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Biogas upgrading and utilization: Current status and perspectives

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ABSTRACT

Biogas production is an established sustainable process for simultaneous generation of renewable energy and treatment of organic wastes. The increasing interest of utilizing biogas as substitute to natural gas or its exploitation as transport fuel opened new avenues in the development of biogas upgrading techniques. The present work is a critical review that summarizes state-of-the-art technologies for biogas upgrading and enhancement with particular attention to the emerging biological methanation processes. The review includes comprehensive description of the main principles of various biogas upgrading methodologies, scientific and technical outcomes related to their biomethanation efficiency, challenges that have to be addressed for further development and incentives and feasibility of the upgrading concepts.

1. Introduction

Biogas is the product of a biologically mediated process, which is known as Anaerobic Digestion (AD). Biogas primarily consists of methane (CH_4) in a range of 50–70% and carbon dioxide (CO_2) at a concentration of 30–50%. The relative content of CH_4 and CO_2 in biogas is mainly dependent on the nature of the substrate and pH of the reactor. Besides these two gasses, biogas additionally contains minor amounts of other compounds, such as nitrogen (N_2) at concentrations of 0–3%, which could originate from air saturated in the influent, vapour water (H_2O) at concentrations of 5–10%, or higher at thermophilic temperatures, derived from medium evaporation, oxygen (O_2) at concentrations of 0–1%, which is entering the process from the influent substrate or leakages, hydrogen sulfide (H_2S) at concentrations of 0–10,000 ppmv, which is produced from reduction of sulfate contained in some wastestreams, ammonia (NH_3) originating from hydrolysis of proteinaceous materials or urine, hydrocarbons at concentrations of 0–200 mg/m^{-3} and siloxanes at concentrations of 0–41 mg m^{-3}, originating for example from effluents from cosmetic medical industries (Muñoz et al., 2015; Petersson and Wellinger, 2009).

Apart from CH_4, all the other gasses contained in biogas are unwanted and are considered as biogas pollutants. The energy content of methane described by the Lower Calorific Value (LCV) is 50.4 MJ/kg-CH_4 or 36 MJ/m^3-CH_4 (at STP conditions). Therefore, it is well understood that the higher the CO_2 or N_2 content is, the lower the LCV in

biogas. For biogas with methane content in the range of 60–65% the LCV is approximately 20–25 MJ/m^3-biogas. H_2S and NH_3 are toxic and extremely corrosive, damaging the combined heat and power (CHP) unit and metal parts via emission of SO_2 from combustion. Moreover, the presence of siloxanes in biogas, even in minor concentrations, is associated with problems. It is well known that during combustion silicone oxides generate sticky residues which deposit in biogas combustion engines and valves causing malfunction (Abatzoglou and Boivin, 2009). Nowadays, there are different treatments targeting at removing the undesired compounds from the biogas expanding its range of applications.

The first treatment is related to "biogas cleaning" and includes removal of harmful and/or toxic compounds (such as H_2S, Si, volatile organic compounds (VOCs), siloxanes, CO, and NH_3). However, it is practically only H_2S which is mainly targeted and many current biogas plants have H_2S removal units commonly based on biological H_2S oxidation by aerobic sulphate oxidizing bacteria. The second treatment is called "biogas upgrading" and aims to increase the low calorific value of the biogas, and thus, to convert it to higher fuel standard (Sun et al., 2015). In case the upgraded biogas is purified to specifications similar to natural gas, the final gas product is called biomethane (Kougias et al., 2017b). Currently, the specifications of the natural gas composition are depending on national regulations and in some countries > 95% methane content is required; however, European Commission has recently issued a mandate for determining harmonised standards for gas quality.

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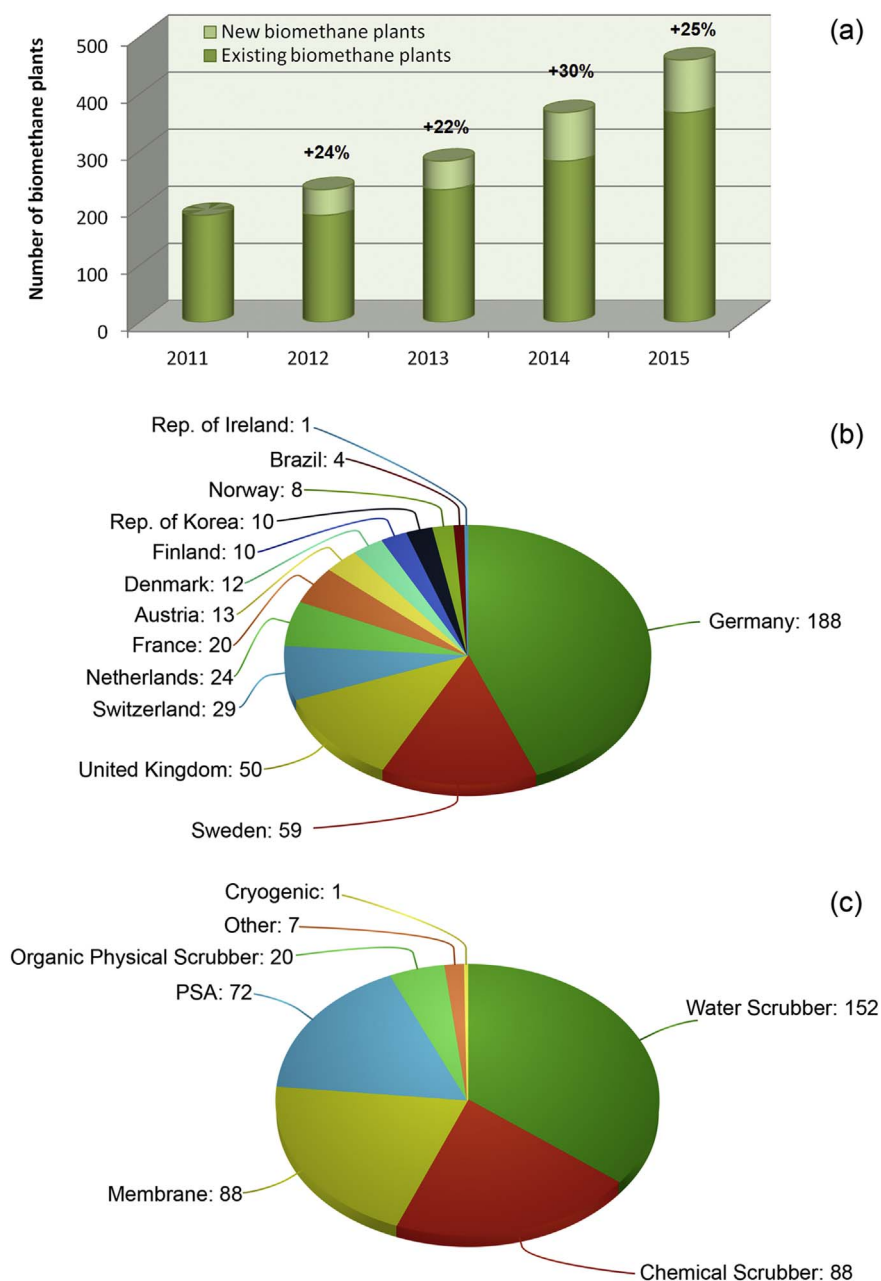
Fig. 1. Development of biogas upgrading technologies distributed according to countries and years; a) number of operating biomethane plants, b) location of existing biomethane plants and c) distribution of applied commercial technologies. Data are according to IEA Bioenergy Task 37 as reported in Hoyer et al. (2016) and European Biogas Association.

It should be noted that in the upgrading process the CO_2 contained in the raw biogas is either removed or is converted to CH_4 by reaction with H_2 (Kougias et al., 2017b). There are several commercial upgrading technologies available. An increasing number of biogas plants with biogas upgrading units are emerging in Europe the recent years (Fig. 1a). Most of the biomethanation plants are in Germany, while other European countries such Sweden, UK, Switzerland and have also constructed biomethanation facilities (Fig. 1b).

The aim of the present work is to provide a comprehensive overview of various biogas upgrading technologies and to present incentives for further development of upgrading concepts. More specifically, the review describes the main principles of commercial or under development physical, chemical and biological methodologies. Particular attention has been given to emerging upgrading bioprocesses since they are envisioned to play a protagonist role in decoupling bioenergy production from biomass availability. Finally, the review presents techno-economic and environmental incentives that encourage the sustainability perspective of biogas upgrading concepts.

2. Biogas upgrading technologies

2.1. Physical and chemical technologies

Currently, five physical/chemical technologies for separation/transformation of CO_2 from CH_4 exist at commercial readiness level (Fig. 1c), involving processes of absorption, adsorption and membrane separation. Moreover, there are other technologies based on cryogenic process or chemical hydrogenation, which are still under development. A more detailed description of the functional principles and the status of these biogas upgrading technologies is given in the next subchapters and a comparison of their biomethanation efficiencies is given at Table 1. In general, the methane recovery from physicochemical processes can reach > 96% and as it will be further discussed increased temperature, high pressure or addition of chemicals are required to ensure an efficient biomethanation.

Table 1

Comparison of different pilot and commercial biogas upgrading technologies (Andriani et al., 2014; Bauer et al., 2013a; Bekkering et al., 2010; Jürgensen et al., 2014; MeGa-stoRE, 2016; Muñoz et al., 2015; Ryckebosch et al., 2011; Serejo et al., 2015; Toledo-Cervantes et al., 2017).

	Cryogenic	Sabatier process	PSA	Water scrubbing	Physical scrubbing	Chemical absorption	Membrane separation
Consumption for raw biogas (kWh/Nm^3)	0.76	nf	0.23–0.30	0.25–0.3	0.2–0.3	0.05–0.15	0.18–0.20
Consumption for clean biogas (kWh/Nm3)	nf	nf	0.29–1.00	0.3–0.9	0.4	0.05–0.25	0.14–0.26
Heat consumption (kWh/Nm^3)	nf	nf	None	None	< 0.2	0.5–0.75	None
Heat demand (°C)	− 196	270			55–80	100–180	
Cost	High	Medium	Medium	Medium	Medium	High	High
CH$_4$ losses (%)	2	nf	< 4	< 2	2–4	< 0.1	< 0.6
CH$_4$ recovery (%)	97–98	97–99	96–98	96–98	96–98	96–99	96–98
Pre-purification	Yes	Recommended	Yes	Recommended	Recommended	Yes	Recommended
H$_2$S co-removal	Yes	No	Possible	Yes	Possible	Contaminant	Possible
N$_2$ and O$_2$ co-removal	Yes	No	Possible	No	No	No	Partial
Operation pressure (bar)	80	8–10	3–10	4–10	4–8	Atmospheric	5–8
Pressure at outlet (bar)	8–10		4–5	7–10	1.3–7.5	4–5	4.-6

nf: not found
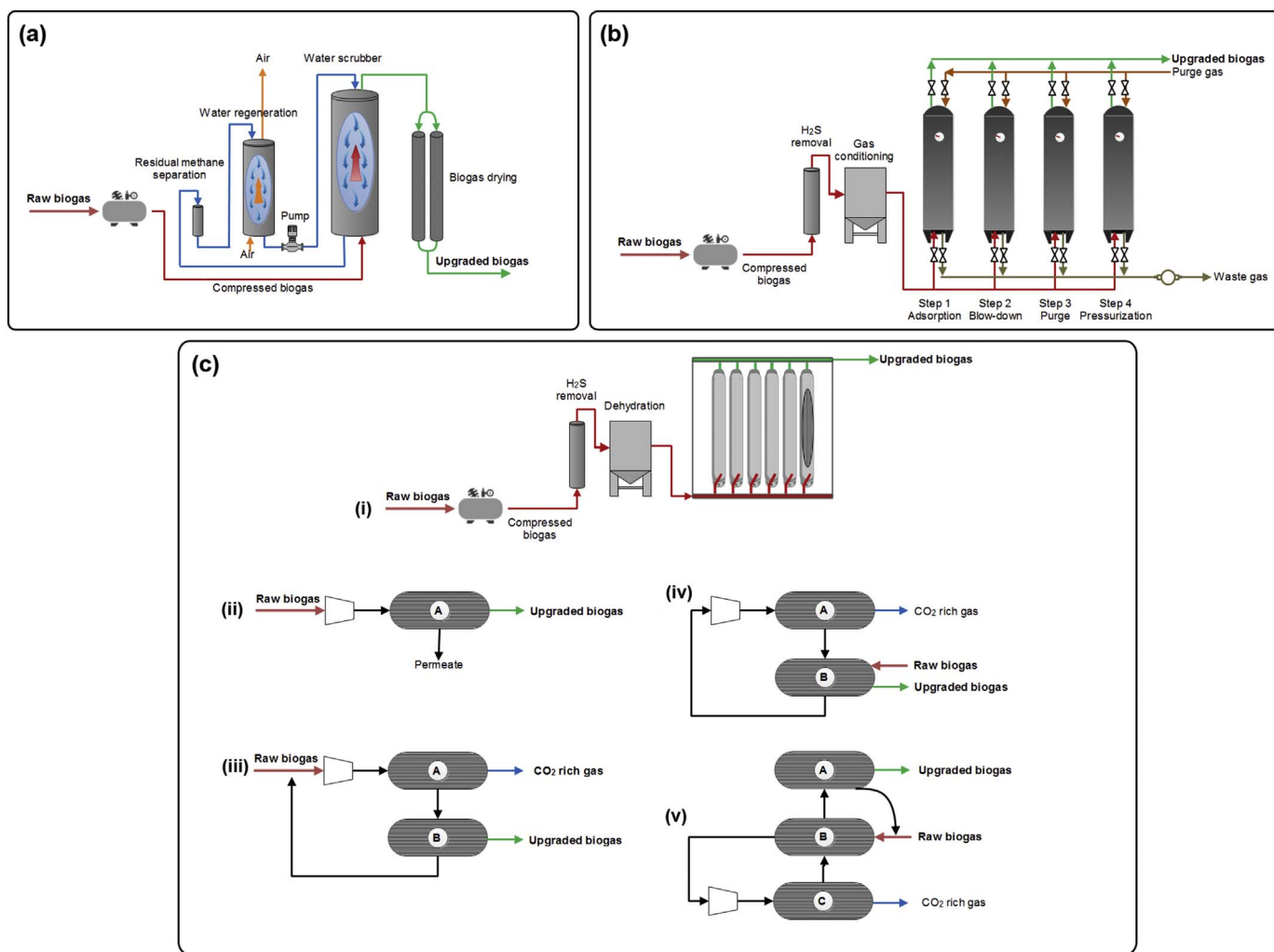
Fig. 2. Flow chart of different physicochemical processes for biogas upgrade; a) water scrubbing system, b) pressure swing adsorption technology and c) membrane cascade separation system for biogas upgrade; i) general design, ii) single stage configuration, iii) two-stage configuration with a recirculation loop, iv) two-stage configuration with sweep and v) three-stage configuration with sweep. Modified based on Bauer et al. (2013b), Makaruk et al. (2010), and Zhao et al. (2010).

2.1.1. Physical absorption method using water scrubbing system

Water scrubbing (Fig. 2a) is the most commonly used technology for biogas cleaning and upgrading (Thrän et al., 2014). This process relies on the separation of CO$_2$ and H$_2$S from the biogas due to their increased solubility in water compared to CH$_4$ (i.e. according to Henry's law, the solubility of CO$_2$ in water at 25 °C is approximately 26 times higher compared to methane). Initially, the biogas is pressurized (6–10 bar, up

to 40 °C) and injected into the absorption column via the bottom side of the tank, while the water is provided from the top (Bauer et al., 2013b). On contrary, water is provided from the top side of the column and flows towards the counter-current flow of the gas. The absorption column is usually filled with random packing material to increase the gas-liquid mass transfer (Ryckebosch et al., 2011). The biomethane is released from the top of the scrubber, while the water phase containing

the CO_2 and H_2S is circulated into a flush column, where the pressure decreases (2.5–3.5 bar) and some traces of CH_4 which were dissolved in the water are recovered. Depending on the water re-use, two methods are commercially available; the "single pass scrubbing", which is employed in cases that the water is derived from sewage treatment plants and the "regenerative absorption". In the latter one, the water can be regenerated in a desorption column by decompression at atmospheric pressure, resulting in the removal of CO_2 and H_2S. Water decompression usually occurs by air stripping. However, in cases that the biogas contains high concentrations of H_2S, steam or inert gas are used in the desorption process to avoid formation of elemental sulphur by the application of air stripping, which will in turn lead to operational problems (Ryckebosch et al., 2011). The regeneration step is crucial for this upgrading technology due to the large quantities of water that are required. The typical water flow that is needed to upgrade 1000 Nm^3/h of raw biogas ranges between 180 and 200 m^3/h depending on the pressure and water temperature (Bauer et al., 2013a). Finally, after a drying step, the CH_4 can reach up to 99% purity (Sun et al., 2015).

2.1.2. Physical absorption method using organic solvents

This method relies on the same principle as water scrubbing, however, the absorption of CO_2 and H_2S is accomplished by the use of organic solvent instead of water (Table 1). Commonly, the used organic solvents are mixtures of methanol and dimethyl ethers of polyethylene glycol. Marketable chemical products are available under the trade names of Selexol® and Genosorb®. The advantage of the solvents compared to the water relies to the considerably higher solubility of CO_2 that can be exhibited. More specifically, Selexol® is able to absorb 3 times more CO_2 than water, which practically means reduced liquid inputs in the system, and therefore, smaller dimensions of the upgrading unit. Nevertheless, the organic solvents are difficult to be regenerated due to the high solubility of CO_2 and this constitutes a major obstacle of the process (Persson, 2003). Furthermore, the solubility of H_2S in Selexol® is significantly higher than the one of CO_2 and therefore its separation during the solvent regeneration requires increased temperatures. It is obvious that the more the concentration of H_2S in the raw biogas is, the higher the temperature should be applied. Thus, to avoid increased energy consumption it is recommended to remove H_2S before the gas is fed to the solvent (Persson, 2003). Initially, the raw biogas is compressed (7–8 bars) and is cooled at around 20 °C prior to its injection from the bottom of the absorption column. Similarly, the organic solvent is cooled down prior to its addition as the temperature affects the Henry's constant (Bauer et al., 2013a). Afterwards, the organic solvent is regenerated by heating it up to 80 °C and adding it in a desorption column in which the pressure is decreased to 1 bar (Bauer et al., 2013b; Sun et al., 2015). The final content of CH_4 in the upgraded biogas using this technology can reach 98% (Bauer et al., 2013a).

2.1.3. Chemical absorption method using amine solutions

Chemical scrubbers use aqueous amine solutions (i.e. mono-, di- or tri-ethanolamine) to bind the CO_2 molecules contained in the biogas. One of the advantages of this technology is that H_2S can also be completely absorbed in the amine scrubber. Amine scrubbing systems mainly consists of an absorber unit and a stripper. In the absorption column, the biogas (at a pressure of 1–2 bars) is provided from the bottom of the tank while the amine solution flows in a counter-current fashion from the top. The CO_2 is bound into the solvent by an exothermic chemical reaction. Subsequently, the resultant rich in CO_2 and H_2S amine solution is routed to a stripping unit for regeneration. The stripping column has a pressure of 1.5–3 bars and is equipped with a boiler that provides heat attaining the temperature at 120–160 °C. The heat aims to disrupt the chemical bonds formed in the absorber phase and also to create a vapour stream that acts as stripping fluid. Finally, the steam that contains CO_2 is cooled in a condenser allowing the condensate to recirculate to the stripper and the entrapped CO_2 to be released. Apart from amine solutions, other aqueous alkaline salts, such

as sodium, potassium and calcium hydroxides, can be involved in order the solvent to chemically react with the CO_2 (Kougias et al., 2010; Zhao et al., 2010). In principle, sodium hydroxide has higher CO_2 absorption capacity compared to amine-based solvents such as mono-ethanolamine. More specifically, in order to capture 1 ton of CO_2, the theoretical amount of mono-ethanolamine that will be needed reaches 1.39 tons, while the corresponding amount of sodium hydroxide is 0.9 tons (Yoo et al., 2013). Main disadvantages of this method include the toxicity of the solvents to human and environment, the significant energy that is needed for regeneration of the chemical solutions, the initial cost of the amine solvents and their loss due to evaporation. Therefore, aqueous alkaline salts are preferred in comparison with amines as they are more cost efficient and more abundant (Yoo et al., 2013). By applying this technology, the final methane content in the output gas can reach 99% purity due to the fact that the chemical reaction is strongly selective and thus the methane loss can be lower than 0.1% (Table 1).

2.1.4. Pressure swing adsorption (PSA)

This technology separates the different gasses from biogas based on their molecular characteristics and the affinity of the adsorbent material (Fig. 2b). The adsorbents can be carbon molecular sieve, activated carbon, zeolites (Zeolite 13 ×, Zeolite 5A) and other material with high surface area (Augelletti et al., 2017). The main principle of PSA technology relies on the properties of pressurized gasses to be attracted to solid surfaces. Therefore, under high pressure, large amounts of gas will be adsorbed, while, a decrease of pressure will result in gas release. The PSA process follows four equal or different duration steps, namely adsorption, blow-down, purge and pressurization (Augelletti et al., 2017). Initially, the compressed biogas (4–10 bars) is injected into an adsorption vessel (column), in which the adsorbent material will selectively retain CO_2, N_2, O_2, H_2O and H_2S, while the methane is able to flow through it and can be collected from the top of the column by decreasing the pressure. In practice, multiple adsorption columns are installed (usually four) to ensure the maintenance of a continuous operation (Bauer et al., 2013b). Once the adsorbent is saturated, the gas stream will continue to the next column. In the saturated column, the adsorbent material will be regenerated by a desorption process, in which the pressure is decreased and the entrapped gasses are released. The gas mixture that is released from the columns contains significant amounts of methane, and therefore, it has to be recycled by leading it to the PSA inlet (Awe et al., 2017). On contrary, the adsorption of H_2S is normally irreversible and for that reason it has to be removed prior the injection of the biogas to the PSA column (Zhao et al., 2010). This method is advantageous due to equipment compactness, it requires low energy and capital investment cost, and finally, due to its safety and simplicity of operation (Augelletti et al., 2017). The raw biogas can be upgraded up to 96–98% methane concentration; however, up to 4% methane can be lost within the off-gas stream (Table 1) (Bauer et al., 2013a; Ryckebosch et al., 2011).

2.1.5. Membrane separation

Membrane technology is a competitive alternative to the conventional absorption based biogas upgrading system. The main principle of the technology relies on the selective permeability properties of membranes allowing the separation of the biogas components. For example, based on the relative permeation rates, the different molecules contained in biogas permeation can be ordered hierarchically from the slowest to the faster permeation as follows C_3H_8, CH_4, N_2, H_2S, CO_2 and H_2O (Bauer et al., 2013a). Depending on the separation media, the process can either be performed with dry (gas/gas separation) or wet (gas/liquid separation) techniques (Fig. 2c). The dry process uses specific membranes (mainly polymeric). The materials of the polymeric membranes able to separate CO_2 and CH_4 are cellulose acetate and polyimide (Baker, 2012). The permeation rate of such membranes is dependent on the sorption coefficients of the gasses and on the membrane construction material, which in turn, affects the mobility

selectivity (Baker, 2012). The sorption coefficient of a gas depends on condensability of the permeant, and thus, smaller molecules are normally less condensable compared to larger ones. On contrary, the diffusion coefficient decreases with increasing molecular size. Considering the diffusion and the sorption coefficient of different gasses as a function of their molar volume, it can be observed that smaller molecules (e.g. CO_2) are less condensable and more favourable to become permeant from the membrane compared to larger molecules (e.g. CH_4) (Baker, 2012). Therefore, in many polymeric membranes the diffusion coefficient and the solubility of CO_2 is higher compared to CH_4 resulting in higher permeability. Consequently, the gas that is rich in CH_4 will remain to the side of the membrane with the higher pressure, while the CO_2 (together with a significant amount of methane that can reach 10–15%) will be diffused to the side with the lower pressure. In real practice, the raw biogas is initially cleaned by removing contaminants such as water and H_2S to avoid problems related to corrosion (Persson, 2003). Afterwards, the biogas is compressed at 5–20 bars prior to its injection to the membrane unit (Bauer et al., 2013b). The CO_2 separation efficiency is strictly dependant on the type and material of the membrane used. An ideal membrane should have large permeability difference between CH_4 and CO_2 so as to minimise the CH_4 losses and efficiently purify the biogas. Currently, there are four main manufacturing configurations for gas/gas membrane cascades (Fig. 2c); the single stage, the two-stage with a recirculation loop, the two-stage with sweep biogas stream and the three-stage with sweep biogas stream (Makaruk et al., 2010). Therefore, as it can be evidenced, single stage configurations (Fig. 2c ii) are simpler, do not include internal rotating equipment, as the two-stage with recirculation loop (Fig. 2c iii), and require less maintenance (Baker, 2012), contributing in minimising the operational cost. Moreover, in two-stage with sweep (Fig. 2c iv), the biogas stream exiting the membrane cascade B is recirculated so as to be mixed with the influent gas and subsequently fed to membrane A as a sweep steam. Finally, the three-stage with sweep biogas stream (Fig. 2c v) has an additional cascade and constitutes a low pressure feed membrane composed by both enriching and stripping sections. The CH_4 content in the upgraded biogas is commonly 95% but it can reach > 98% under certain conditions (Table 1) (Bauer et al., 2013a).

The difference between the dry and the wet process is related to the hydrophobic properties of the micro-porous membranes used in the latter one. The wet membrane technology combines the advantages of the membranes with those from the absorption method. Practically, the installed membrane separates the gas feed and the liquid, and the gas molecules are able to diffuse through the membrane and be absorbed by the liquid media that flows counter-wise. The liquid solution can be regenerated under high temperature, while the released CO_2 is pure and can be exploited in other industrial applications. Major disadvantages of this technology are the high cost of the membranes and also that they are fragile. It is estimated that the lifetime of the membranes for biogas purification varies between 5 and 10 years (Bauer et al., 2013a).

2.1.6. Cryogenic separation process

This technology is conducted through a gradual decrease of biogas temperature separating the liquefied CH_4 from both CO_2 and rest components (Muñoz et al., 2015) in order to obtain a product in accordance with the quality standards for Liquefied Natural Gas (LNG) (Grande and Blom, 2014). The separation is carried out by initially drying and compressing the raw biogas up to 80 bars followed by a stepwise temperature drop up to − 110 °C (Ryckebosch et al., 2011). Thus, the low contained impurities (i.e. H_2O, H_2S, siloxanes, halogens etc.) and subsequently, CO_2 which is the second most dominant component of biogas are gradually removed in order to recover almost pure biomethane (> 97%). Despite the promising results, the cryogenic separation process is still under development and only few facilities are operating in commercial scale (Bauer et al., 2013a). The high investment and operation costs, losses of CH_4 and practical problems (e.g. clogging) derived from either the increased concentration of solid CO_2

or presence of rest impurities limit the wider establishment of this technique (Bauer et al., 2013a; Muñoz et al., 2015; Ryckebosch et al., 2011).

### 2.1.7. Chemical hydrogenation process

The reduction of CO_2 with H_2 can be either conducted biologically (presented in following subchapter) or chemically, based on Sabatier reaction. Regarding the chemical hydrogenation process, various catalysts, with Nickel and Ruthenium to be the most commonly used in industrial applications (Jürgensen et al., 2015), have already been tested under elevated temperature (e.g. 300 °C) and pressure levels (e.g. 5–20 MPa) (Xia et al., 2016). Due to high selectivity, complete conversion of CO_2 and H_2 can be practically achieved (Jürgensen et al., 2014). Nevertheless, despite the high process efficiency, specific drawbacks still remain. For instance, the sustainability is affected by the presence of trace gasses in the biogas, which degenerate the catalysts leading to increased need for periodical replacement (Guebitz et al., 2015). Additional technical challenges of the process are the scarcity of elements to synthesize efficient catalysts, the need for pure gasses and the high energy cost to maintain the operational conditions.

2.2. Biological technologies

The biological biogas upgrading technologies can be generally classified into chemoautotrophic and photosynthetic. Most of these configurations have been experimentally proven and are at an early stage of pilot or full scale implementation. As it will be discussed extensively, the major advantage of such technologies is related to the fact that the CO_2 is converted into other energy containing or high value added products at mild operational conditions (i.e. atmospheric pressure, moderate temperature levels) contributing significantly to a sustainable bio-based and circular economy.

2.2.1. Chemautotrophic methods

The chemoautotrophic biogas upgrading methods are based on the action of hydrogenotrophic methanogens that can utilise H_2 to convert CO_2 to CH_4 based on the following equation:

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O \quad \Delta G^0 = -130.7\,KJ/mol \tag{1}$$
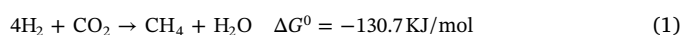
However, in order to make the biological upgrading method renewable, the H_2 required in the reaction should derive from renewable source. Therefore, the concept of using renewable electricity to hydrolyse water for production of H_2 has attracted increased attention, especially in cases that residual electricity from wind mills or solar panels exploiting is exploited. This method is also serving the purpose of storing the surplus energy generated by wind turbines or photovoltaic modules creating a new technology called power to gas (P2G). Solar and wind energy are point energy sources which need buffering for delivering the energy when it is dark and the wind is still. Batteries used for electricity storage have still several drawbacks such as low capacity for storing large amounts of electricity, high production cost, and often require toxic and caustic materials. Water electrolysis using renewable electricity is splitting the water to O_2 and H_2. In such way, the generation of H_2, which is an energy carrier by itself, is a clean power source free of CO_2 emissions. However, H_2 has some disadvantages before a practical application is possible. More specifically, H_2 has the inherent disadvantage of a very low volumetric energy density, which renders difficult its storage (Jürgensen et al., 2014). Additionally, the exploitation of H_2 as a fuel for the transportation sector is still under development (Muñoz et al., 2015). Therefore, integration of P2G technology for conversion of H_2 to CH_4 is very attractive as it integrates wind or solar energy technology with biogas technology. This process is a promising means to convert electricity to a chemical energy carrier, which can easily be stored in the existing natural gas infrastructure. The energy content of CH_4 (36 MJ/m^3) is remarkably higher compared with the corresponding one of H_2
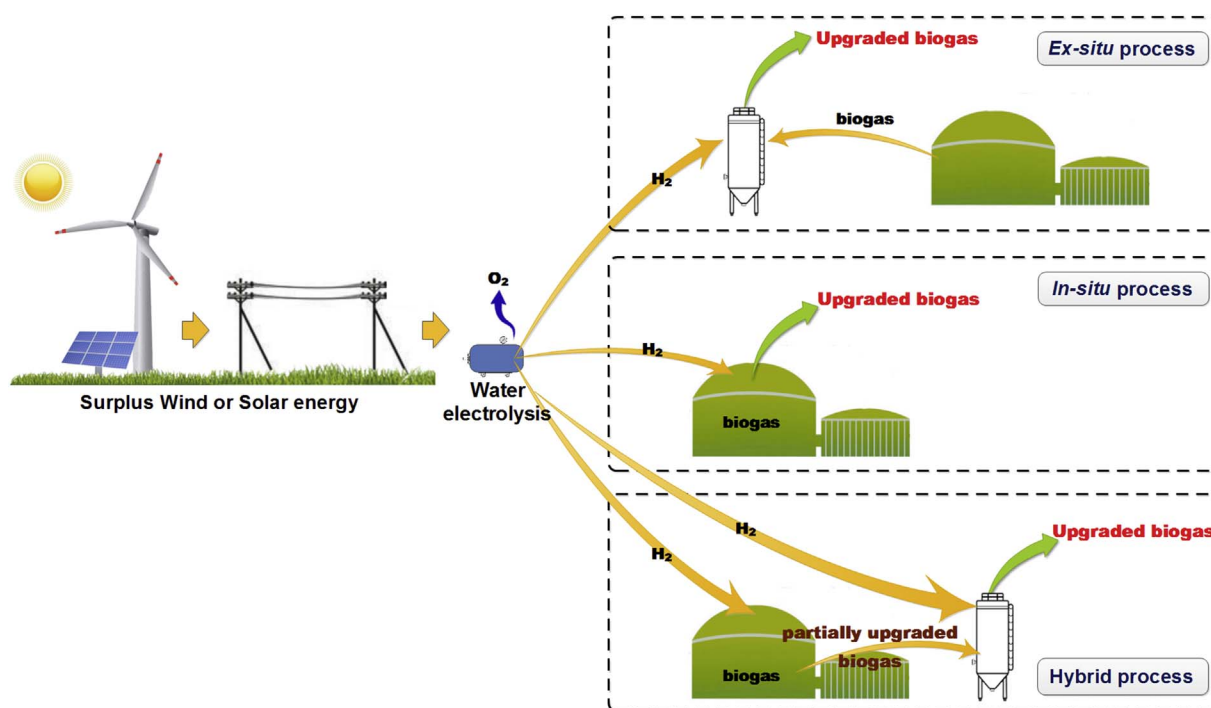
Fig. 3. In-situ, ex-situ and hybrid biological biogas upgrading technologies based on hydrogen methanation.

(10.88 MJ/m^3) (Luo et al., 2012). Moreover, the upgrading process exploits the existing facilities of the biogas plants and therefore reduces the initial investment cost. Furthermore, during the chemoautotrophic methods, the CO_2 is not separated or absorbed but converted to CH_4 leading to a significant increment of the final energy value of the output "windgas" (i.e. methane produced using the surplus energy from wind turbines) or "solargas" (i.e. methane produced using the surplus energy from solar panels) (Kougias et al., 2017b). Finally, this technology serves as a precondition for the sustainability of the ambitious biogas implementation plan of decoupling the biogas production from the biomass availability. The configurations in which hydrogen assisted biogas upgrading occurs can be classified into three categories (Fig. 3), namely in-situ, ex-situ and hybrid designs (Kougias et al., 2017b). Till now, the in-situ and ex-situ processes are experimentally proven and several research works are available in the literature. On the contrary, the hybrid concept is currently under development and the first results related to that technology will be soon available.

2.2.1.1. In-situ biological biogas upgrading. In the in-situ concept, H_2 is injected inside a biogas reactor in order to be coupled with the endogenous CO_2 which is produced in the anaerobic digester and be converted into CH_4 by the action of autochthonous methanogenic archaea (Kougias et al., 2017b). As seen in Table 2, the process can lead up to approximately 99% methane recovery only in cases that

operational parameters (e.g. pH) are fully monitored and controlled. A main technical challenge that this technology faces is related with the increment of pH level to values above 8.5, leading to inhibition of methanogenesis. The elevation of pH is attributed to the removal of bicarbonate which is the key buffer in the biogas process. As shown in Eq. (2), CO_2 dissolved in the liquid phase of the reactor is dissociated to H^+ and HCO_3^-. The utilization of CO_2 will lead to a decrease of H^+, causing a concomitant increase in the fermentation pH.

$$H_2O + CO_2 \leftrightarrow H^+ + HCO_3^- \qquad (2)$$

Previous experiments in in-situ biogas upgrading reactors showed a slight inhibition of methanogenesis due to bicarbonate consumption (Luo et al., 2012) verifying the argument that in conventional biogas production systems a pH of 8.5 is the threshold for optimum bio-methanation process both for mesophilic and thermophilic conditions (Bassani et al., 2015). In order to alleviate this technical challenge, co-digestion with acidic waste was proposed to arrest increase of pH (Luo and Angelidaki, 2013a). More specifically, it was demonstrated that the co-digestion of manure with cheese whey wastewater maintained the pH in an optimal range during the whole biogas upgrading process. An alternative approach to circumvent this challenge was the application of pH control permitting successful upgrading to almost pure bio-methane (Luo et al., 2014).

Another important issue that has to be considered during the in-situ

Table 2
Comparison of in-situ biological upgrading processes.

Reactor type	Substrate	Temperature, °C	HRT, d	H$_2$ flow, L/L/d	H$_2$ conversion efficiency, %	CH$_4$, %	CO$_2$ removal, %	pH	Reference
Batch	Maize leaf	52			100	89.4	66–70	7.0–8.0	(Mulat et al., 2017)
UASB	Potato-starch	55	7	1.8	67	82	76	8.38	(Bassani et al., 2016)
CSTR	Cattle manure	55	14	0.68	> 90	65		8.3	(Luo et al., 2012)
CSTR	Cattle manure and whey	55	15	1.7		75	85	7.7–7.9	(Luo and Angelidaki, 2013a)
CSTR	Sludge	38	20	0.3–1.7	58–99	76.8–100	43.3–100	7.89–8.43	(Agneessens et al., 2017)
CSTR	Cattle manure and whey	55	15	0.93–1.76		78.4–96.1	53–91	7.61–8.31	(Luo and Angelidaki, 2013b)
CSTR	Sewage sludge	37	10	0.92	96	98.9	99	8	(Wang et al., 2013)

process is related with the oxidation of the Volatile Fatty Acids (VFA) and alcohols which is only thermodynamically feasible in cases that H_2 concentration is very low (Batstone et al., 2002). On contrary, high H_2 levels (> 10 Pa) inhibit the anaerobic digestion, and promote the accumulation of electron sinks such as lactate, ethanol, propionate, and butyrate (Liu and Whitman, 2008). It would be expected that if sudden and high H_2 concentrations are introduced in the biogas reactor the VFA degradation would no longer be possible (Batstone et al., 2002). As a consequence, the system could become imbalanced or even, in the worst case, can totally be fatally deteriorated due to excess acidification caused by VFA accumulation. A recent study concluded that the injection of H_2 in batch reactors at a concentration that exceeds the stoichiometric amount for hydrogenotrophic methanogenesis led to an accumulation of acetate, which could be attributed to stimulated homoacetogenic pathway, and/or decreased methanogenic activity of acetoclastic archaea (Agneessens et al., 2017). However, after longer term H_2 exposure, increase of the hydrogenotrophic population enhances the H_2-utilization capacity and reverts the inhibition (Reeve et al., 1997).

An additional key parameter is the solubilisation of H_2 to the liquid phase as it must cross the interface between the gas and the liquid phase in order to be available for the microorganisms. Thus, the aqueous solubility of most gasses is rather low, which limits the gas–liquid mass transfer and hampers the performance of the bioreactor (Tirunehe and Norddahl, 2016). For that reason, the material and type of the module that is used to inject H_2, the application of gas recirculation flows and the reactor designs are considered as fundamental elements for the implementation of sufficient in-situ biogas upgrading (Bassani et al., 2016). In batch experiments, it was found that the H_2 uptake rate decreased rapidly at CO_2 concentrations $< 12\%$ (Agneessens et al., 2017) and the maximum CH_4 content in biogas reached 89% (Mulat et al., 2017). On contrary in continuously fed reactors, Luo and Angelidaki (2013b) who used hollow fiber membranes to inject H_2 in an anaerobic reactor treating cattle manure and cheese whey, achieved up to 96% methane at the final output gas. In another research performed in up-flow anaerobic sludge blanket reactor, hollow fiber membrane was installed in an external degassing unit and the obtained efficiency of the in-situ biogas upgrading reached 94% (Luo et al., 2014). However, as the cost of such membranes has to be considered for full scale applications, other porous devices, such as ceramic sponges, have been proven to benefit the coupling of CO_2 and H_2 and their consequent transformation to CH_4 (Bassani et al., 2016). A comparison of different in-situ configurations is presented in Table 2.

2.2.1.2. Ex-situ biological biogas upgrading. The ex-situ biogas upgrade concept relies to the provision of CO_2 from external sources and H_2 in an anaerobic reactor that contains (pure or enriched) hydrogenotrophic culture, resulting in their subsequent conversion to CH_4 (Kougias et al., 2017b). This method has several advantages compared to the in-situ process as; a) it secures the stability of the conventional biogas process because the upgrading is occurring in a separate unit, b) the biochemical process is simpler since there is no degradation of organic substrate (i.e. initial steps of anaerobic digestion, such as hydrolysis and acidogenesis are not performed), c) it is a biomass independent process, d) other external source of waste CO_2 (e.g. syngas) can be used making the process more flexible, and e) by this process it is feasible to supply power to remote from the centralized grid rural areas. As evidenced by Table 3, the ex-situ process can handle high volumes of influent gasses decreasing the gas retention time even to 1 h, which minimises the dimensions of the biogas upgrading chamber. The biogas upgrading efficiency, strongly depending on the reactor type, can result in final methane content between 79 and 98%. Technical challenge in this technology remains the low gas-liquid mass transfer rate, which in case of H_2 is described by the following equation:

$$r_t = 22.4 k_L a (H_{2gTh} - H_{2l}) \tag{3}$$

Table 3
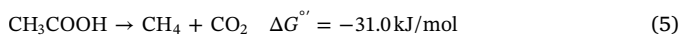Comparison of ex-situ biological upgrading processes.

Reactor type	Liquid media	Temperature, °C	Gas retention time, h	Gas recirculation, L/LR.h	CH$_4$, %	CO$_2$ removal, %	H$_2$ conversion efficiency, %	pH	Reference
Batch	Anaerobic digestate	55	24	-	92	-	-	7.7–8.2	(Guneratnam et al., 2017)
Trickle-bed reactor	Immobilized enriched hydrogenotrophic culture	37	2.5–3.5	-	> 96	> 96	-	7.4–7.7	(Rachbauer et al., 2016)
Trickle-bed reactor	Immobilized hydrogenotrophic culture	37	4	No	98	100	100	7.2–7.4	(Burkhardt et al., 2015)
Trickle-bed reactor	Digested sludge from sewage treatment plant	37	2–7	Yes	92.8–97.9	-	94–100	-	(Burkhardt and Busch, 2013)
Fixed bed reactor	Anaerobic digestate from sewage treatment plant	35	1.5–6.5	-	-	68–100	-	-	(Lee et al., 2012)
Fixed bed reactor	Methanogenic culture	50	~ 4	No	> 90	> 90	97.1	6.9	(Alitalo et al., 2015)
Biofilm plug flow reactor	Mixed anaerobic microbial culture	37	0.24		> 98	> 98		-	(Savvas et al., 2017)
Up-flow	Enriched hydrogenotrophic inoculum	55	4–15	2.88–20.14	89.5–96.3	85.5–100	96.8–100	8.03–8.81	(Bassani et al., 2017)
Up-flow in series	Anaerobic digestate	55	16	4	98	~ 50	< 100	8.5	(Kougias et al., 2017b)
CSTR	Anaerobic digestate	55	8	4	79	~ 33	> 60	8	(Kougias et al., 2017b)
Bubble column reactor	Anaerobic digestate	55	8	4	98	~ 83	< 100	8.3	(Kougias et al., 2017b)
CSTR	Enriched hydrogenotrophic culture	55	1–8	-	95	88–96	72–95	7.8	(Luo and Angelidaki, 2012)
CSTR	Anaerobic digestate	37	-	-	88.1	71	93	8.17	(Bassani et al., 2015)
CSTR	Anaerobic digestate	55	-	-	88.9	80	92	8.49	(Bassani et al., 2015)
CSTR	Anaerobic sludge from municipal wastewater plant	35	-	-	92	98	< 100	7.1–7.3	(Kim et al., 2013)
CSTR	Pure culture (*M. thermautotrophicus*)	60	4	Yes	-	-	89	7.35	(Martin et al., 2013)

where r_t is the H_2 gas–liquid mass transfer rate ($L/(L_{Reactor}.day)$), 22.4 is the corresponding volume that occupies 1 mol of gas at standard condition of temperature and pressure (L/mol), k_La is the gas transfer coefficient (day^{-1}), H_{2g} is the H_2 concentration in the gas phase (mol/L), and finally H_{2l} expresses the dissolved H_2 in the liquid phase (mol/L). Therefore, it is obvious the H_2 gas-liquid mass transfer rate is proportionally correlated with the k_La, which in turn is dependent on specific operational parameters such as the gas recirculation flow (Guiot et al., 2011; Kougias et al., 2017b), the reactor configuration (Bassani et al., 2016; Kougias et al., 2017b), the installed diffusion device (Bassani et al., 2017; Díaz et al., 2015; Luo and Angelidaki, 2013b) and the stirring intensity (Luo and Angelidaki, 2013b, 2012).

A number of research publications are proposing different novel concepts for increased biomethanation efficiencies. A comparative summary of these configurations is given in Table 3. It was demonstrated that the operating temperature was important for the bio-methanation efficiency. More specifically, it was shown that enriched thermophilic culture resulted in > 60% higher H_2 and CO_2 bio-conversion compared to the mesophilic culture in batch assay (Luo and Angelidaki, 2012). Another study concluded that an increment of the operating temperature from 55 °C to 65 °C leads to more efficient bio-methanation operation (Guneratnam et al., 2017). Nevertheless, in-dependently from the temperature conditions, an adaptation period is needed for the microorganisms to be able to efficiently ferment the CO_2 and H_2 gasses. For example, in a recent study, it was shown that by operating a mesophilic trickle-bed reactor with immobilized hydro-genotrophic culture for a period of 8 months, it was possible to obtain an output gas with CH_4 content over 96% (Rachbauer et al., 2016). The biomethanation efficiency achieved is similar to the one recorded under thermophilic conditions (Bassani et al., 2017; Luo and Angelidaki, 2012). The types of the reactor along with the application of gas re-circulation or liquid mixing are other essential parameters for designing a biogas upgrading system. It was demonstrated that upflow in series or bubble column reactors are able to achieve higher than 98% methane concentration at the output gas, even by injecting the H_2 through conventional spargers instead of advanced membrane modules (Kougias et al., 2017b). Moreover, in relation to other reactor types, trickle bed reactor systems can achieve an increased CO_2 and H_2 con-version efficiency up to 98–99% methane, due to the formation of biofilm of mixed anaerobic consortia that serves as a good biocatalyst for the completion of the process (Burkhardt et al., 2015; Savvas et al., 2017). Finally, intensive stirring speed (Luo and Angelidaki, 2012), or diffusion devices with pore sizes that create gas-bubbles able to mix the reactor demonstrate best kinetics and output gas quality (Bassani et al., 2017).

2.2.1.3. Microbial communities in biological biogas upgrading systems. In anaerobic digestion context, biological biogas upgrading can be obtained via two different processes (Fig. 4). The first one is mediated by hydrogenotrophic methanogenic archaea performing the direct conversion of CO_2 to CH_4 with the use of external H_2 as a source of electrons. This pathway, known as hydrogenotrophic methanogenesis, is highly energetically favourable at pH 7, according to Eq. (1), with negative Gibbs free energies (Stams and Plugge, 2009).

The second metabolism responsible for biogas upgrading is indirect; it involves homoacetogenic bacteria and is based on the conversion of CO_2 to acetate via the Wood-Ljungdahl pathway, which is also an ex-ergonic process (Eq. (4)). Subsequently, this low energy gain is com-pensated by acetoclastic methanogenic archaea that convert the acetic acid into CH_4 (Eq. (5)).

$$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O \quad \Delta G^{\circ\prime} = -104.5\,kJ/mol \quad (4)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad \Delta G^{\circ\prime} = -31.0\,kJ/mol \quad (5)$$

Under standard methanogenic conditions, H_2 derives from acetate oxidation (or syntrophic acetate oxidation) via an endergonic reaction

and the energy loss is compensated when H_2 partial pressure is kept low by hydrogenotrophic methanogens. In this case, the low H_2 partial pressure is fundamental to enable proton reduction and energy con-servation (Stams and Plugge, 2009).

Due to the crucial role of H_2 concentration on equilibrium of bio-chemical reactions, addition of external H_2 has a strong selective pressure on the microbial community, shaping its composition with a massive increase of both hydrogenotrophic methanogens and homo-acetogenic species producing acetate from H_2 and CO_2, such as *Acetobacterium woodii*, *Moorella thermoacetica* and different species be-longing to and *Clostridium* (Schuchmann and Müller, 2014). In contrast, exogenous addition of H_2 is responsible for inhibiting syntrophic acetogens (involved in propionate and butyrate degradation) and syn-trophic acetate oxidizers (SAO) (Demirel and Scherer, 2008).

Hydrogenotrophic methanogens are the key players for efficient biogas upgrading process and their abundance can be increased using different strategies (i.e. bioaugmentation with pure cultures or en-dogenous enrichment of hydrogenotrophic populations). For practical applications, the utilization of mixed adapted cultures is more ad-vantageous compared to pure cultures because the H_2 adapted micro-bial communities are more robust and do not require sterile conditions, which would add extra costs to the process. Moreover, the development of a microbial acclimatized consortium was found to be more efficient in H_2 conversion, with larger yields of CH_4 compared to utilization of pure cultures represented for example by *M. thermoautotrophicum* (Peillex et al., 1990). Finally, by using of mixed adapted cultures, the costs of growing specific strains in large quantities for the initial in-oculation of full-scale digesters are avoided.

Microbial analysis performed during biogas upgrading, revealed that the most frequently found hydrogenotrophic methanogenic genera were *Methanobacterium*, *Methanoculleus*, *Methanomicrobium* and *Methanothermobacter* (Agneessens et al., 2017; Bassani et al., 2017; Luo and Angelidaki, 2013a; Mulat et al., 2017), whereas *Methanosarcina* and, more generally, acetoclastic methanogens are usually present at lower abundance (Agneessens et al., 2017; Bassani et al., 2015; Mulat et al., 2017). *Methanobacterium* and *Methanothermobacter* species were found to be dominant in various biogas upgrading configurations (i.e. recirculation liquid of upflow reactors, immobilized on trickle-bed re-actor and on biofilm created on top of H_2 diffuser surface) (Kougias et al., 2017b; Rachbauer et al., 2016). Recently, a provisional name as "*Candidatus* Methanoculleus thermohydrogenotrophicum" was given to a new hydrogenotrophic archaea species which was found to increase in abundance upon H_2 in thermophilic reactors (Kougias et al., 2017a).

The limiting step in hydrogen assisted methanogenesis is not always the biological conversion catalyzed by the microbial species but more often the H_2 diffusion in the liquid medium (Díaz et al., 2015). In the presence of high H_2 concentrations, the hydrogenotrophic archaea consume H_2 for CH_4 production instead of using it for microbial growth (Reeve et al., 1997). This will in turn promote the formation of a close syntrophic association between methanogens and fermentative bac-teria. In fact, Reeve and colleagues found a decreased growth yield (Y_{CH4}) of *M. thermoautotrophicum* at high H_2 concentration (expressed as grams of biomass synthesized per mole of CH_4 produced), which was partially attributed to the transcriptional activity of some specific genes involved in methanogenesis (Reeve et al., 1997). Due to the difficulty in isolation and cultivation of methanogens and syntrophic bacterial species, most of the studies recently performed on these microbial communities were performed using high throughput 16S rRNA am-plicon sequencing (Agneessens et al., 2017; Bassani et al., 2017; Kougias et al., 2017b; Mulat et al., 2017). It has been shown that H_2 addition has multiple effects on the microbial species and it can influ-ence not only species abundance but also their transcriptional activity (Reeve et al., 1997). For this reason a thorough investigation requires more complete analyses of the gene expression level performed using metatranscriptomic approaches. Among other results, analysis of the gene expression evidenced that hydrogenotrophic methanogenesis was
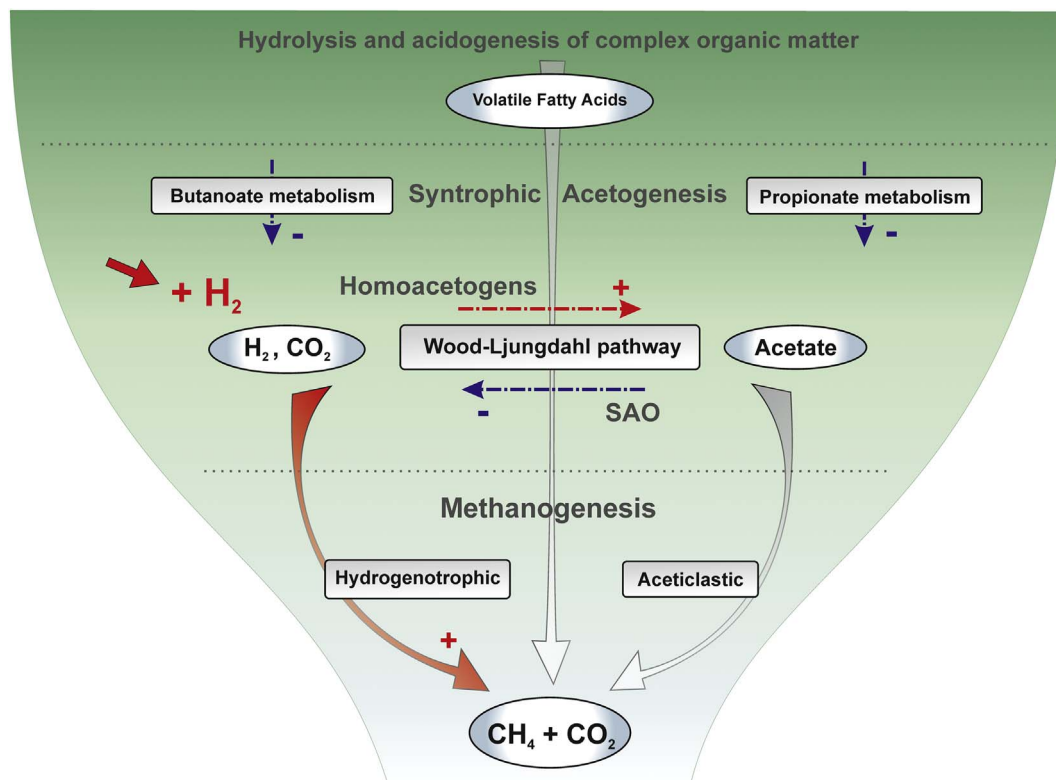
Fig. 4. Metabolic pathways for hydrogen assisted methanogenesis.

highly expressed in biogas reactors (Bremges et al., 2015; Treu et al., 2016) suggesting this as a possible explanation for the efficiency of methanogens in H_2 utilization.

2.2.2. Photoautotrophic methods

The photosynthetic biogas upgrading is an alternative method to sequester the CO_2 in order to obtain a CH_4-rich gas. As presented in Table 4, by these methods H_2S removal is additionally achieved, while > 54% of CO_2 is consumed. The methane recovery of photoautotrophic technologies can reach up to approximately 97% depending on the reactor type and the selected algal species. This biotechnological process is catalyzed by phototrophic organisms like algae in enclosed (e.g. tubular) or open (e.g. high rate algal ponds)

photobioreactors (Table 4). Specifically, the closed systems have high photosynthetic performance and low requirements in terms of land and water needs, but their high investment cost and energy demands appear as the main bottlenecks. In contrast, the pros and cons of open photobioreactors differ markedly, as they need insignificant resources for construction and operation but they have lower photosynthetic CO_2 uptake and higher natural sources requirements. In the upgrading process, the biogas is injected either directly in the photobioreactors or externally in an absorption column where microalgal broth stream is recirculated from the major tank. Subsequently, photoautotrophic microorganisms, as for instance prokaryotic cyanobacteria or eukaryotic microalgae, can efficiently uptake CO_2 utilizing solar irradiation, water and nutrients to produce biomass, oxygen and heat. Thus, the CH_4

Table 4
Comparison of different photoautotrophic biogas upgrading technologies.

Indoor/ outdoor	System	Species	H_2S removal	CO_2 removal, %	O_2, %	CH_4 recovery, %	Reference
Indoor	HRAP	*Chlorella vulgaris*	Yes	80%	< 2		(Serejo et al., 2015)
Indoor	HRAP	*Planktolynga brevicellularis* (81%), *Stigeoclonium tenue* (14%) and *Limnothrix planktonica* (5%)	Yes	72–79	1.2–0.7	81	(Posadas et al., 2015)
Outdoor	Enclosed photobioreactor bag	*Chlorella vulgaris* *Scenedesmus obliquus* *Neochloris oleoabundans*		55.39 62.31 54.39	0.62	80.4 82.64 80.06	(Zhao et al., 2015)
Indoor	Open photobioreactor	*Nannochloropsis gaditana*		81	1.2		(Meier et al., 2015)
Outdoor	HRAP	*Picochlorumsp.* and *Halospirulina* sp.	Yes	94	2.6		(Franco-Morgado et al., 2017)
Indoor	Enclosed photobioreactor	*Scenedesmus* spp. Mixotrophic Autotrophic	Yes	66.7	17.8	64.7	(Prandini et al., 2016)
Indoor	HRAP	*Mychonastes homosphaera*	Yes	98.8	0.7	96.2	(Toledo-Cervantes et al., 2017)
Indoor	HRAP	*Geitlerinema* sp. (61.5%), *Staurosira sp.* (1.5%) and *Stigeoclonium tenue* (37%)	Yes	98.8	0.03	97.2	(Toledo-Cervantes et al., 2016)
Outdoor	HRAP Open-photobioreactor	*Chlorella* sp. *Chlorella sorokiniana*	Yes	95 89–93	0.1–2.0 < 1	94	(Posadas et al., 2017) (Meier et al., 2017)

content is increased satisfying the existing regulations of having maximal 2–6% CO_2 in the final gas (Meier et al., 2015). Moreover, side benefit of this method is the production of active biomass that can be used either for the extraction of high value added products (Guedes et al., 2011) or as feedstock for biogas production oriented to circular economy (Mussgnug et al., 2010). Hence, the CO_2 is efficiently valorised and transformed into other products and is not simply entrapped in the liquid media.

Interestingly, a variety of cyanobacteria or microalgae with high photosynthetic efficiency were successfully utilized for biomethane production among which *Chlorella*, *Arthrospira* and *Spirulina* species to be the most commonly studied (Muñoz et al., 2015). For instance, *Chlorella* sp. MB-9 (Kao et al., 2012a), *Arthrospira platensis* (Kao et al., 2012a), *Spirulina platensis* (Bahr et al., 2013) upgraded the biogas to CH_4 concentration up to 90%, 82% and 74%, respectively, while they performed a parallel photosynthetic CO_2 assimilation of 85%, 100%, and 86%, respectively.

Apart from the CO_2 consumption, the removal of other biogas pollutants is also of high importance. For instance, the efficiency of photoautotrophic technology is not favoured using pure microalgal photobioreactors due to the fact that the fixation of 1 mol of CO_2 stoichiometrically leads to 1 mol of released O_2, and thus, the composition of the final product is negatively affected (Meier et al., 2017). However, this drawback can be turned into advantage utilizing diverse cultures. On this context, Bahr et al. (2013) used a mixed consortium of microalgae and sulphur-oxidizers in order to oxidize the containing H_2S of the injected biogas to sulphate using the generated O_2 as an electron acceptor. Hence, the calorific value of biomethane can be further improved by the combined CO_2 capture and H_2S removal. In parallel, H_2S removal is very important for increased process sustainability as even at concentrations close to 100 ppmv can be toxic to the microalgal cells (Kao et al., 2012b). Similarly, the surplus of CO_2 can also slow down the microalgal growth rate driven by a pH drop (Meier et al., 2015). In another concept the produced gas consisting of methane and oxygen was utilized for production of single cell proteins by methanotrophs (van der Ha et al., 2011).

In addition, other operational conditions, such as temperature and dissolved oxygen concentrations, directly affect algal growth and thus, indirectly the upgrading efficiency (Muñoz and Guieysse, 2006). Furthermore, light wavelength and intensity are known to highly influence the photoautotrophic populations. On this topic, artificial light source using various LED strategies seem to be more promising for biogas upgrading purposes than natural solar light due to regulated light wavelengths, photoperiods and intensities towards optimal conditions (Yan et al., 2016). Finally, the gas retention time (Muñoz et al., 2015) and liquid to biogas ratio are additional technical parameters that should be always carefully considered to produce biomethane that compiles with the specifications of national legislations (Toledo-Cervantes et al., 2016).

2.2.3. Biogas upgrading through other fermentation processes

Although CO_2 in biogas can be biologically converted to methane with the addition of H_2 to achieve biogas upgrading, the production of valuable liquid products (e.g. acetate, ethanol, butyrate, butanol, etc.) from CO_2 in biogas is more attractive (Agler et al., 2011; Kennes et al., 2016). The produced fatty acids such as acetate and butyrate are also important precursors for liquid biofuels production (Agler et al., 2011; Martin et al., 2016; Zhang et al., 2013). Diverse microorganisms (e.g. *Acetobacterium woodii*, *Butyribacterium methylotrophicumn*, *Clostridium scatologenes*, etc.) are known to be able to convert CO_2 and H_2 to liquid products (Schiel-Bengelsdorf and Dürre, 2012), and most of the microorganisms are acetogens, which assimilate CO_2 by Wood-Ljungdahl pathway (also known as reductive acetyl-CoA pathway) (Latif et al., 2014). A homoacetogic strain *Blautia coccoides GA-1* was isolated from a continuously stirred tank reactor (CSTR) treating organic wastewater, which could produce acetate from CO_2 and H_2 with the acetate yield of

5.32 g/g dry cell weight after 240 h of incubation (Liu et al., 2015). The study also showed that the presence of fermentable organics (e.g. glucose) could repress autotrophic metabolism remarkably. The ethanol production from syngas, containing H_2 and CO_2, was studied in a trickle bed reactor with *Clostridium ragsdalei* as the microbial catalyst, which demonstrated the importance of gas–liquid mass transfer during the fermentation process (Devarapalli et al., 2016). However, the products consist not only of ethanol (5.7 g/L), but also acetate (12.3 g/L). Compared to the pure culture fermentation, the mixed culture fermentation of CO_2 and H_2 has potential advantages such as no need for sterilisation and possibility of using wastewaters for nutrients supply. It was also demonstrated in previous studies that CO_2 and H_2 could be converted to acetate by mixed culture (Nie et al., 2008, 2007). It should be noted that acetate has high solubility and is energy-intensive to be separated from the liquid (Perez et al., 2013). Therefore, it was proposed to produce medium chain fatty acids (caproate and caprylate) from CO_2 and H_2 (Zhang et al., 2013), which not only have better fuel value than bioethanol but also are easier to be separated from the liquid (Agler et al., 2012; Kucek et al., 2016). Zhang et al. (2013) demonstrated that medium chain fatty acids (caproate (0.98 g/L) and caprylate (0.42 g/L)) could be produced from CO_2 and H_2 in hollow-fiber membrane biofilm reactor by mixed culture. However, acetate (7.4 g/L) and butyrate (1.8 g/L) with relatively high concentrations were also produced, indicating the low selectivity for medium chain fatty acids in such process. The above mentioned technologies for valuable liquid products production from CO_2 and H_2 have not been applied to biogas upgrading. The effects of impurities (e.g. H_2S) in biogas on the above fermentation technologies need to be investigated, and also the methods to enhance the selectivity of the products remain to be explored.

Biogas upgrading by conversion of CO_2 in biogas together with H_2 has the inherent challenge that needs availability of cheap H_2 sources. Alternative fermentation processes exist where CO_2 is coupled with sugars to produce carboxylic acids. In this way, CO_2 in biogas can be converted to succinic acid during the glucose fermentation by *Actinobacillus succinogenes* or any other bacteria capable of producing succinic acid (Zeikus et al., 1999), which is a four-carbon diacid with the chemical formula $C_4H_6O_4$. Succinic acid is a platform chemical and a precursor for the synthesis of numerous commodities in agri-food, chemical, and pharmaceutical industries (e.g. chemicals (1,4-butanediol, tetrahydrofuran, 2-pyrrolidinone, and gamma-butyrolactone), green solvents (like 2-Methyltetrahydrofuran (2-MeTHF)) and biodegradable polymers (polybutylene succinate (PBS) and polyamides) (Cukalovic and Stevens, 2008). Gunnarsson et al. (2014) made the first investigation on the feasibility of biogas upgrading by integration with biosuccinic acid production utilizing the bacteria *Actinobacillus succinogenes 130Z*. It showed that slight over-pressure during fermentation was advantageous for increasing the solubility of CO_2, and thereby increases the final succinic acid yield and titer, CO_2 consumption rate, and CH_4 purity. The methane content of 95% in the biogas was achieved by this technology. The technology is very promising compared to those based on H_2, since H_2 has low solubility and generally requires high energy to achieve high gas-liquid mass transfer (Luo et al., 2012). It is known that there are different bacteria (e.g. *Saccharomyces cerevisiae*, *Escherichia coli*, etc. (van Heerden et al., 2013; Yan et al., 2014) that can produce succinic acid from glucose. Therefore, further studies are needed to identify other bacteria for succinic acid production coupled with biogas upgrading.

2.2.4. Biogas upgrading through microbial electrochemical methods

CO_2 removal in biogas to produce CH_4 by bioelectrochemical systems has been presented as sustainable and cost-effective way to upgrade biogas (Lovley and Nevin, 2013; Van Eerten-Jansen et al., 2012). In a microbial electrolysis cell (MEC), electrons released by bacteria from the oxidation of organics in anode can combine with protons to generate hydrogen in the cathode chamber (Lu and Ren, 2016; Zhang

and Angelidaki, 2014). The hydrogen formed in the cathode can be used for biogas upgrading. In fact, Cheng et al. (2009) for the first time reported that methane could directly be produced by the reduction of CO_2 in the cathode using a biocathode in MEC, and methane was produced at an overall energy efficiency of 80%, which provided a potential technology for biogas upgrading. It was also demonstrated later that the reduction of CO_2 to methane was attributed to both extracellular electron transfer and abiotically produced hydrogen (water electrolysis), which was dependent on the set potential of cathode (Villano et al., 2010). Later, biogas upgrading by MEC was studied by Xu et al. (2014), and both in-situ (the cathode of MEC was used as biogas reactor) and ex-situ (biogas was introduced to the cathode) biogas upgrading methods were tested. The removal of CO_2 by in-situ biogas upgrading method was found to be better than ex-situ biogas upgrading method in both batch and continuous experiments, and the CO_2 content in the biogas below 10% were obtained by both methods. Interestingly, it was found that the CO_2 removal was attributed to not only the production of methane but also the CO_2 ionisation due to alkalinity generated in the cathode.

Recently, another method was presented, in which the CO_2 was removed from the gas to a separate chamber (Zeppilli et al., 2016). The comparison of MEC equipped with proton exchange membrane (PEM) and anion exchange membrane (AEM) for the CO_2 removal from simulated biogas was conducted (Zeppilli et al., 2016). It was found that PEM-MEC showed higher COD removal efficiency (78 ± 7%) and methane production rate (83 ± 24 meq/Ld) but needed more energy per unit of removed CO_2 (2.36 vs 0.78 kWh/Nm^3 $CO_{2removed}$) than AEM-MEC. The main CO_2 removal mechanism was the sorption of CO_2 converted to bicarbonate due to the generation of alkalinity, and also part of the bicarbonate was transferred to anode in AEM-MEC, which might be related with its lower methane production rate. It should be noted that organic wastewater is not necessary in the anode since electricity can provide electrons from water, for CO_2 reduction in the cathode, which was also demonstrated in a previous study (Van Eerten-Jansen et al., 2012). It was found that oxygen produced in the anode during water oxidation could diffuse into the cathode, and therefore decreased the coulombic efficiency of the biocathode. However, the diffusion of oxygen to cathode did not have obvious negative effect on the methane production rate.

The production of valuable liquid products from CO_2 can also be achieved in MEC (Sadhukhan et al., 2016; Wang and Ren, 2013). The reduction of CO_2 to formic acid by using multiwalled carbon nanotubes and cobalt tetra-amino phthalocyanine as the cathode in MEC was reported previously (Zhao et al., 2012). In addition, biocathode immobilized by *Methylobacterium extorquens AM1* was also shown to be promise for formic acid production from CO_2 (Hwang et al., 2015). Furthermore, Nevin et al. (2010) reported the production of acetate and 2-oxobutyrate from CO_2 in a MEC with *Sporomusa Ovata* growing on the cathode, and enriched mixed culture grown on the cathode was also feasible for acetate production from CO_2 in MEC (Xiang et al., 2017). It is obvious microbial electrochemical method is an environmental-friendly way to couple several positive actions together, including consumption of CO_2 to upgrade biogas, COD removal in the anode and production of valuable gas and liquid products. However, most of the current researches are based on lab-scale experiments; the technical and economic limitations for scaling up of the technologies for biogas upgrading remain to be explored.

3. The incentives and feasibility of biogas upgrading

The incentive for biogas upgrading relate to the larger scale transition of energy systems to renewable energy that is presently pursued by many countries. When releasing the energy supply from fossil fuels, the nature of the energy system changes towards a high share of fluctuating energy from wind and solar power and towards a high dependency on biomass resources (Danish Energy Agency, 2014a; Lund

et al., 2011). With respect to the role of biogas in the energy system, this creates economic and environmental incentives for biogas upgrading. On the short term, upgrading by physical/chemical CO_2 removal is both economically and environmentally attractive, in some countries this is already the case. On the longer term, in a global larger scale renewable energy scenario, also upgrading by hydrogenation is judged to be both environmentally and economically attractive to other non-fossil alternatives. The reasoning for these statements is found in the following sections.

3.1. Feasibility of physicochemical CO_2 removal

Biogas upgrading by physicochemical CO_2 removal is rapidly developing in many countries (Fig. 1b). As it can be illustrated by the case of Denmark, this is mainly due to the economical pay off compared to producing electricity and/or heat directly from the raw biogas. Fluctuating electricity production from wind power has in Denmark increased to a level close to 50%, meaning that wind power production equals 50% of total electricity consumption on an annual basis. With a high share of fluctuating wind power, the relative benefit of biogas upgrading compared to heat/power production from the raw biogas increases, because the heat/power production must run continuously as raw biogas cannot cost-efficiently be stored for more than a few hours, whereas the upgraded gas can be stored on the gas grid for months. Storing the gas provides the flexibility and added value of using it in periods of highest value. It is foreseen that all new biogas plants in Denmark are likely to upgrade and store the gas on the grid (Danish Energy Agency, 2014b). Also with respect to environmental impacts, the upgrading applications are more beneficial compared to direct heat/power production. This can be explained by the fact that the continuous generation of heat/power increasingly replaces wind or solar power and biomass; however, stored CH_4 allows replacing fossil based transport fuels and fossil electricity marginal supply, especially in periods with low wind (Wenzel et al., 2014).

The cost of upgrading is highly dependent on the biogas flow and the economy of investment scale (Fig. 5). Whereas Fig. 5a reflects the spectrum of investment costs of all types of physicochemical upgrading technologies on the market, Fig. 5b provides the total amortized investment (CAPEX) plus operation and maintenance costs (OPEX) pr. kWh of upgraded biogas for small scale pressure swing adsorption units (PSAs). An upgrading cost of e.g. 2 €c/kWh of upgraded biogas shall be seen relative to a sales price including subsidy of around 8.4 €c/kWh in Denmark in e.g. 2017. This upgrading cost allows selling the gas directly to the grid and, thus, further saves the investment in gas motor or turbine for heat/power production for new biogas facilities, where such a unit is not already installed. According to a recent study from EA Energianalyse and SDU (2016) the total cost of biogas upgraded by physicochemical CO_2 removal (including OPEX and all amortized CAPEX) is found to lie in the interval 5.8–7.8 €c/kWh of upgraded biogas.

3.2. Incentives for physicochemical or biological biogas upgrading

Upgrading the raw biogas by reacting CO_2 with H_2 is more expensive than CO_2 removal per kWh of biomethane produced due to the relative high cost of H_2. Compared to a production cost of around 7 €c/kWh of total upgraded biogas by CO_2 removal, the cost of H_2 itself lies around 9 €c/kWh, and on top of this comes the investment in and operation of a methanation plant which adds a further 15–20% on this cost. This means that a total cost of biomethane from hydrogenating the CO_2 part of raw biogas (assuming a 60%/40% CH_4/CO_2 mix) by physicochemical hydrogenation lies around 8–9 €c/kWh (EA Energianalyse and SDU, 2016). The cost of the biological hydrogenation is difficult to be concretely estimated, but is believed to be similar to physicochemical upgrading at present, as the cost of H_2 is judged to be dominating in both cases.
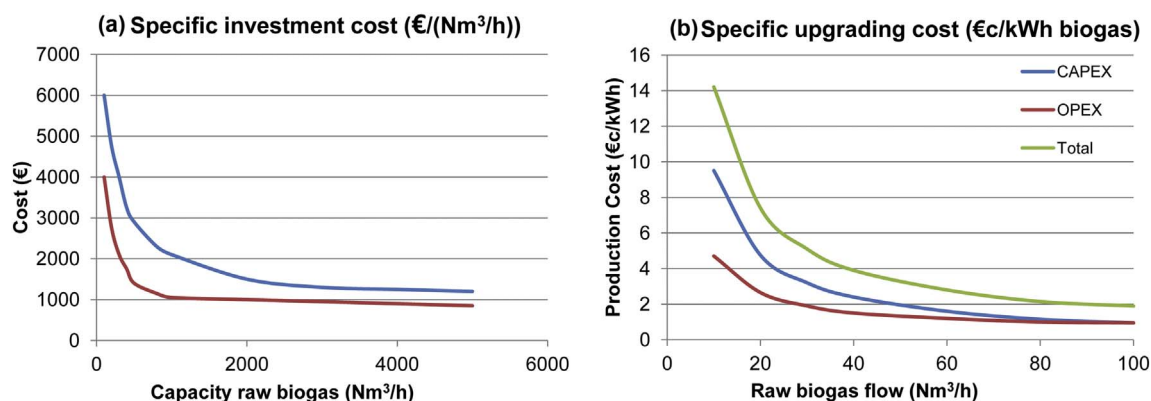
Fig. 5. Economic feasibility of biogas upgrading; a) Cost data and economy-of-scale of the investment in physicochemical biogas upgrading. High-low interval including all existing upgrading technologies. Based on data from Hoyer et al. (2016), b) Specific total biogas upgrading costs including amortized CAPEX and OPEX for small scale PSA units. Based on data from Blom et al. (2011).

However, a rapid decrease in production cost of renewable electricity, both solar power and wind power, was experienced during the last decade and is expected to continue. In the decade 2005 to 2014, the cost of photovoltaic power production fell from 40 €c/kWh to 9 €c/kWh under German solar radiation conditions, and this trend is expected to continue without any foreseeable levelling out and be around 2–4 €c/kWh in 2050 by a conservative estimate (Fraunhofer, 2015). This cost may turn to end up even lower. With rapidly decreasing renewable electricity production cost, the CAPEX part of the cost becomes more dominating. This means that on a longer term, the future winning technology will probably be found as the one with lowest CAPEX, but if this turns out to be microbiological upgrading or physicochemical upgrading is yet too early to say.

The incentive for upgrading biogas by H_2 is, thus, not a short term economic benefit as it already is for physicochemical CO_2 removal. But on a medium to longer term, further incentives are expected to evolve, both in terms of the just described fall in electricity production price and in terms of potential increase in biomass and gas prices relative to electricity price. Biogas hydrogenation may, thus, prove to be a key to a sustainable renewable energy system due to its ability to release energy systems from being over-dependent on biomass supply. Refraining from using fossil resources implies a challenge in providing propulsion means for a larger part of the transport sector, which cannot be electrified within a foreseeable future, i.e. aviation and long distance heavy duty transport on road and sea. If not based on fossil fuels, the most attractive source of carbon for hydrocarbon transport fuels is biomass, but comparing demand and supply potentials for hydrocarbon fuels and biomass shows that biomass must be considered a constrained resource (Wenzel et al., 2014). The most recent expert consensus on the global availability of biomass for energy is found in a report from the Intergovernmental Panel on Climate Change, IPCC (Chum et al., 2011), and it concludes that biomass available for energy will lie in the region of 100–300 EJ/year in 2050, equal to around 10–30 GJ/person/year at that time. To understand the significance of this figure, one can compare it to the scale of biomass demand in a renewable system design. In the last 5–10 years a large number of scenarios for a fully renewable energy system were made in Denmark. The developed energy system design, all being based on 100% renewable energy, vary from some being very dependent on biomass and bioenergy on the one side to some being very advanced with a high degree of electrification of heat and transport sectors and a high integration of electrolysis and H_2. All the scenarios with large scale H_2 assume that it is used for hydrogenation of carbon from biomass, both in the form of CO_2 in biogas and in syngas from thermal gasification of wood.

Even though the studies were done independently and by different parties using different methods and modelling tools at different time points, there is an interesting consensus among these studies. The

system designs being very dependent on biomass and bioenergy all need above 100 GJ/person/year of biomass resources to satisfy the system demands. When the system reaches a high degree of electrification, the demand falls to around 80 GJ/person/year (still without H_2), and when large scale electrolysis and H_2 is integrated, the demand falls to 40–50 GJ/person/year. The scenarios with the lowest biomass demand assume even hydrogenation of CO_2 (Lund et al., 2011; Mathiesen et al., 2015; Wenzel et al., 2014). A summary of H_2 integration and biomass demand in these studies is given in Table 5.

As evident from Table 5, it seems that even very advanced renewable energy system designs with highest degree of electrification and large scale electrolysis and hydrogenation of bio-carbon implies a higher demand for biomass than the around 20 GJ/person/year that is available as a global average according to Chum et al. (2011).

In this light, and as renewable energy is a targeted approach for meeting the climate challenge based on the agreement from the Climate Summit in Paris 2016, a strategy for including H_2 for the upgrading of bio-carbon, including the CO_2 of biogas, is judged to be an attractive approach to avoiding excessive demands for biomass for energy. The environmental benefit of avoiding excessive use of land for energy crops and forestry biomass is very large (Wenzel et al., 2014) and in a world of constrained biomass availability, hydrogenation may also prove to be economically favourable compared to excessive use of biomass and dependency on biomass imports.

Table 5
A summary of results regarding the relation between hydrogen integration and biomass demand in fully renewable energy system designs from Danish studies.

Study	Scenario	Hydrogen	Biomass
		(GJ/person/year)	
(Lund et al., 2011)	'Recommended scenario'	18	43
(Mathiesen et al., 2015)		19	43
(Danish Energy Agency, 2014a)	Bio +	0	130
(Danish Energy Agency, 2014a)	Bio	0	85
(Danish Energy Agency, 2014a)	Wind	11	47
(Danish Energy Agency, 2014a)	Hydrogen	15	44
(Wenzel et al., 2014)	Bio	0	120
(Wenzel et al., 2014)	Electrification	0	82
(Wenzel et al., 2014)	Electrolysis	14	51
(Wenzel et al., 2014)	CO_2 hydrogenation	18	40

4. Perspectives - Conclusions

Besides heat and power production, new applications of biogas have emerged the recent years. Conversion of biogas to biomethane is already a strategic target in many countries. Physicochemical methods are in general at high technology readiness levels, while biological methods are still new and not commercial yet. However, they offer huge potential in respect to feasibility, technological easiness, and potential. Development of biological technologies is rapid as challenges have been identified and solved. Biological upgrading opens new horizons for integrating different forms of renewable energy and besides upgrading can offer electricity storage advances and decoupling bioenergy production from biomass availability.

Acknowledgement

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