrading unit are required. CSTR systems frequently rely on high mixing speeds to increase $k_L a$ due to reduced gas bubble size and improved gas distribution. Yet, because of the high

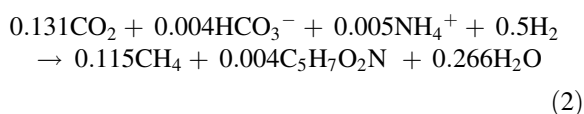
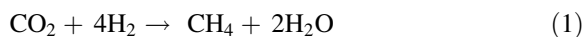
energy demand for mixing, upscaling is limited (Strübing et al. 2017). *Ex-situ* BM utilizing TBR, on the other hand, was considered to be the most promising because it may overcome process scale-up constraints. The TBR provides a large contact area between methanogenic archaea with gas phase, which enhances the conversion of H_2 and CO_2 into CH_4 (Kougias et al. 2020). In this kind of configuration, about four orders of magnitude higher diffusion coefficient is achieved (Aryal et al. 2018). Besides, no additional energy for mixing is required, as in CSTR. In consequence, the number of studies on TBR in correlation to hydrogenotrophic methanogenesis has increased in the last years. Therefore, this review aims to sum up the recent findings regarding optimal operational conditions, configurations, performance, and microbiology of TBR in *ex-situ* BM concept.

2 Factors affecting *ex-situ* biomethanation

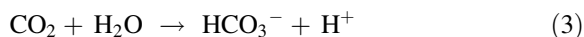
2.1 Stoichiometry

The *ex-situ* BM is based on the catabolic reaction between H_2 and CO_2 (molar ratio 4:1) that are

converted into CH₄ (Eq. 1). Additionally, CO₂ serves as a carbon source for anabolic reaction of microbial growth that changes the molar ratio to ca. 3.7:1 (Eq. 2) when both anabolism and catabolism are accounted. However, the theoretical uptake for anabolic reaction is minor compared to catabolic reaction (Dupnock and Deshusses 2017). It has been found by Martin et al. (2013) that the experimental growth rate of hydrogenotrophic methanogen (*Methanothermobacter thermautotrophicus*) was lower than theoretical.



During *ex-situ* BM, substrates are supplied in the gaseous form, and they exchange with the liquid phase, where, CO₂ dissolves in the liquid phase according to Eq. 3. Depending on pH during the process, the CO₂ solubility sharply increases around pH = 8.0 where the twofold higher CO₂ concentration can be dissolved in the liquid phase compared to pH = 6.0. With increasing pH, the CO₂ is represented by ionized forms such bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) where the equilibrium point (pK) for CO₂/HCO₃⁻ is pH = 6.3 while for HCO₃⁻/CO₃²⁻ is pH = 10.3 (Goldberg et al. 2002).



HCO₃⁻ is a key buffer in AD and plays an important role in pH control. Removal of HCO₃⁻ due to CO₂ conversion (e.g., at high H₂ supply H₂/CO₂ > 4) may lead to the pH increase above optimal level for microbial growth. Therefore, studies on *ex-situ* BM are frequently performed under strict pH control.

2.2 Reactors configuration

The frequently reported constraint in previous studies (regardless reactor's design) was the gas–liquid mass transfer of H₂ due to its low solubility (1.44 mg/kg of water at 50 °C) (Kolev 2011). In comparison to CO₂, H₂ is nearly 25 times less soluble in water (Sieborg et al. 2020). CSTR was commonly used for BM in recent years, where improvement on the gas liquid mass-transfer rate of H₂ was the main focus. A number

of studies on optimization of agitation, reactor shape, gas diffusion systems and impeller design were performed to enhance gas–liquid mass transfer by decreasing the gas bubble size (Orgill et al. 2013; Wahid and Horn 2021). For example, stirring speeds of up to 1500 rpm were demonstrated as efficient at the laboratory scale (Seifert et al. 2014). However, in return the accelerated agitation, special impeller design or reactor shape increase both the capital and operational costs of BM in CSTR, making it energy intensive.

In comparison to CSTR, TBR for *ex-situ* BM mitigates several problems that were faced with other configurations. The TBR is frequently used e.g., for hydrogen sulfide (H₂S) removal from biogas where the number of different methods was developed in the last years (Naegele et al. 2013). The TBR configuration for *ex-situ* BM is based on the hydrogenotrophic methanogens activity that are immobilized as a biofilm on the packing material that results in a large contact area between biofilm and fed gases (Ashraf et al. 2020). The substrate gases are introduced most frequently under atmospheric pressure (or pressure between 1.5 and 9 bar) either downwards or upwards through the packing material (Fig. 2). Elevated pressure improves gas–liquid mass transfer in the reactor and is unlikely to affect BM (Ullrich et al. 2018). To ensure nutrients supplementation, the liquid substrate is continuously or periodically recirculated. Therefore, the operation of TBR does not require a high energy input for continuous mixing or bubbling. It has been shown that in comparison to other configurations, TBR has a higher specific CH₄ production reaching up to 15.4 m³/(m³d)¹ (CSTR = 3.7 m³/(m³d); up-flow reactor 0.25 m³/(m³d)) (Bassani 2017; Strübing et al. 2017; Voelklein et al. 2019). At the same time, the quality of produced biomethane allows for the grid injection in most of cases.

2.3 Packing materials

Concerning the packing material, studies were performed using commercially available random packing carriers (i.e., glass ring, Bioflow 40, Hel-X) or structured packing (i.e., polyurethane foam) (Dupnock and Deshusses 2017; Ashraf et al. 2020; Dahl Jønson

¹ volume of feed gas per volume of reactor per day.

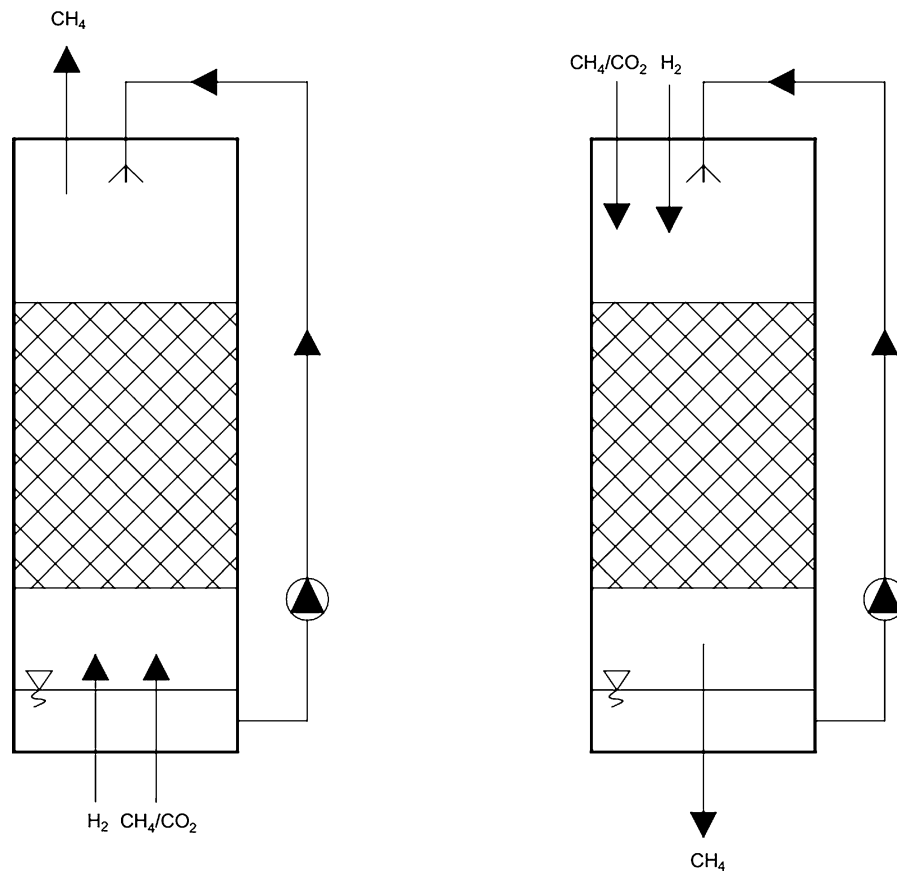


Fig. 2 Typical configurations of trickle bed reactor for *ex-situ* biomethanation **a** counter-current, **b** concurrent

et al. 2020; Sieborg et al. 2020). Random packing was commonly used in the recent studies, that could be related to their clogging resistance (compared to e.g., polyurethane foam). The surface area of reported packing materials ranges from $300 \text{ m}^2/\text{m}^3$ ² (RFK 25 L type carrier, Strübing et al. (2017); Bioflow 40, Burkhardt et al. (2019); Hiflow rings type 15–7, Rachbauer et al. (2016)) to $859 \text{ m}^2/\text{m}^3$ (Hel-X bio carrier HXF12KLL, Strübing et al. (2017)). Generally, biofilm growth at large surface area is beneficial by providing high contact area between methanogenic archaea and substrate gases. In addition, the shape of the carrier is critical, e.g., glass rings, can halt part of recirculation liquid when positioned horizontally, preventing the even wetting of biofilm (Porté et al. 2019). Another example is clogging that was raised by Ashraf et al. (2020) when polyurethane foam was used

during long term operation (200 days), caused by accumulated solids originating from used liquid media.

2.4 Operational conditions

Various operational conditions were tested during the TBR operation for *ex-situ* BM (Table 1). Most of the studies were performed in the laboratory scale, under working volumes ranging from < 1L to 61 L. Reactors were run mostly at thermophilic (ca. $55 \text{ }^\circ\text{C}$) (Strübing et al. 2017, 2018, 2019; Porté et al. 2019; Ashraf et al. 2020; Dahl Jønson et al. 2020; Sieborg et al. 2020) or mesophilic (ca. $37 \text{ }^\circ\text{C}$) (Burkhardt and Busch 2013; Burkhardt et al. 2015, 2019; Rachbauer et al. 2016; Dupnock and Deshusses 2017) conditions. The operating temperature was shown to be crucial for the efficiency of BM. Typically, higher methane production rates were observed for reactors operating

² surface area per packing material volume.

Table 1 Operational conditions and performance comparison

Temperature (°C)	Working volume	Carrier material—name	Carrier material—surface area	Configuration	Liquid phase—source	Liquid recirculation
55 ± 1	58.1 L	RFK 25 L type carrier, Hel-X bio carrier HXF12KLL	313 m ² /m ³ , 859 m ² /m ³	counter-current	Anaerobic sludge from a mesophilic wastewater treatment plant digester	10 L/h
55 ± 1	58.1 L	RFK 25 L type carrier, Hel-X bio carrier HXF12KLL	313 m ² /m ³ , 859 m ² /m ³	counter-current	Anaerobic sludge from a mesophilic wastewater treatment plant digester	3 L/h
55 ± 1	58.1 L	RFK 25 L type carrier, Hel-X bio carrier HXF12KLL	313 m ² /m ³ , 859 m ² /m ³	counter-current	Anaerobic sludge from a mesophilic wastewater treatment plant digester	10 L/h
54 ± 1	1 L	Glass rings (5 × 6 mm)	0.002 m ² /g	counter-current / concurrent	Digestate from a biogas plant	0.1 L/h for 30 s/ 0.5 h
52	0.291 L	Polyurethane foam filling	560–580 m ² /m ³	concurrent	Pasteurized cow manure	3 L/h for 3 min/d
52	0.291 L	Polyurethane foam filling	560–580 m ² /m ³	concurrent	Pasteurized cow manure	n.a.*
52	0.291 L	Polyurethane foam filling	560–580 m ² /m ³	concurrent	Pasteurized cow manure	4.2 L/h for 3 min/ d
38 ± 1	61 L	Bioflow 40	305 m ² /m ³	counter-current	Liquid trace element solution	0.24 L/h with 30 min delay
37 ± 2	5.78 L	Hiflow rings type 15–7	313 m ² /m ³	counter-current	Mineral media	15 L/h
37 ± 0.5	61 L	Bioflow 40	305 m ² /m ³	counter-current	Liquid trace element solution	15.6 L/h
37	26.8 L	Bioflow 40	305 m ² /m ³	counter-current	Liquid trace element solution	11.9 L/h
35	0.2258 L	Open pore polyurethane foam (PUF)	600 m ² /m ³	concurrent	Mineral media	0.612 L/h
Temperature (°C)	pH	Gas ratio (H ₂ :CO ₂)	Gas loading (m ³ /m ³ ·d)	Effluent CH ₄ content (%)	Conversion (%)	Reference
55 ± 1	6.0–8.0	3.75:1/4:1	6.5–77.6	71.4 ± 12.1–99.1 ± 1.3	> 99	Strübing et al., 2017
55 ± 1	7.0 ± 0.25	3.78:1	62.7–66.4	72.8 ± 26.1–97.5 ± 0.9	99	Strübing et al., 2018
55 ± 1	7.7 ± 0.1	3.78:1	78.5	98.1 ± 2.1	> 98	Strübing et al., 2019
54 ± 1	8.29 ± 0.03–8.60 ± 0.09 / 8.12 ± 0.14–8.63 ± 0.11	4.13:1:1.53 (CH ₄)	1.8–11.6	95.1 ± 0.5–98.7 ± 0.3 / 94.9 ± 0.6–99.1 ± 0.1	> 99	Porté et al., 2019
52	7.19 ± 0.02–9.49 ± 0.34	3.155–4.065:1:0.5–1 (N ₂)	13.7–44.1	80–98 (with N ₂)	> 99	Ashraf et al., 2020
52	7.5–8.0	3.71:1:1 (N ₂)	6.0–18.2	67.1 (without N ₂)	n.a	Sieborg et al., 2020
52	7.73–8.51	4:1:1(N ₂)/4:1:2 (N ₂)	14.9	95.3 ± 4.4 (with N ₂)	n.a	Dahl Jønson et al., 2020

Table 1 continued

Temperature (°C)	pH	Gas ratio (H ₂ :CO ₂)	Gas loading (m ³ /(m ³ d))	Effluent CH ₄ content (%)	Conversion (%)	Reference
38 ± 1	7 ± 1	4:1	16.4	96.6	n.a	Burkhardt et al., 2019
37 ± 2	6.8–7.0	6.7–3.7:1	5.8–13.9	95.4–97	97.2	Rachbauer et al., 2016
37 ± 0.5	7.2–7.4	4:1	4.83	98	n.a	Burkhardt et al., 2015
37	n.a	4:1	2.3–11.6	92.8–97.9	99 (H ₂)	Burkhardt and Busch, 2013
35	4.0–9.0	3.6:1 (N ₂)	151.4–214.9	0–44 (without N ₂)	n.a	Dupnock and Deshusses, 2017

*n.a. – not available

at thermophilic temperatures due to increased microbial growth rates (Angelidaki et al. 2018). Nonetheless, Rachbauer et al. (2016) reported an output gas with a CH₄ content (> 96%) using a mesophilic TBR in a long-term experiment (8 months), demonstrating that a long adaptation period affects reactor performance regardless of temperature conditions.

2.4.1 Gas loading rates

Performed studies reported wide ranges of influent gas loading rates. The gas loading rates of the feed gases vary between 1.8 and 214.9 m³/(m³d) though most studies used gas loading rates in the range of 5–16 m³/(m³d) (Table 1). Higher loadings of around 70 m³/(m³d) were used by Strübing et al. (2019, 2018, 2017) while Dupnock and Deshusses (2017) studied extreme high flow rates between 151.4 and 214.9 m³/(m³d). Depending on the operational conditions, the process performance of the BM was significantly influenced by the applied gas loading rate. However, no clear correlation can be established based on the applied gas loading rate and used packing materials.

2.4.2 Reactors inoculation

To inoculate TBR for *ex-situ* BM, digestate from biogas reactors (Rachbauer et al. 2016; Dahl Jønson et al. 2020) or sludge from wastewater treatment plants (Burkhardt and Busch 2013; Burkhardt et al. 2015, 2019; Strübing et al. 2017, 2018, 2019) were mainly used. Often, these cultures were enriched (containing a high abundance of hydrogenotrophic methanogens) to shorten the lag phase or adaptation period. Different inoculation procedures were reported in the literature while most studies performed inoculation by recirculating the liquid inoculum for a certain period of time. Some reported short recirculation time (2 h) (Ashraf et al. 2020; Dahl Jønson et al. 2020; Sieborg et al. 2020), while Porté et al. (2019) recirculated inoculum for 24 h. Much longer inoculation period (72 h) was reported by Burkhardt et al. (2019) and Rachbauer et al. (2016). In most cases, substrate gases were introduced after inoculation period, though Strübing et al. (2019, 2018, 2017) supplied substrate gases during the inoculation period.

2.4.3 Nutrient requirements

Continuous supplementation of nutrients to the microbes in TBR is crucial to maintain the stability of the process. In recent years, the media used for *ex-situ* BM in TBR can be categorized into synthetic and non-synthetic. Non-synthetic liquid media originated mostly from digested wastewater sludge (Strübing et al. 2017, 2018, 2019), digestate from biogas plant (Porté et al. 2019) and pasteurized cow manure (Ashraf et al. 2020; Dahl Jønson et al. 2020; Sieborg et al. 2020). The possibility to use non-synthetic and rather easily available media is a strong advantage of this process increasing its sustainability. However, the non-synthetic media require pretreatment to prevent the growth of unintended microorganisms, that can potentially produce biogas through the acetoclastic pathway or use gas substrates e.g., to produce acetate through homoacetogenesis. In the literature, several pre-treatment methods have been published, for example, Porté et al. (2019) incubated the digestate for more than 3 months under thermophilic conditions to minimize biogas generation from organic matter in the medium. Strübing et al. (2019, 2018, 2017) flushed the digested sewage sludge repeatedly with nitrogen and sieved it (100 μm) to remove the solid particles before use. Pasteurization at 70 °C was performed by Ashraf et al. (2020), Sieborg et al. (2020) and Dahl Jønson et al. (2020) to inhibit bacterial activity in cow manure. The supplementation with synthetic media was described by Strübing et al. (2018, 2017) following the procedure adopted by Seifert et al. (2014). Application of mineral buffer solution, as e.g., phosphate buffer was also performed to maintain pH of medium (Dupnock and Deshusses 2017; Strübing et al. 2017, 2018; Dahl Jønson et al. 2020). In these studies, buffer solution was supplied when necessary without any fixed rhythm. Instead of using phosphate buffer, Porté et al. (2019) neutralized medium twice a week with HCl and introduced it back into the reactor to stabilize the pH value. Consequently, different procedures applied in the previous studies had also focused on a wide pH range that spanned from 7.0 up to around 8.6.

The frequency of nutrients supplementation in TBR varied between the studies. Often irregular nutrient supply was reported (Rachbauer et al. 2016; Ashraf et al. 2020; Dahl Jønson et al. 2020). This indicates that the studies optimizing the liquid phase exchange

were not comprehensive enough, making it difficult to compare findings from different studies.

2.5 TBR performance

In this review, the performance of TBR from previous studies were compared based on the efficiency of CO₂ and H₂ conversion into CH₄ and the effluent CH₄ content. In general, most studies reported a nearly full conversion rate (around 99%) while few studies reported slightly lower conversion values ranging between 97–98% (Table 1). The high conversion rate was correlated with high CH₄ content in the effluent gas in nearly all previous studies (> 95%). However, in these calculations, some studies used the N₂ in the experiments to mimic the CH₄ in the supplied gas (Ashraf et al. 2020; Dahl Jønson et al. 2020). Similar addition of N₂ was also performed by Sieborg et al. (2020) where the CH₄ content without recognition of the added N₂ as CH₄ was 67.1% in the effluent gas. However, without reported conversion, it is not possible to relate this information with two previously mentioned studies.

On the other hand, Dupnock and Deshusses (2017) reported a very low conversion rate with the effluent CH₄ content of 44%. These results were related to the extremely high gas loading applied to the reactor (151.4 m³/(m³d)–214.9 m³/(m³d)) that is about 3 times higher than the loadings reported by others. Extreme gas loading led to a decrease in product gas purity and low conversion efficiency that can be caused by the shear force impacted on biofilm resulting in its detachment. Therefore, the optimum gas loading rate should be determined according to the packing material used. A study by Strübing et al. (2019, 2018, 2017) obtained good results with nearly full conversion when high gas loading (> 16 m³/(m³d)) was used, showing that higher loadings can be adapted in the TBR for BM. On the other hand, extreme high loadings as used in Dupnock and Deshusses (2017) seem to be too challenging for this reactor configuration.

Regarding to H₂ injection configurations, the literature comparing concurrent and counter-current configurations are scarce. Therefore, the proper validation of the most appropriate configuration is not currently possible. To our knowledge, only Porté et al. (2019) compared these two configurations indicating comparable results for both configurations (CH₄

content—97.6% for concurrent and 97.8% for counter-current). However, this study was performed using only one kind of packing material (glass rings) and relatively low gas loading rate (up to $11.6 \text{ m}^3/(\text{m}^3\text{d})$).

The use of different liquid phases with a wide pH range (from 7.0 up to 8.6) had no significant influence on the purity of the effluent gas. Comparable CH_4 content with an average of 97 to 98% were observed (Fig. 3). Similar observations have been reported when different operating temperatures were tested (mesophilic vs. thermophilic), as the performance of the reactors were comparable. Though, the microbial communities and the hydrogenotrophic methanogens differ because of temperature.

2.6 Typical process disturbances

The TBR for *ex-situ* BM offers many advantages compared to different configurations. However, the difficulties regarding several issues were previously reported. The most common difficulties are related to the establishment of archaea in the TBR that leads to a non-efficient CH_4 production or acetate synthesis

(homoacetogenesis) (Eq. 4) (Logroño et al. 2020). The acetate accumulation was previously reported by e.g., Kougiyas et al. (2017). The acetate synthesis during the process leads to the pH decrease and lower CH_4 production. Therefore, the appropriate operational conditions are critical to manage microbiota towards selective CH_4 production.



Another problem typically connected with TBR operation is clogging, that is caused by the uncontrolled biomass growth on the packing material. Clogging causes significant technical problems leading to the process performance limitation (Burkhardt et al. 2019). Due to the clogging, the packing material needs to be replaced, that in case of e.g., foam-like packing requires a new acclimatization of microbiota with packing material (Alfaro et al. 2018). Aside from clogging, the high loading gas supplied to the TBR may cause the detachment of the biofilm developed on the packing material leading to the biomass wash out.

Based on the Eq. 1 the *ex-situ* BM in addition to CH_4 produces H_2O as a co-product. The H_2O

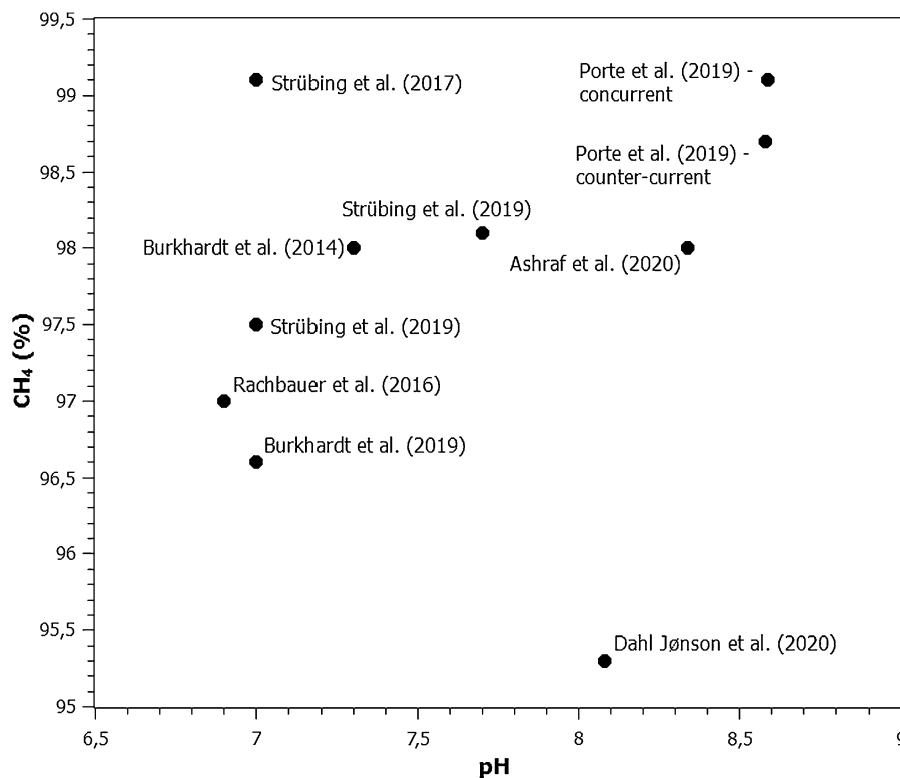


Fig. 3 Relationship between effluent CH_4 content and operational pH at different studies (the reference to the study is included)

production during TBR causes the dilution of the liquid phase in TBR. In consequence, it causes the dilution of e.g., trace elements and nutrients required for microbial growth that need to be balanced during the reactor operation.

3 Microbiology of *ex-situ* biomethanation

The *ex-situ* BM process is based on the biological activity of hydrogenotrophic methanogens (archaea) that use CO₂ and H₂ as substrates. Hydrogenotrophic methanogens are typically present in the regular AD where they theoretically contribute to around 30% of CH₄ production (70% is accounted for acetoclastic methanogens) (Sawayama et al. 2004). The hydrogenotrophic methanogens were found to be less sensitive to the presence of ammonia than the acetoclastic methanogens, leading to an increase in their share at elevated ammonia presence during the regular AD (Angenent et al. 2002; Sposob et al. 2020). This trait of hydrogenotrophic methanogens can potentially facilitate the use of other ammonia-rich and non-synthetic nutrients sources or enhance the system tolerance on ammonia presence in biogas as the feedstock to *ex-situ* BM.

Based on the previous studies, it has been found that the *ex-situ* BM conditions selectively enriched hydrogenotrophic methanogens leading to their predominance. Therefore, the information about bacteria and their role in *ex-situ* BM is rather limited. Although, previous studies on bacterial communities revealed that the phyla Firmicutes, Proteobacteria, and Bacteroidetes typically predominate in TBR (Dupnock and Deshusses 2017; Kougias et al. 2017; Porté et al. 2019; Ashraf et al. 2020). Several bacterial taxa from phyla Firmicutes (mainly *Clostridia*) were suspected to be responsible for homoacetogenesis (Logroño et al. 2020). Also, previous research indicated *Clostridia* members to be abundant in TBR biofilm and liquid media, while acetate-utilizing bacteria prevailed in liquid samples (Porté et al. 2019). However, their further identification at e.g., genus level was challenging to achieve. The two main orders of hydrogenotrophic methanogens such as Methanobacteriales and Methanomicrobiales were found characteristic for *ex-situ* BM (Table 2). It has been suggested that their dominance during BM systems is regardless the operating temperature (Logroño et al. 2020).

Order Methanobacteriales is widespread and known for mediating the hydrogenotrophic methanogenesis both under mesophilic and thermophilic conditions (Karakashev et al. 2005). In the last years different species of Methanobacteriales were identified. For example *Methanothermobacter thermoautotrophicus* was frequently reported in the case of thermophilic *ex-situ* BM (Martin et al. 2013; Kougias et al. 2017). Furthermore, they are capable to thrive in high H₂S concentrations conditions (Kaster et al. 2011). Therefore, this methanogen was widely used for bioaugmentation of *ex-situ* BM, similarly as *Methanothermobacter marburgensis* expressing their stable performance over the time. Additionally, some of the hydrogenotrophic methanogens such as *Methanobrevibacter arboriphilus* express the capability to survive in the oxygen (O₂) exposures up to 3 days enhancing the system ability to recover (Dupnock and Deshusses 2017).

The second order present during the *ex-situ* BM, Methanomicrobiales, is usually represented by a lower relative share in comparison to the *Methanobacteriales*. Genera of *Methanoculleus* and *Methanospirillum* were previously reported in context of *ex-situ* BM. *Methanoculleus* has also been reported in high salt and ammonia AD processes (maize and manure as a substrate) (Maus et al. 2012; Dahl Jønson et al. 2020). The lower presence of Methanomicrobiales, especially *Methanospirillum* can be related to the fact that no thermophilic *Methanospirillum* genus has been identified so far while most of the previous studies operated at thermophilic conditions (Jain et al. 2020). Although, their presence was previously reported in mesophilic AD reactors treating cattle and pig manure.

4 Techno-economic analysis

There has been little research focus on the cost analysis of the TBR in the power-to-methane concept; therefore, this section will assess the relevant factors related to the economy of power-to-methane technology using BM reactors in general.

4.1 Power-to-methane with BM reactor

To our knowledge, only one study, Bekkering et al. (2020), used TBR as an *ex-situ* BM reactor in estimating the cost of farm-scale power-to-methane

Table 2 Dominating hydrogenotrophic methanogens

Classification				Reference
Order	Family	Genus	Species	
Methanobacteriales	<i>Methanobacteriaceae</i>	<i>Methanobrevibacter</i>	<i>Methanobrevibacter arboriphilus</i>	(Dupnock and Deshusses 2017)
			–	(Jensen et al. 2019)
		<i>Methanobacterium</i>	<i>Methanobacterium formicicum</i>	(Porté et al. 2019)
			<i>Methanothermobacter</i>	<i>Methanothermobacter marburgensis</i> **
		<i>Methanothermobacter thermotrophicus</i> **		(Martin et al. 2013; Alfaro et al. 2018)
		<i>Methanothermobacter wolfeii</i>		(Guneratnam et al. 2017)
		sp. 1		(Porté et al. 2019)
		sp. 12		(Kougias et al. 2020)
		–		(Dupnock and Deshusses 2017; Jensen et al. 2019; Ashraf et al. 2020; Dahl Jønson et al. 2020; Logroño et al. 2020)
		–	–	(Luo and Angelidaki 2012; Savvas et al. 2017b)
Methanomicrobiales	<i>Methanomicrobiaceae</i>	<i>Methanoculleus</i>	–	(Wang et al. 2013; Ashraf et al. 2020; Logroño et al. 2020)
			<i>Methanospirillaceae</i>	<i>Methanospirillum</i>

**these species were also inoculated at the beginning of the studies

technology. The authors compared the costs of four different scenarios in the study: (a) without BM, biogas is upgraded using membrane technology, (b) with BM, (c) BM combined with membrane upgrading, and (d) BM combined with membrane upgrading with surplus renewable electricity. Scenario (a) had the lowest renewable gas production costs, whereas scenarios (b–d) had higher energy efficiencies and environmental benefits (due to the consumption of renewable energy). The higher costs of BM scenarios are primarily the result of electrolysis. The investment cost for *ex-situ* TBR (including compressor) for a 500 Nm³ h⁻¹ biogas production unit was estimated to be 1.5 × 10⁶ €.

The production cost of BM for 5 MW plant size is slightly higher than catalytic methanation, while at 110 MW plant size, these costs are about 2.5 times higher than for catalytic methanation (Götz et al. 2016). For both processes, the costs are heavily dependent on the electrolyzer investment cost. The cost of the BM process in 2017 was around 1200 € kWel⁻¹ (related to the electrical power input of

electrolyzer) and is expected to drop to 300 € kWel⁻¹ in 2050 (Golling et al. 2017). In 2030, the cost of BM is predicted to fall to 700 € kWel⁻¹. The cost reduction could be due to lower cost of electrolyzer and economy scale with the development of the technology (Golling et al. 2017). Hidalgo and Martín-Marroquín (2020) mentioned that the investment costs for electrolysis and methanation technologies are expected to fall from > 1000 € kWel⁻¹ to about 500 € kWel⁻¹ in the future. The decrease in the investment cost clearly indicates that the market implementation of the power-to-methane concept is ongoing.

Consideration of environmental effects during the economic feasibility assessment of BM is crucial. Bekkering et al. (2020) reported that GHG savings improved better with BM technology than without. It is expected that the cost of energy may be at the similar level of the cost of natural gas if CO₂ emission saving is included or if the CO₂ emitted from natural gas is taxed. Another point to be considered is that BM can minimize the expansion of electricity grid infrastructure and raise the share of green energy in the

transportation and heating sector. In this light, BM itself plays an important part in the realization of the ambitious transition of the energy system (Götz et al. 2016).

4.2 Electrolysis

Water electrolysis is one of many H₂ processing technologies that produces high purity H₂ in an environmentally friendly manner (Kumar and Himabindu 2019). The production costs of H₂ from water electrolysis are influenced by various technical and economic factors, with CAPEX requirements, conversion efficiency, electricity costs and annual operating hours being the most important. The cost of producing H₂ alone is estimated to be 0.09 € kWh⁻¹, which is higher than the cost of conventional physicochemical biogas upgrading by CO₂ removal (0.07 € kWh⁻¹) (Angelidaki et al. 2018).

Currently, there are three water electrolysis technologies available: alkaline electrolysis (AE), polymer electrolyte membrane electrolysis (PEM) and solid oxide electrolysis (SOE) (Hosseini and Wahid 2016; Gorre et al. 2020). CAPEX requirements for AE are in the range of 416–1165 € kW_e⁻¹ and 916–1498 € kW_e⁻¹ for PEM electrolyzers, while estimates for SOEC electrolyzers range across 2230–4660 € kW_e⁻¹. Further reduction in CAPEX is projected in the future (Fig. 4). The main reasons for the reduction are related to the increase in automation and production capabilities, together with the enhancement in electrolyzers

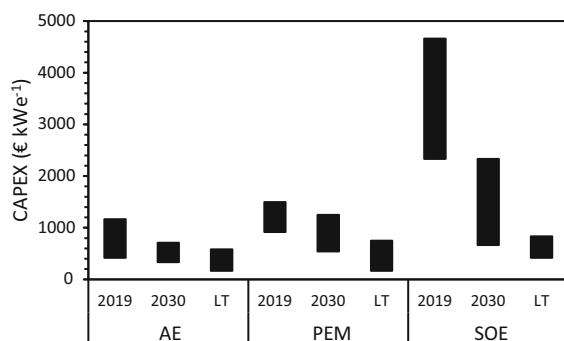


Fig. 4 CAPEX of different types of electrolyzers (LT—long-term, AE—Alkaline electrolysis, PEM—polymer electrolyte membrane electrolysis, SOE—solid oxide electrolysis. CAPEX represents system costs, including power electronics, gas conditioning and balance of plant; CAPEX ranges reflect different system sizes and uncertainties in future estimates)

technology due to development of power-to-gas. The operation and maintenance (O&M) costs shared about 9% of the total H₂ production cost.

At present, AE technology is more suitable for large scale implementation because of the cost and maturity (Brauns and Turek 2020; Hu et al. 2020). However, the main drawbacks are low current densities, corrosion and limitation when working in dynamic condition (e.g. slow start-up and loading response) (Hosseini and Wahid 2016; Dutta and Hussain 2020; Grimm et al. 2020). On the other hand, the PEM technology is more efficient and flexible to handle fluctuating input currents but is restricted by expensive materials cost, short life span and complexity due to high operating pressure (Hosseini and Wahid 2016; Brauns and Turek 2020; Dutta and Hussain 2020). SOE is the latest development in water electrolysis technology. Positive aspects of SOE include high electrical efficiency, low material cost and possibility to operate in reverse mode as fuel cell or in co-electrolysis way (Hidalgo and Martín-Marroquín 2020). Nevertheless, the technology has a limited lifetime due to thermal cycles (Pääkkönen et al. 2018; Dutta and Hussain 2020). Future cost reductions, increased lifetime and improved efficiency in these technologies may be realized through the development of new materials and manufacturing processes.

4.3 H₂ storage and transportation

Typically, electrolysis can be performed more dynamically than the operation of methanation reactor. As a result, H₂ storage is needed. If the cost of H₂ storage is considered, it is the second main contributor to the investment cost of a power-to-methane plant (Götz et al. 2016). Currently, gaseous storage at different pressure levels are mainly used at large BM plants (Gorre et al. 2020). The costs of storage may vary between 375 € kg⁻¹ for 50 bar and 490 € kg⁻¹ for 200 bar (Gorre et al. 2020). The size of H₂ storage system depends on the dynamic behavior of methanation and the profile of electrical input of electrolyzer (Götz et al. 2016; Gorre et al. 2020). For example, larger H₂ storage is required for full load operation, while smaller storage is needed for dynamic operation. Besides, electrolyzer operating in a smaller number of full-load hours may greatly reduce the investment cost. Dynamic operation is the best option in term of cost, however, the variability in H₂ input

may affect the process performance of the BM reactor because the anaerobic microbes are sensitive to changes. Further research is crucial to examine the response of anaerobic microbes towards intermittent H₂ supply.

The cost for transportation could be close to zero if the H₂ can be utilized directly to where it is produced. Though, if the H₂ has to be transported for long distance, the costs of transmission and distribution could be three times as large as the cost of H₂ production (Birol 2019). H₂ has a low energy density, meaning that it is expensive to transport H₂ over long distances. Different types of H₂ transportation methods are available, including cryogenic liquid tankers, pressurized H₂ tube trailers and gas pipelines. The selection of economical H₂ transportation varies based on the distance and amounts of H₂. For short distances (< 500 km) and small amounts, liquid H₂ transport by trucks is the best option, meanwhile, pipelines and ship are the potential option for long distances (> 1000 km) and transport of large amounts of H₂ (Nazir et al. 2020). The estimated cost of H₂ distribution for 500 km in 2030 using pipelines and liquid H₂ trucks is below 0.5 € kg⁻¹ while around 1.7 € kg⁻¹ when H₂ is compressed and transported by trucks. However, the choice of H₂ transportation also depends on the required form of H₂ (gases or liquid) at the utilization purpose.

4.4 Economic potential of by-products

By-products such as O₂ or heat generated during electrolysis and recovered from AD effluent could be valorized to increase the economic viability of BM (Zauner et al. 2018; Bekkering et al. 2020; Hidalgo and Martín-Marroquín 2020). O₂ for example can be sold (price of O₂ is 50 € t⁻¹) for industrial use (Zauner et al. 2018). Another option is to use it for aeration process (e.g., nitrification) in the wastewater treatment plant or for desulfurization of biogas (Götz et al. 2016). Though, additional cost for liquefaction of O₂ for transportation purposes and the intermittent O₂ production (based on electrolyzer operation) need to be considered. In this case, direct utilization of O₂ at the electrolyzer site could be the best scenario. The waste heat from BM can be utilized for heating the digester or drying the digestate (Bekkering et al., 2020; Gorre et al., 2020). Waste heat recovery should be considered wherever possible in order to increase the resource and overall process efficiency.

5 Sources of CO₂

The sources of CO₂ for BM can originate from fossil power plants, biomass, industrial product gasses or ambient air (Schiebahn et al. 2015; Gorre et al. 2020; Hidalgo and Martín-Marroquín 2020). CO₂ captured from fossil power plants are widely investigated in the context of carbon capture and storage (CCS). Several separation technologies are available including adsorption, membrane separation, chemical and physical absorption, and cryogenic separation. The related costs are calculated around 20–60 € tCO₂⁻¹. While, large amounts of CO₂ can be extracted from fossil power plants, the fact that CO₂ is not biogenic makes it difficult to be classified as the product of renewable power CH₄ (Schiebahn et al. 2015). Fermentation of biomass to produce biogas or bioethanol generates CO₂ as by-products and thus, no extra energy or cost involved for producing biogenic CO₂. CO₂ from raw biogas can be used directly in BM without the need of CO₂ separation (Schiebahn et al. 2015).

The energy and industry sectors contribute to more than one third of global CO₂ emissions (Hidalgo and Martín-Marroquín 2020). Thus, CO₂ from these sectors can serve as a potential substrate for BM decreasing the CO₂ emissions. CO₂ separation technology in industrial processes is technically feasible. The most relevant industries are cement and steel, due to the high CO₂ generations (Schiebahn et al. 2015). Combining the biomass gasification technology with power-to-methane could be an interesting approach to increase the availability of H₂ and CO₂ for BM (Götz et al. 2016). The gases (CO, CO₂ and H₂) produced from the biomass gasification process could be used as substrates for BM, together with H₂ generated from electrolysis. The integration of biomass gasification and power-to-methane during the steel production process has been already evaluated by Rosenfeld et al. (2020). During the steel production, three gases such as coke oven gas (COG), blast furnace gas (BFG) and basic oxygen furnace gas (BOFG) are produced. COG contains a high share of CH₄ and H₂ while BFG and BOFG consist of CO₂, CO and N₂ (Rosenfeld et al. 2020). These gases can be indicated as another substrate source for BM. Besides steel industry, other relevant CO₂ or CO sources are from cement manufacturing and chemical industry (Baier et al. 2018; Hidalgo and Martín-Marroquín 2020). However, further studies on the profitability of such system in terms of mass and

energy balance, economy and CO₂ reduction are needed.

CO₂ from ambient air can be separated using strong alkali such as potassium or sodium hydroxide. This process has the advantage of being able to supply biogenic CO₂ without relying on spatially accessible CO₂ sources. Furthermore, there is no requirement for CO₂ transportation. According to the literature, the cost of CO₂ generated by air capture varies between 100 and 1000 € tCO₂⁻¹ (Schiebahn et al. 2015; Bos et al. 2020). Keith et al. (2018), on the other hand, reported a lower levelized cost per ton CO₂ captured from the atmosphere, ranging from 78 to 193 € tCO₂⁻¹.

6 Perspectives

Since the TBR was quite recently applied for *ex-situ* BM, the understanding of the process is limited specifically regarding optimal conditions and maximum performance. Due to that, further work focusing on operational parameters optimization (e.g., gas loading rate, hydraulic retention time, pH) and packing materials should be performed to increase the process productivity and describe its limitations.

TBR configuration also has its drawbacks for which solutions can be found in the future such as: bacterial contamination (homoacetogenesis), clogging and H₂O production. Additionally, better understanding of *ex-situ* BM could be achieved through the mathematical modeling of hydrogenotrophic methanogens at TBR. However, so far, the modeling approaches regarding hydrogenotrophic methanogenesis are scarce.

Appropriate optimization of the process will provide an answer to the mass and energy balance of this process and its economic feasibility. At the same time, further development of electrolyzers for H₂ production is expected that could potentially decrease the price of H₂, which is an economically crucial factor for the process. The future answers to these considerations will probably facilitate the scale up of *ex-situ* BM using TBR and its application at the full-scale AD plants.

7 Conclusions

Ex-situ biomethanation is one of the most promising solutions addressing the power-to-methane concept

that is going to significantly develop in the next years. In this review the attention was given to TBR as the most efficient for this application describing its principals, operational conditions, performance, and microbiology.

From an economic point-of-view, the prospects of power-to-methane will be dependent on the reduction of H₂ costs and developments in electrolyzers technology. Therefore, the related costs influencing power-to-methane technology with BM reactor such as electrolyzers and H₂ storage and transportation were also discussed in this work. Furthermore, we explored the possibility of using CO₂ generated from various sources as an influent substrate for BM.

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