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REVIEW ARTICLE

Evaluation of biogas upgrading technologies and future perspectives: a review

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Abstract

Biogas is acknowledged as one of the foremost bioenergy to address the current environmental and energy challenges being faced by the world. Commonly, biogas is used for applications like cooking, lighting, heat and power production. To widen the scope of biogas application, like transportation, natural gas grid injection and substrate for the production of chemicals and fuel cells, mainly CO_2, H_2S and other impurities need to be removed by various upgrading technologies. It is an important process to produce biomethane with above 90% methane. There are various physico-chemical (adsorption, absorption, cryogenic and membrane separations) and biological (in situ and ex situ) processes for biogas upgradation, and each process is site and case specific. The aim of the present paper is to thoroughly evaluate the existing and emerging biogas upgrading technologies. Analysis of each technology with respect to basis of operations, energy requirement, methane purity and recovery and cost economics has been carried out. A thorough analysis has been done on the major hurdles and the research gaps in this sector. For a wider and successful implementation of the biogas upgradation technology, the trends in research and development (R&D) such as development of efficient biogas upgrading technologies, adsorbents, reduction in cost and methane loss have been thoroughly evaluated.

Keywords Biogas upgrading · Biomethane · CO_2 removal · Future perspectives

Introduction

Fossil fuels are the dominant source of energy providing 80% of the global energy needs. In the current trend of fuel consumption, carbon dioxide emissions are estimated to increase to 37 Gt by 2035 (IPCC 2013). Considering the limited fuel reserves, increasing greenhouse gas emissions and climate change, a transition from fossil-based (coal, petroleum and natural gas) to zero-carbon renewable fuels has been experienced worldwide. For sustainable economic growth, there is a need for accelerated and synergistic deployment of renewable and efficient energy measures by the second half of this century (IRENA 2017a).

Renewable resources form the nucleus of energy transition to make it less carbon intensive and compatible to the international climate goals (REN21 2017). To adequately limit the rise in global temperatures, energy use would have to be totally decarbonized in less than 50 years (IRENA 2017b). To meet this goal, International Renewable Energy Agency (IRENA) analysed that renewables must grow to 65% of global energy supply by 2050 (IRENA 2018). World Bioenergy Association estimated that renewable energy contributed approximately 18.6% of the total global energy consumption, in which bioenergy accounted for nearly 14% (Fig. 1) (Kummamuru 2017). Bioenergy is projected to sustainably supply between a quarter and a third of future global primary energy mix in 2050 (Devi P, Devi 2012). There is an increasing inclination towards using modern technologies and efficient bio-energy conversion routes for biofuels production to fulfil the global energy demand.

Biogas is a potential alternative to the world's unquenchable demand for energy and concurrently reduces waste and greenhouse gas (GHG) emissions. Wastes like sewage sludge, agricultural and crop residues, animal dung and industrial organic wastes and wastewaters can be converted into biogas through anaerobic digestion. Biogas production is predicted to

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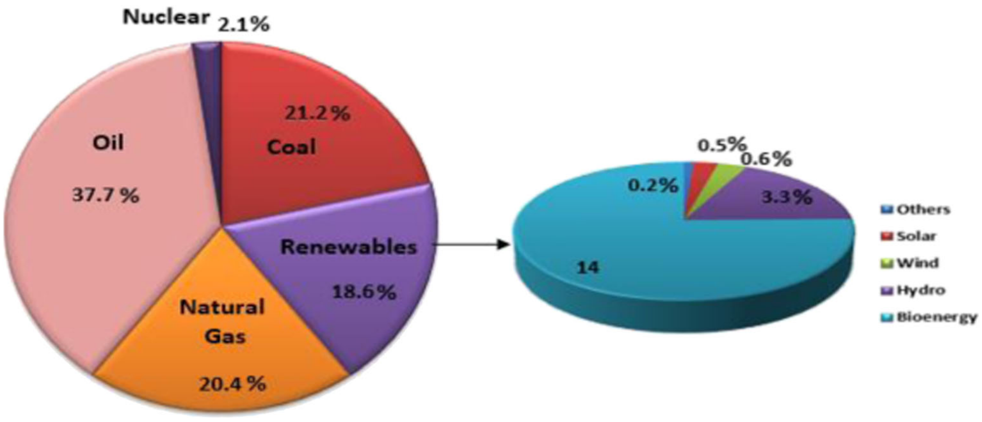
Fig. 1 Gross final energy consumption globally in 2014



increase to 40.2 Mt by 2030 (World Energy Council 2013). The major constituents of biogas is methane (CH_4; 50–70%) and carbon dioxide (CO_2; 30–50%) with traces of nitrogen (0–3%), hydrogen sulphide (H_2S), carbon monoxide (CO), oxygen(O_2; 0–1%), ammonia (NH_3), siloxanes, volatile organic compounds (VOCs) and hydrocarbons. The composition of biogas depends upon nature of raw materials used for digestion and pH of the medium (Muñoz et al. 2015). Biogas alike natural gas has CH_4 as a major component. The market for biogas is being earnestly encouraged for cooking, power, heat and transport and is predicted to increase to 29.5 GW by 2022 (World Energy Council 2013).With increasing research and development in this sector, there has been establishment of state-of-the-art biogas production and upgradation processes, technologies and equipment for its effective utilization.

The presence of CH_4 makes biogas a combustible fuel. The concentration of CH_4 in biogas fixes its calorific value as the other constituents do not contribute to the energy content. Raw biogas has calorific value in the range of 21 MJ/m^3 assuming 50% CH_4 in raw biogas and density of 1.22 kg/Nm^3 similar to air (1.29 kg/Nm^3) (Rutz and Janssen 2008). CH_4 concentration of biogas should be appreciably high (> 90%) to find use in different applications. Table 1 provides a comparison of the calorific values of various fuels.

CO_2 is the non-combustible portion of biogas. Its presence decreases the energy content per unit mass/volume (calorific value) of biogas, making it suitable only for those applications in which low-quality energy is needed, for example cooking and lighting. It not only lowers the power output from the engine but also reduces the effective volume of the storage cylinders. Due to its presence, frequent refilling of fuel tank of vehicle would be required which would result in more energy consumption in compression of biogas. CO_2 forms dry ice upon compression which results in lump formation and freezing problems at metering points and valves. This makes it difficult to be stored in containers for transportation and limit its utility. Therefore, removal of carbon dioxide from biogas becomes necessary to increase use of biogas for wider range of applications. The H_2S and water vapour present in small amount in biogas are corrosive to the metallic parts of equipments, engines, pipes and valves fittings and reduce the lifespan of equipment. These contaminants need to be removed from biogas before its application. After upgradation and compression, upgraded biogas (biomethane) meets the standards comparable to natural gas for injection into a natural gas grid or for use as a vehicle fuel.

Table 1 Calorific value of various fuels (SGC 2012; Huguen and Le Saux 2010)

Fuel	Energy (kWh)
1 Nm^3 biogas (60% CH_4)	6.0
1 Nm^3 biomethane (97% methane)	9.67
1 Nm^3 natural gas	11.0
1 l petrol	9.06
1 l diesel	9.8
1 Nm^3 biomethane is equivalent to approx.	1.1 L of petrol
1 Nm^3 natural gas is equivalent to approx.	1.2 L petrol

The utilization of biogas as a fuel is determined by its composition. There is a considerable difference between the composition requirements of stationary engine applications and fuel gas or pipeline quality (Allegue and Hinge 2012). Biogas utilization in boilers for gas heating only requires H_2S removal < 250 ppmv and moisture removal (Khan et al. 2017), whereas use of biogas in stationary engines for combined heat and power (CHP) generation requires the removal of moisture and H_2S below < 1000 ppmv. However, for vehicular fuel and gas grid injection applications, CO_2, H_2S, moisture and most of the other impurities need to be removed as recommended in country standards (Sun et al. 2015). At present, no international standard for upgraded biogas utilization as a vehicle fuel or injection in the natural gas grid is available. Some countries have developed national standards, policies and procedures for the same. There are differences in values and units of measurement (vol.%, mol.%, ppm). Although there is a common view regarding the permissible level of minor and trace components of biogas. Some parameters that are crucial to measure the gas quality such as CH_4, CO_2, O_2, H_2, moisture, sulphur compounds, heating value and Wobbe Index are relatively in the same range in the specifications developed by different countries. Some countries like Switzerland, Netherlands, Germany, Michigan and India have stringent defined standards and specifications for utilization of biomethane as vehicle fuel or for grid injection which are in the range of CH_4 80–96%, $CO_2 < 2–3\%$, $O_2 < 0.2–0.5\%$, $H_2S < 5$ mg/m^3, $NH_3 < 3–20$ mg/m^3 and siloxanes $< 5–10$ mg/m^3 (Table 2).

Biogas upgrading is a popular, well-developed and commercially available technology. It is being increasingly implemented around the world but is still infancy as compared to the biogas production sector. However, this sector is on its growth trajectory with above 503 biogas upgrading plants in operation till the 2016 (Fig. 2) from 187 plants in 2011 (EBA 2017). This paper reviewed and critically evaluated biogas upgrading technologies. The upgrading approaches deliberated comprehensively in this paper have the capability to simultaneously separate CO_2, H_2S and other impurities. Conventional and emerging biogas upgrading technologies based on adsorption, absorption, cryogenic, membrane separation and biological methods are proficient enough to upgrade biogas to high quality biomethane for various applications. Biogas upgrading technologies discussed in this paper have a wide range of physical, chemical and biological principals, operating conditions, biomethane quality, CH_4 loss, energy consumption and costs. Each technology is site and case specific and mainly dependent on the requirements of final application of biomethane. Each upgrading technology has different advantages and disadvantages over one another.

A number of reviews and literature studies have provided considerable information on performance of existing biogas cleaning and upgrading technologies; they mainly focus on the technological details. The primary objective of this review paper is to provide a comprehensive literature summary on research and development and recent progress in biogas upgrading technologies. This paper provides perspectives on the selection of technology according to the final utilization of biogas/biomethane along with insights on the efficiency, investment, operational and maintenance costs of the technologies. This review highlights challenges related to the improvement of the processes for enhancing biomethane production. This review concludes that a lot of research is required to decrease CH_4 loss, environmental impacts, capital, operating and maintenance costs, energy consumption and development of support policies, subsidies and governmental support. The study could provide guiding principles for establishing efficient biogas upgradation plants. The paper promulgates essential information and general research directions to those who are involved or interested in the field of biogas upgradation.

Biogas cleaning

The first step in the treatment of biogas is 'biogas cleaning'. It includes removal of harmful and/or toxic compounds (such as H_2S, moisture, siloxanes, volatile organic compounds (VOCs), and NH_3). The removal of water, hydrogen sulphide and other possible contaminants is required for all commonly used gas applications for example in boilers, CHP engines, vehicles or the injection in the natural gas grid (Table 3). Biogas needs cleaning to reduce the chance of damaging downstream equipment which is due to the formation of harmful compounds (Ryckebosch et al. 2011).

Water vapour present in biogas is in the range of 1–5% (Sun et al. 2015). It is the main component which causes damage to pipes and engines by corrosion; hence, its removal is essential because it produces corrosive acids in combination with toxic impurities such as hydrogen sulphide or halogenated compounds to. Water vapour can be removed in a number of ways, for example adsorption with silica gel, glycerol, refrigeration, activated carbon or molecular sieves. Hydrogen sulphide (H_2S) in biogas is present in different concentrations depending upon the digester feed substrate and inorganic sulphate content varies with the feedstock. It is both toxic and corrosive causing substantial harm to equipment, instruments and piping. Different applications have different tolerance limits for H_2S. Boilers can tolerate H_2S up to 1000 ppm, internal combustion engines perform well when H_2S is maintained below 100 ppm and for natural gas applications below 4 ppm (Allegue and Hinge 2012). There are several methods usually employed to remove hydrogen sulphide. The techniques used commercially are precipitation, adsorption with activated carbon, chemical absorption and biological treatment (Ryckebosch et al. 2011). Addition of oxygen or air directly into the digester is the simplest, commonly used and very cost-effective method of desulphurization. Siloxanes are compounds containing a silicon-oxygen bond (Si–O bonds) with organic groups like methyl, ethyl and other organic groups mainly used in the manufacturing of cosmetics, medicines, drugs, deodorants and shampoos. These are generally found in significant concentrations of 1–400 mg/m^3 in biogas produced by sewage sludge, landfill gas and municipal waste (Kajolina et al. 2015). The possible techniques for the removal of siloxanes are absorption, adsorption or condensation processes (Ajhar M et al. Ajhar et al. 2010). However, most of the methods available for hydrogen sulphide removal are also selective for the removal of siloxanes. Halogenated hydrocarbons like higher hydrocarbons are commonly found in landfill gas. These become very corrosive when they combine with water. These are detrimental to human health and also to the environment. These are most commonly removed by absorption with activated carbon but its regeneration done only for a limited number of times (Ryckebosch et al. 2011).

Table 2 Natural gas/biomethane standards in some countries (Persson et al. 2006; Huguen and Le Saux 2010; Bauer et al. 2013; Sun et al. 2015; BIS 2015; Khan et al. 2017)

Country	Austria	France	Germany	Netherlands	Sweden	Switzerland	British Columbia	California	Michigan	India
Calorific upper value (MJ/Nm^3)	38.5–46.1	38.5–46.1 (H gas) 34.2–37.8 (L gas)	30.2–47.2	31.6–38.7		38.5–47.2		36.9–42.8		
Wobbe Index (MJ/Nm^3)	47.9–56.5 (upper)	48.2–56.5 (H gas) 42.5–46.8 (L gas upper)	46.1–56.5 (H gas) 42.5–46.8 (L gas upper)	43.6–44.41 (upper)	44.7–46.4 (type A)[1] 43.9–47.3 (type B)[1] (lower)	47.9–46.1 (unlimited injection)	48.2–56.5 (H gas) L: 42.5–46.8 (L gas upper)	47.6–51.6 (upper)		
Qualities										
CH_4 (%)[2]	> 96			> 80	97 ± 1 (type A) 97 ± 2 (type B)	> 96 (unlimited injection) > 50 (limited injection)	> 95.5		> 93.5	> 90
CO_2 (%)[2]	< 2	< 2.5[3]	< 6	< 6 (< 10–10.3 for regional grid)	< 3	< 6 (unlimited injection) < 4 (limited injection)	< 2	3	< 2	< 4
$CO_2 + O_2 + N_2$ (vol.%)					< 4 (type A)[1] < 5 (type B)[1]					< 10
H_2 (%)[2]	< 4	< 6	< 5	< 12	< 0.5	< 4		0.1		
O_2 (%)[2]	< 0.5	< 0.01[3]	< 3	< 0.5	< 1	< 0.5	< 0.2	< 0.2	< 3	< 0.5
CO(%)[2]		< 2		< 1		< 0.5				
Total inert (vol.%) (CO_2, N_2, O_2, CO, H_2)								4		
Water content max. (mg/Nm^3)				< 32	< 32		< 65		No condensation	16 mg/m^3
Total sulphur (mg/m^3)	< 10	< 30	< 30[4]	< 45	< 23	< 30		265		
H_2S	< 5 mg/m^3	< 5 mg/m^3 (H2S + COS)	< 5 mg/m^3	< 5 mg/m^3	< 10 ppm = < 15.2 mg/m^3	< 5 mg/m^3	4.3 ppm	88 mg/m^3	4.1 ppm	< 30.3 mg/m^3

[1] Type A: biogas as a vehicle fuel—engines without lambda control; type B: biogas as a vehicle furl—engines with lambda control

[2] Vol.% or mol.%

[3] France allows some flexibility on parameters. Oxygen and CO_2 content may be increased to 3 vol.% and 11.3 vol.% respectively under some conditions

[4] Exclusive odourization

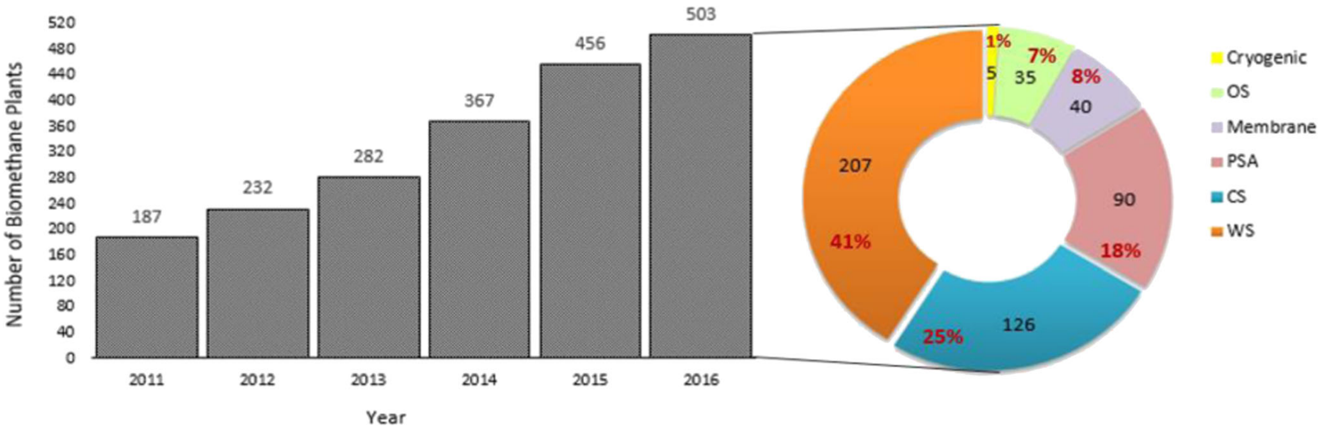


Fig. 2 Growth of biogas upgradation market since year 2011

Established biogas upgrading technologies

The established biogas upgrading technologies are those that are basically derived from natural gas purification industry. These are separation techniques designed to exploit the physical, chemical and thermodynamic or transport properties of gas components. Currently, six physical/chemical technologies for separation of CO_2 from CH_4 exist at commercial readiness level involving water scrubbing, pressure swing adsorption, organic scrubbing, chemical scrubbing, cryogenic separation and membrane separation. Moreover, there are other technologies based on biological methods 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 following text. The performance of physical/chemical upgrading technologies is compared (Table 4) in terms of different parameters: basis of operation (physical/chemical), gas pre-cleaning requirements (H_2S/moisture removal), working pressure, CH_4 concentration in upgraded biogas, CH_4 loss (ratio between the CH_4 flow rate in the off gas and the CH_4 flow rate in the biogas), CH_4 recovery (ratio between the CH_4 flow rate in upgraded biogas and CH_4 flow rate in the biogas), specific energy consumption (kWh/Nm^3 upgraded biogas), heat requirement, quality of upgraded gas, investment cost €/Nm^{3}biogas, technical availability, etc.

Water scrubbing

Basis of operation

Water scrubbing is the simplest, environmentally benign, cost economic and widely implemented method for biogas cleaning and upgrading (Sun et al. 2015). Among the commercially available technologies, it is the most common and well-developed technology for CO_2 and H_2S removal from biogas accounting for approximately 41% share in the global biogas upgrading market (UNIDO 2017). This process is based on the principle of physical absorption of gases like CO_2 and H_2S in water. The water solubility of CH_4 is 26 and 73 times lower than that of CO_2 and H_2S at 25 °C respectively (Perry 1984; Cozma et al. 2013). Hence, H_2S gets removed along with CO_2 from biogas due to its higher solubility in water. This method can tolerate H_2S concentrations of 300–2500 ppmv, but higher H2S concentrations are detrimental to the scrubbing system (Muñoz et al. 2015). H_2S dissolution in water causes decrease in pH. This causes reduced solubility of CO_2 in water and clogging of the packing material due to microbial growth which also results in limited gas–liquid mass transfer (Persson 2003). Dissolved H_2S gets desorbed from water along with CO_2 in the desorption tank at atmospheric pressures. Release of high concentrations of H_2S into the atmosphere not only causes unpleasant odour but also is harmful to environment. Thus, it is highly recommended to remove H_2S prior to the scrubbing process. Constant renewal of water

Table 3 Qualitative requirements for removal of main components from biogas according to its applications

Application	H_2S	CO_2	H_2O
Gas heater (boiler)	Recommended	No	No
Stationary engine (CHP)	Yes	No	No condensation
Vehicle fuel	Yes	Recommended	Yes
Natural gas grid	Yes	Yes	Yes

Table 4 Comparison of different biogas upgrading technologies (Allegue and Hinge 2012;Galante et al. 2012; Muñoz et al. Muñoz et al. 2015; Sun et al. 2015; Khan et al. 2017; Sahota et al. 2018)

Parameter method	Basis of operation	Temperature (°C)	Gas pre-cleaning requirement	Working pressure (bar)	Solvent/adsorbent/ consumables	Heat requirement	Energy consumption (kWh/Nm^3 upgraded biogas)	% Purity of CH_4 in upgraded gas
Water scrubbing	Physical absorption	20–40	Generally, not required, H_2S removed along with CO_2	6–10	Water, antifouling agents, drying agents	No	0.2–0.5	95–98
Physical organic scrubbing	Physical absorption	10–20	Not required	4–7	Organic solvents, polyethylene glycol	Medium,70-80 °C	0.10–0.33	> 96, < 93–98
Chemical absorption	Chemical absorption	35–50	Required and recommended	1	Amines (MEA, DMEA), alkali solutions, antifouling, drying agents	Too high 120–160 °C	0.05–0.25	> 98
Pressure swing adsorption	Adsorption	5–30	Required and highly recommended	4–8 bar	Adsorbents, molecular sieves	No	0.16–0.43	> 96–98
Membrane separation	Gas–Gas Permeation Gas–Liquid Absorption	25–60	Required and recommended	20–36	Membranes of silicone rubbers, cellulose acetate, hollow fibres	No	0.18–0.35	90–92 96
Cryogenic separation	Multistage compression and condensation	− 59 to − 45	Recommended	40	Glycol refrigerant	No	0.2–0.79	99

Parameter method	Methane loss (%)	N_2, O_2 separation	Investment cost (€/Nm^3 biogas)	Maintenance costs (€/year)	Ease of operation	Technical availability (%)	Advantages	Disadvantages
Water scrubbing	1–3%	No	Cheapest, 0.13–15	15,000	Simplest	96	• Easily scalable • Inexpensive • Easy to operate •Co-removal of H2S • Needs no special chemical or equipment	• High water demand even with regeneration • H2S damages equipments • Clogging due to bacterial growth • Foaming possibility • Biomethane drying is essential
Physical organic scrubbing	1.5–4	No	0.25	39,000	Difficult in operation	96	• Higher CO_2 solubility than water • Relatively low methane loss • Co-removal of H2S and other impurities	• Expensive investment and operation • Difficult to operate • Heating required for complete regeneration
Chemical absorption	0.04–0.1	No	0.28	59,000	Difficult in operation	91	• Highest biomethane quality • High CO2 removal efficiency • Low methane loss • No gas pressurization required	• High investment cost • High heat requirement for regeneration • Corrosion of equipment • Salt precipitation • Foaming possible
Pressure swing adsorption	1–3.5	Yes	0.26	56,000	Extensive process control needed	94	• No heat and chemicals required • Relatively inexpensive • Easily scalable	• High methane loss • Complicated process control

Table 4 (continued)

							• Compact	• H2S and water pre-treatment required
Membrane separation	0.5–20	Partly	Cheap, 0.22	25,000	Easy	98	• Simple and compact construction • Easy operation and maintenance • Modular configuration • No chemical or heat demand • High reliability	• Multiple steps required for high purity • Medium to high methane losses • Membrane replacement required in 1–5 years • Clogging and fouling of membranes • Expensive
Cryogenic separation	0.5–3	No	0.40–0.44, Most expensive	nf	Complex, multifaceted	–	• High biomethane purity • Least methane losses • Pure CO2 as a by-product • Low energy required for liquified natural gas production	• Expensive capital and O and M costs • Contaminant pre-treatment required • Technically complex procedure

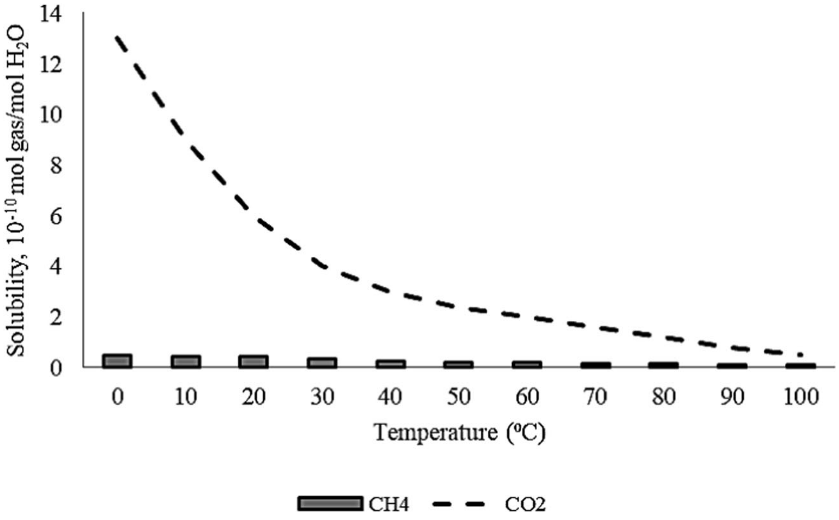
and use of antifoaming agents or adding alkalinity is necessary to avoid H_2S poisoning, corrosion and fouling (Tynell 2007). Temperature is one of the significant factors in water scrubbing process. Solubility of gases increases with decreasing temperatures. The solubility of CO_2 and CH_4 in water with respect to temperature is shown in Fig. 3 below. The CO_2 absorption in water is a physical process in which a large amount of dissolution heat is released. Low temperatures in the absorption column are thus advantageous for the enhancement of CO_2 absorption in water.

Lantela et al. (Läntelä et al. 2012) observed a decrease in CO_2 removal efficiency from 88.9 to 87.3% at 25 bar as the temperature increased from 10–15 to 20–25 °C. Xiao Y et al. (Xiao et al. 2014) observed that the CO_2 removal efficiency decreased from 85.3 to 52.2% as the temperature increased from 7 to 40 °C. Hence, temperature control in water scrubbing column for efficient biogas upgradation should be given great attention, especially when the plant is operated in summers. A cooling system should be used in such cases.

Initially, pressurized biogas is injected through the bottom of the absorption column, while water is channelled into the column from the top (Fig. 4). CO_2 absorption in water scrubbing process is often carried out at 8–10 bar, although pressures in the range of 10–20 bar are also used (Kapoor et al. 2017). The scrubbing column is packed with randomly filled packing material which helps in increasing the time of contact between the phases and surface area for mass transfer. Biogas flows upwards into the column and water flows from the top towards the bottom of the column. The counter current interaction between the two phases over the random packing material results in high mass transfer. Biomethane with above 90% CH_4 is obtained from the top of the scrubber, while the water containing absorbed CO_2 and H_2S is channelled from the bottom of the column into a flash vessel, where the pressure decreases to 2.5–3.5 bar (Nock et al. 2014). This reduction in pressure in the flash vessel results in the release of a CO_2 rich gas mixture (80–90% CO_2 and 10–20% CH_4) which can be further processed for methane loss recovery and bio-CO_2 production. It should be noted that N_2 and O_2 cannot be separated because they are non-condensable gases (Bauer et al. 2013).

Large quantities of water (m^3/h) are usually required for the scrubbing process which depends upon the pressure in the column and temperature of the gas. Based on the quantity, quality and cost of water available for the process, two methods are commercially used in water scrubbing technology, single pass and regenerative absorption (Angelidaki et al. 2018). Single-pass scrubbing employs water derived from wastewater treatment plants in which water is used only once. The spent water obtained from the bottom of the water scrubbing column is depressurized in a flash vessel and released into the environment (Fig. 5). In regenerative absorption process, water is regenerated in a two-stage regeneration step.

Fig. 3 Effect of temperature on the solubility of CO_2 and CH_4 in water (Perry 1984)



Water is first depressurized at 2–3 bar in the flash vessel followed by water decompression and regeneration in a desorption/stripping column at atmospheric pressure. Water is then recycled and reused for the scrubbing process. In single-pass scrubbing process, flow rates of water in the range of 0.1–0.2 m^3/Nm^3 biogas are generally required depending on the operating pressure and temperature in contrast to 0.18–0.23 m^3/Nm^3 biogas in regenerative absorption units (Bauer et al. 2013; Muñoz et al. 2015). In spite of the fact that regenerative absorption water recycling reduces water consumption, for biogas flow rates of 100-1000 Nm^3/h, 20–200 L/h freshwater is purged into the water line to avoid the accumulation of harmful compounds. High operating pressures require low water flow rates which in turn increases cost for biogas compression and water pumping and decreases the lifetime of the upgrading plant.

CH_4 loss, energy requirements and cost economics

CH_4 losses are an integral part of the upgradation process. With water scrubbing technique, plant developers guarantee a maximum of 2% CH_4 loss, but it depends upon various factors. Petersson and Wellinger (2009) reported CH_4 loss of 1–2%, and Pertl et al. (2010) reported CH_4 loss of 1.5% in their study. CH_4 loss from 8 to 10% has also been reported from some plants due to optimized operation of the system (Khan et al. 2017). Energy requirement during the process is mainly for gas compression, water pumping and regeneration. Investment costs of water scrubbing systems depend upon the scale of the plant (Bauer et al. 2013). As the plant capacity increases, the cost decreases. With plants having scale of operation of 100 to 500 Nm^3/h, investment costs decrease from 5500 to 2500 €/Nm^3/h and it remains relatively constant for

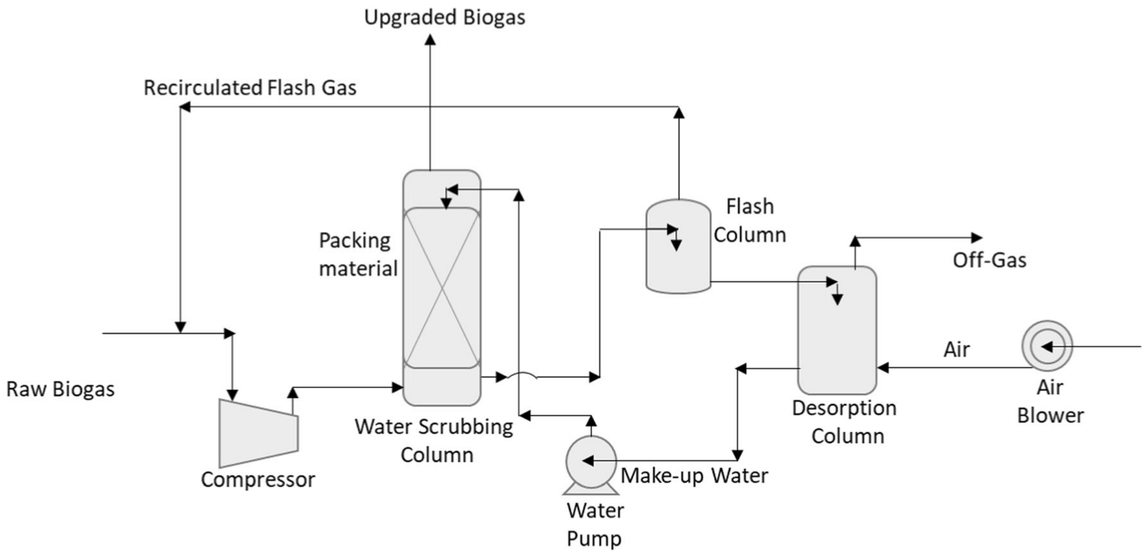


Fig. 4 Process flow diagram of biogas upgrading by water scrubbing process with regeneration of water

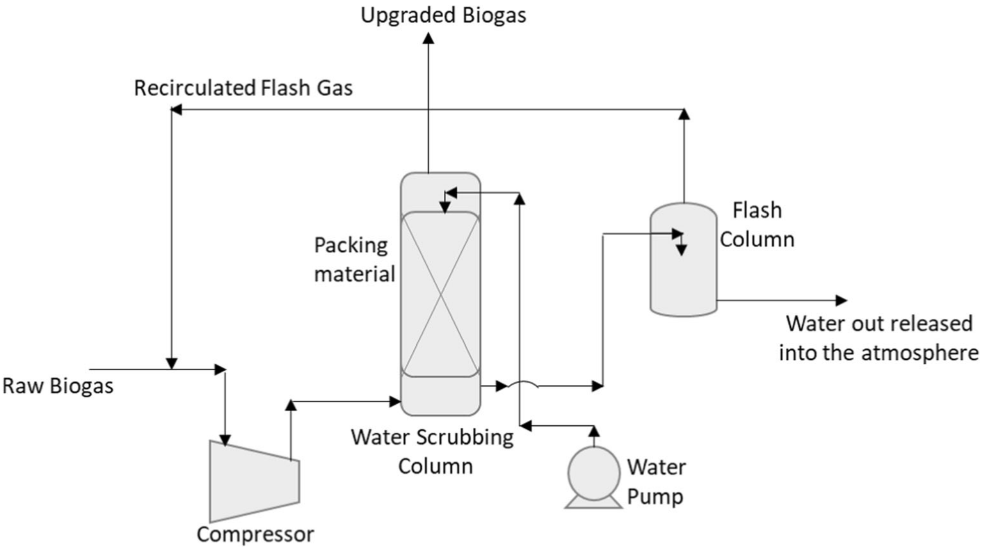


Fig. 5 Process flow diagram of biogas upgrading by water scrubbing process without regeneration of water

plant capacities over 1000 Nm^3/h at 1800–2000 €/Nm^3/h (Galante et al. 2012; Muñoz et al. 2015). Conversely, the operating costs due to energy consumption range from 0.11 to 0.15 €/Nm^3 for plant capacities 200–300 m^3/h. Energy consumption however decreases from 0.3 kWh/Nm^3 at 500Nm^3/h to 0.2 kWh/Nm^3 at 2000 Nm^3/h. Majority of energy is required for gas compression (0.10–0.2 kWh/Nm^3 for 8–10 bar compression) and water compression (0.05–0.1 kWh/Nm^3) (Cucchiella and D'Adamo 2016; Khan et al. 2017). Annual maintenance costs are usually 2–3% of the investment costs assuming the costs of consumables as negligible (Persson 2003).

Organic scrubbing

Basis of operation

Organic scrubbing is a physical absorption process comparable to water scrubbing but instead uses organic solvents to absorb CO_2 from biogas. Besides CO_2, H_2S and H_2O can also be separated. The organic solvents most commonly used in the process are mixtures of methanol and dimethyl ethers of polyethylene glycol (Khan et al. 2017). Solvents are available in different forms and brands. Solvents commercially available are under the trade names of Selexol® and Genosorb® (Allegue and Hinge 2012; Petersson and Wellinger 2009). Organic solvents have significantly higher solubility of CO_2 in the solvent in comparison to water. For example, Selexol® has the capacity to absorb five times more CO_2 than water, which fundamentally reduces solvent requirement for the process (Tock et al. 2010). The use of the organic solvents not only results in reduction in absorbent recycling rates and plant size but also reduces investment and operating costs. Additionally, the anticorrosive property of these solvents does not require special construction and coating materials for the scrubber. Moreover, another advantage of organic solvent is low vapour pressure of polyethylene glycol dimethyl ethers which leads to low loss of solvent during the scrubbing process and hence minute requirement of solvent for make-up. Conversely, the regeneration of organic solvents is difficult due to the high solubility of CO_2 in the solvent. Likewise, the solubility of H_2S in Selexol® is significantly higher as compared to CO_2, which causes regeneration of solvent at high temperatures with the help of steam or inert gas in order to avoid a sulphur-mediated solvent deterioration. It is therefore apparent that the high concentrations of H_2S in raw biogas require higher temperature for regeneration of solvent. Hence, to avoid increased energy consumption, H_2S removal is suggested before the process of organic scrubbing (de Hullu et al. 2008). As shown in Fig. 6, during the process of biogas upgrading by organic solvents, raw biogas is compressed to 7–8 bar and before injection into the absorption column it is cooled down to 20 °C (Angelidaki et al. 2018). Likewise, the organic solvent is also cooled before injecting it from the top. After scrubbing, the organic solvent is regenerated by heating and depressurising to 80 °C and 1 bar respectively in a desorption column (Muñoz et al. 2015).

CH_4 loss, energy requirements and cost economics

The biomethane quality that can be achieved using this technology is 98% CH_4 (Angelidaki et al. 2018). In fact, biomethane content of 96–98.5% and CH_4 loss less than 2% can be achieved in an optimized full-scale plant, but with the comparable energy consumption as water scrubbing (Persson 2003; Bauer et al. 2013; Muñoz et al. 2015). High purity CO_2 can be obtained as a by-product from the process. This process has the advantage that an additional drying of upgraded biogas is not required because moisture and halogenated hydrocarbons are easily absorbed by the organic solvent. In spite of the

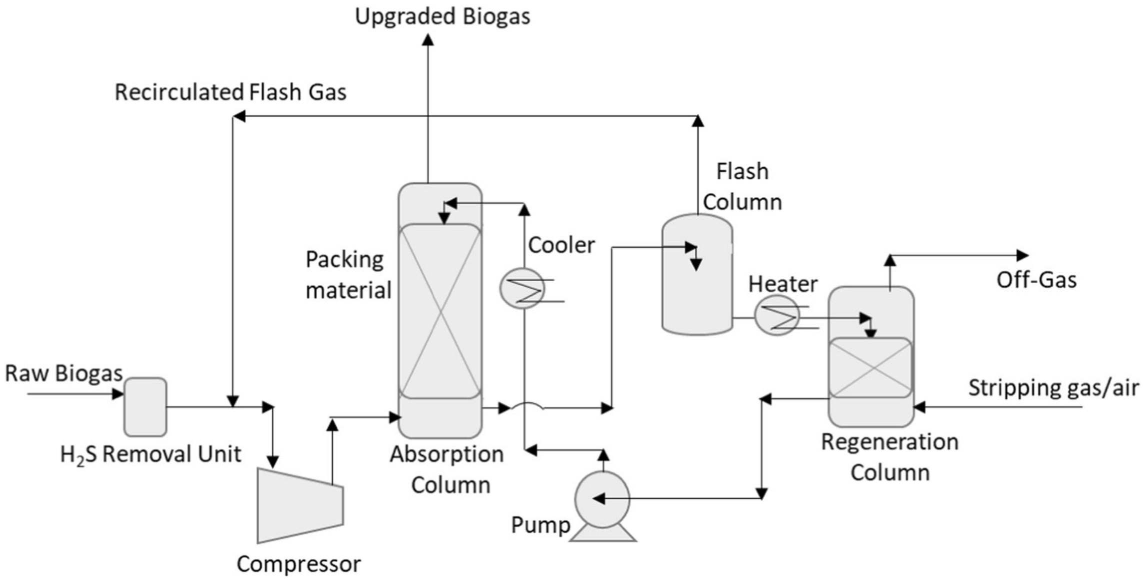


Fig. 6 Process flow diagram of biogas upgrading by organic scrubbing process

lucrative benefits of this technology, it has only 6% market share in the biogas upgrading market (Thrän et al. 2014).

The capital costs of organic scrubbing decrease from 4500 €/Nm^3/h for plants having capacity of 250 Nm^3/h plants to 2000 €/Nm^3/h for scale of 1000 Nm^3/h (Cucchiella and D'Adamo 2016). Capital costs for large-scale plants having capacities over 1500 Nm^3/h becomes constant at 1500 €/Nm^3/h. Operating costs are mainly because of 0.2–0.25 kWh/Nm^3 of electricity required for compression of biogas and pumping of solvent and maintenance costs are 2–3% of the investment cost (Patterson et al. 2011). Even though waste heat of the exhaust gases of incineration or combustion plants is usually used for solvent regeneration, still, higher energy requirements in the range of 0.4–0.51 kWh/Nm^3 have been reported in literature (Muñoz et al. 2015; Cucchiella and D'Adamo 2016).

Chemical absorption

Basis of operation

Typically, chemical scrubbing is based on the fundamentals of reversible chemical reaction between absorbed gases and chemical solvent. It has almost comparable biogas–liquid mass transfer principles to physical scrubbing. But the configuration of chemical scrubbing is much simpler with improved performance because of the use of highly reactive chemical absorbents having high CO_2 solubility (Andriani et al. 2014). Commonly used as chemical solvents for removing acidic gases like CO_2 and H_2S are amines (derivatives of ammonia, NH_3). The amines that are normally used for biogas upgrading include mono-, di-, and tri-ethanolamine (Maile and Muzenda 2014) mainly monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA) and sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) (Kadam and Panwar 2017). MEA is the cheapest amine for absorbing CO_2 as a scrubbing agent (Abdeen et al. 2016). Due to its high selectivity for CO_2 and high absorption capacities, it is the most commonly used amine (Mani et al. 2006). Commercially, up to 30 wt%, MEA has been employed successfully with 80–95% CO_2 removal efficiency. DEA is the second most widely used alkanolamine in the gas processing industry for the purification of gases containing CO_2 and H_2S. It has a lower regeneration energy requirement than MEA, but a much lower absorption rate and capacity (Table 5). However, it is also prone to losses and degradation, but relatively to a lesser extent than MEA. MDEA is a very popular solvent for the removal of high concentrations of acidic gases. It is the most preferred amine due to its high capacity, relatively low regeneration energy requirement, low tendency to form degradation products and low corrosion rates, excellent thermal and chemical stability. Its major drawback is the relatively slow kinetics which results in low absorption capacity of CO_2. MDEA solvents have low vapour pressure and basicity allows it to be used in high concentrations of up to 60 wt%, which results in lower circulation rates, smaller plant size and low costs (Bernhardsen and Knuutila 2017). AMP is the most common sterically hindered amine used for CO_2 absorption. AMP is two orders of magnitude slower in oxidative degradation and more resilient to thermal degradation than MEA. The CO_2 absorption capacity of AMP is high due to the presence of a large tertiary carbon near the amino functional group which results in a faster reaction with CO_2 than tertiary amine. CO_2 absorption rates of MEA, DEA, AMP are higher than MDEA in the order of MEA > DEA > AMP > MDEA and CO_2 absorption capacity

Table 5 Absorption capacity, advantages and disadvantages of some chemical absorbents (Rufford et al. 2012, Maile et al. 2015, Abdeen et al. 2016)

Name	Absorption capacity (molCO_2/ mol amine)	Advantages	Disadvantages
Monoethanolamine (MEA)	0.45–52 (Rufford et al. 2012)	• High reactivity • Low solvent cost • Low molecular weight • Reasonable thermal stability and degradation rate	• High regeneration energy requirement • Uneconomical process • Relatively low CO_2 loading capacity results in large recirculation rates which eventually demands for large equipment sizes and high capital cost • High solvent losses and degradation and high vapour pressure
Diethanolamine (DEA)	0.21–0.81 (Rufford et al. 2012)	• Lower regeneration energy requirement • Low heat of reaction	• High losses and degradation but relatively to a lesser extent than MEA • Regeneration of the spent DEA solutions is more complex as vacuum distillation may be required
N-methyldiethanolamine (MDEA)	0.20–0.81 (Rufford et al. 2012)	• Relatively low regeneration energy requirement for regeneration • Less degradable and corrosive • Low vapour pressure and basicity • lower circulation rates, smaller plant size and costs	• Relatively slow kinetics • Low absorption capacity
2-Amino-2-methyl-1-propanol (AMP)	0.84 (Choi et al. 2009)	• Slow in oxidative degradation • More resilient to thermal degradation than MEA • CO_2 absorption capacity of AMP is high as compared to other amines • Faster reaction with CO_2 than tertiary amines • Low cost for solvent regeneration	• Absorption rate is low as compared to MDEA
MDEA and piperazine (PZ), known as activated MDEA (AMDEA)	0.41 (Rochelle et al. 2011)	• High absorption capacity significantly as compared to MDEA	• Limited solvent solubility as solid precipitation occurs at both low and high CO_2 loading
Ammonia (NH3)	1.76 (Mani et al. 2006)	• Non-degradable • Non-corrosive	• NH_3 is highly volatile and could be lost as an air pollutant • High saturated vapour pressure of ammonia introduces NH3 in the gas phase • Ammonia washing equipment at the outlet of the gas absorption column which will on the other hand increase both capital cost and energy demand

in the order of AMP > MEA > DEA > MDEA (Rinprasertmeechai et al. 2012). Recently, piperazine (PZ) is being used as an activator for amine systems to improve absorption kinetics such as MEA/PZ and MDEA/PZ blends which allows for increased solvent capacity and faster kinetics. A mixture of MDEA and piperazine (PZ), known as activated MDEA (AMDEA), is becoming popular for CO_2 absorption from biogas because of its higher absorption capacity compared to MDEA (Muñoz et al. 2015) due to the presence of primary and secondary amines in PZ and the tertiary amine in MDEA which increases reaction rate for CO_2 absorption (Li et al. 2013). Aqueous-free ammonia (NH_3) is an alternate chemical absorbent for CO_2 removal from biogas (Mcleod et al. 2014). It has highest absorption capacity, is not degradable, corrosive and requires up to 75% less energy than MEA for regeneration due to weaker bonding of CO_2 to ammonia (Budzianowski 2011; Mani et al. 2006; Makhloufi et al. 2014).

Inorganic solvents generally used for chemical scrubbing are aqueous solutions of alkaline salts such as sodium, potassium, ammonium and calcium hydroxides (Abdeen et al. 2016). Solubility of CO_2 in sodium hydroxide is higher as compared to amines, theoretically, to absorb 1 ton of CO_2, 1.39 tons of mono-ethanolamine will be required, as compared to 0.9 tons of sodium hydroxide (Angelidaki et al. 2018). However, absorption of CO_2 in alkaline solutions is supported by agitation to increase turbulence and the contact time between biogas and solvent which subsequently increases the diffusion and hence mass transfer. Aqueous alkaline salts are more competent, cost economic and easily available as compared to amines. As compared to amines, alkali solvents suffer major drawback of slow absorption rate of CO_2 compared to amines and caustic solvents and regeneration of aqueous alkali salts of NaOH and KOH. Regeneration is complex and challenging because of the formation of thermally stable products of absorption process, i.e. Na_2CO_3 and K_2CO_3 salts. For regeneration of spent NaOH solution, temperature of 160 °C is required for the decomposition of $NaHCO_3$ into Na_2CO_3, H_2O and CO_2. But very high temperature of 800 °C is required to form Na_2O which is a suitable source of NaOH (Maile et al. 2017). The regeneration of the alkali solutions is expensive due to the high energy requirement. Also, causticization of sodium hydroxide using lime requires high temperature, is highly inefficient and produces low alkalinity solvent and produces low alkalinity solvent. However, if the carbonation products of inorganic absorption process are used in some applications like chemical manufacturing, then the process can be advantageous.

A chemical scrubbing system consists of a packed bed column integrated to a reboiler equipped desorption unit. During chemical scrubbing, biogas is injected in the packed bed absorber operating at 1–2 bar from the bottom and the chemical solvent is provided from the top counter currently (Bauer et al. 2013) as shown in Fig. 7. Both structured and random packings can be used as the risk of clogging of packings due to biomass growth is controlled by the high pH of chemical solvent (Ryckebosch et al. 2011).

Chemical scrubbing of biogas is an exothermic reaction. During the process, absorber temperature increases to 45–65 °C from 20 to 40 °C (Khan et al. 2017). The exothermic reaction produces intermediate chemical compounds (CO_3^{2-}, HCO_3^-) which results in an increased CO_2 absorption capacity due to enhanced mass transfer of CO_2 from biogas. This results in smaller and compact units with decreased absorbent recycling rates. The spent solution rich in CO_2 and H_2S obtained from the bottom of the absorber is pumped to a stripping column though a heat exchanger. Regeneration of the spent is accomplished in the stripping column at a pressure of 1.5 bar and heating it to 120–160 °C (Petersson and Wellinger 2009; Khan et al. 2017). The stripping column is equipped with a reboiler to provide heat of reaction for desorption of CO_2 from the spent chemical solution. The heat disrupts the chemical bonds formed during absorption. The exiting steam containing CO_2 is cooled in a condenser and channelled to the stripper to release the entrapped CO_2 into the environment. If H_2S is also absorbed during chemical scrubbing, higher temperature will be required for regeneration of spent solvent for H_2S desorption. It is therefore suggested to remove it before the scrubbing process. Toxicity of the solvents to the environment, huge requirement of energy for regeneration of spent solvent carried out at 120–150 °C, cost of the chemicals, solvent loss due to evaporation and the contaminant build-up make the process complex. Low operating pressures significantly reduces energy requirements for biogas compression and solvent pumping. In spite of its high CO_2 removal efficiency, energy consumption is comparatively high due to requirement of high heat demand for regeneration. There is also a possibility of salt precipitation, foaming and O_2 poisoning of amine and other chemicals. Foaming, amine degradation, solvent losses and make up problems, corrosion and the operational problems make this system complex as compared to other techniques. These disadvantages contribute to limited share of this developed technology to 22% in the global upgrading market (Thrän et al. 2014).

CH_4 loss, energy requirements and cost economics

Biomethane with high concentration of > 99% of CH_4 leaves the column from the top with CH_4 loss lower than 0.1%. CH_4 recovery of 99.5–99.9% can be attained with high purities due to low solubility of CH_4 in chemical solvents (Khan et al. 2017; Kadam and Panwar 2017), even though CH_4 loss up to 4% has been reported in some modelling reports due to CH_4

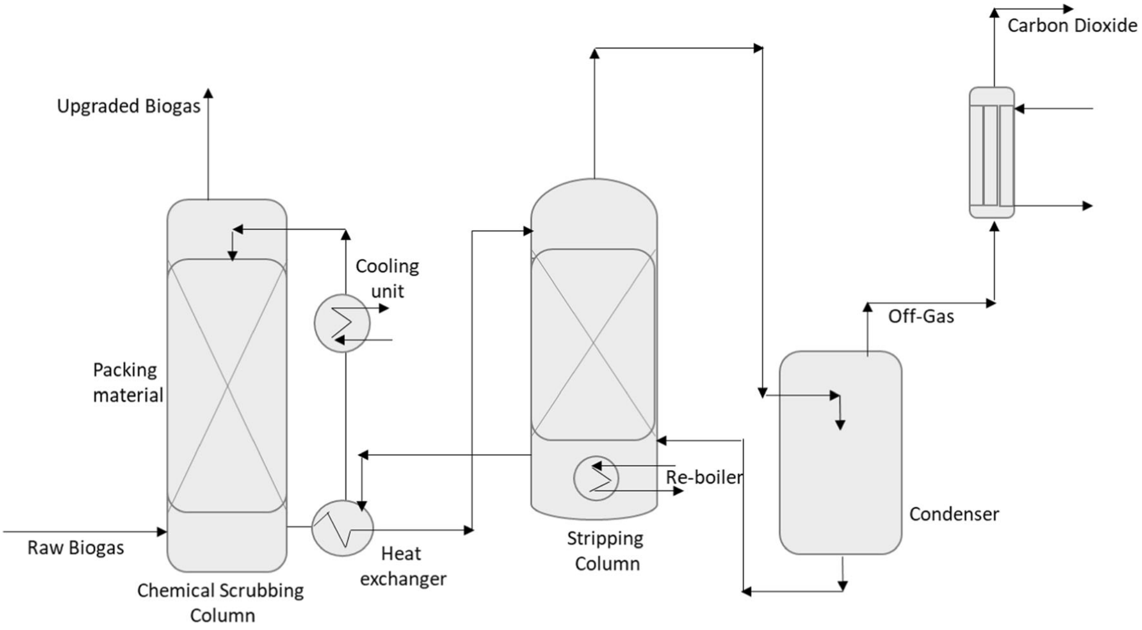


Fig. 7 Biogas upgrading by chemical absorption (amine scrubbing)

dissolution in alkanolamine (Sun et al. 2015, Awe et al. 2017, Huertas et al. 2011; Lasocki et al. 2015). One of the advantages of this technology is that up to 300 ppmv of H_2S present in biogas can be tolerated which can be completely absorbed in the amine scrubber (Muñoz et al. 2015). However, removal of high concentrations of H_2S is highly recommended before the scrubbing process to prevent solvent poisoning.

The investment cost of chemical scrubbing decrease as the treatment capacities increase. For treatment capacity of 600 Nm^3/h, the investment costs are 3200 €/Nm^3/h, which decreases to 1500 € per Nm^3/h for upgrading plants having capacity of 1800 Nm^3/h (Bauer et al. 2013; Cucchiella and D'Adamo 2016). Although, the costs associated with the expenses of chemicals, antifoaming agents and chemical make-up are marginal, the electricity requirements for gas compression and liquid pumping are reasonable in the range of 0.12–0.15 kWh/Nm^3; the costs for energy required for amine regeneration (0.55 kWh/Nm^3) are the major contributors to the operating costs (Bauer et al. 2013; Muñoz et al. 2015; Cucchiella and D'Adamo 2016).

PSA

Adsorption and types of adsorbents

Pressure swing adsorption (PSA) technology was originally developed in the 1960s primarily for the separation of industrial gases like nitrogen. It is an established and mature technology for biogas upgradation as well with a market share of 21% (Persson 2003; UNIDO 2017). This method is second most popular after water scrubbing. PSA process is a mass-transfer process based on the mechanism of selective adsorption of at least one selective gaseous component (adsorbate) to the surface of the adsorbent according to molecular size due to physical or van der Waals forces or electrostatic forces while excluding other gaseous components under elevated pressure (Grande 2012; Galante et al. 2012). The efficiency of this process depends on several factors, like, pore size of adsorbent material, partial pressure of adsorbate, system temperature and interaction forces between adsorbate and adsorbent material. Moreover, the regeneration capacity of the adsorbent material under specific conditions also influences efficiency of the process. Different types of adsorbing materials are available for the separation of CO_2 from CH_4 present in biogas. Adsorbent property is the most critical factor determining the performance of PSA based biogas upgrading. The separation mechanism is based on the molecular size exclusion and adsorption affinity of the adsorbent. The physico-chemical properties of gases are reported in Table 6.

Table 6 Physico-chemical properties of gaseous components present in biogas (Perry 1984; Rufford et al. 2012)

Gaseous component	σ (Å)	α ($Å^3$)	μ (D)	Θ (D-Å)	Tc (K)
CH_4	3.80	2.448	0.000	0.02	190
CO_2	3.40	2.507	0.000	4.30	304
H_2S	3.60	3.630	0.970	3.74	373
H_2O	2.65	1.501	1.850	2.30	647
N_2	3.64	1.710	0.000	1.54	126

σ kinetic diameter (Å: Angstrom), *α* polarizability ($Å^3$: Angstrom^3), *μ* dipole moment (D: coulomb-metre), *Θ* quadrupole moment, *Tc* critical temperature

The adsorption mechanism is based on one or combination of the following selectivity: (1) *Equilibrium selectivity or thermodynamic selectivity*: differences between the intensity of microporous solid surface interactions of the adsorbate and/or loading interactions of the adsorbate when the process attains equilibrium. The strongly adsorbed constituents are retained from the gas mixture in the column, while the effluent gas stream contains gaseous species with less interactive and loading intensity with the adsorbent. Materials like activated carbon, zeolite 13X, silica gel and metal–organic frameworks are termed as equilibrium-based adsorbents, present stronger surface interactions and higher selectivity with CO_2 and can adsorb larger loadings of CO_2 as compared to CH_4 because these material surface groups create stronger bonds with CO_2 than CH_4. (2) *Kinetic selectivity* is principally time dependent selectivity (Tagliabue et al. 2009). It is based on the differences between the diffusional rates of constituent molecules through the adsorbent pores. The components with comparatively fast diffusional rates are retained in the microporous adsorbent and the effluent gas has the slower diffusing constituents. For biogas application, adsorbent can be selected which have pores big enough to allow CO_2 (kinetic diameter 3.4 Å) to simply enter into their structure while bigger CH_4 molecules (kinetic diameter 3.8 Å) have size limitations to diffuse through them (Perry 1984; Tagliabue et al. 2009). Materials like carbon molecular sieves, clinoptilolites, titanosilicates, DDR zeolites and SAPO-30 have similar separation characteristics for CO_2 and CH_4. In these adsorbents, kinetic separation takes place by controlling the diffusional rates of the constituents by constricting the size of the micropores, thereby allowing more CO_2 to retain per unit time (Ruthven 1994; Li et al. 2009).

The adsorbents commonly used for biogas upgradation process are zeolite and carbon-based adsorbents. Furthermore, innovative materials like magnesium-based metal organic framework (MOF), silicalite or silico-aluminophosphate sorbents (SAPOs) are also being considered for biogas upgrading due to their large pore size (Grande 2011). This results in large volume, high specific surface area and consequently high gas adsorption capacity (Tagliabue et al. 2009). MOFs' have significantly higher CO_2 and CH_4 adsorption capacities than zeolite 13X under similar conditions (Chaemchuen et al. 2013). Zeolite-based adsorbents have stronger surface interactions with CO_2 than

CH_4 and are generally known as equilibrium-based adsorbents. These are based on the differences in the adsorbate–microporous solid surface interactions and/or adsorbate packing interactions when the system reaches equilibrium. Zeolites can be classified into different categories according to pore size, for example, zeolite 13X, zeolite 5A and zeolite 4A (Sarker et al. 2017). Other adsorbents are termed as kinetic-based adsorbents, i.e. carbon molecular sieve 3 K. These are based on different gas diffusion rates, for example, CO_2 diffuses at a faster rate in the micropores of the adsorbent materials than CH_4, leading to a kinetic separation. Adsorbents with molecular sieve having average pore size of 3.7 Å are used to retain CO_2 (3.4 Å) inside the pores, while eliminating CH_4 (3.8 Å). CH_4 flows unretained through the interstitial spaces of the adsorbent, resulting in a CH_4 rich stream. Low polarity and heat of adsorption are the characteristics of carbon-based adsorbents. Both equilibrium and kinetic adsorbents are well developed and commercially available for biogas upgrading applications. The equilibrium and kinetic selectivity of some adsorbents is presented in Table 7. Due to strong nonlinearity of the isotherms, kinetic-based adsorbents exhibit better upgrading performance as compared to equilibrium-based (Grande and Rodrigues 2007). Grande and Rodrigues (2007) studied a five-step PSA cycle for biogas upgrading using two different adsorbents, carbon molecular sieve 3 K (CMS-3K) and zeolite 13X. They reported that both adsorbents were capable enough to attain CH_4 purity of 98%, but CMS-3K presented 33% higher CH_4 recovery ratio and 50% less energy consumption as compared to zeolite 13X (Grande and Rodrigues 2007). Apart from high selectivity, adsorbents must be non-toxic, mechanically and thermally stable over long lifetimes, commercially available and exhibit a linear adsorption isotherm (Cavenati et al. 2004; Canevesi et al. 2018).

Basis of operation

PSA is a dynamic process operated in a cyclical mode. Interconnected vertical columns packed with adsorbents are operated in sequence under pressure with raw biogas or upgraded biogas. The columns are operating in parallel with either of the stage, i.e. adsorption, pressure equalization(s), blow down and purge pressurization, feed, blow down and purge. PSA columns are often operated at 4–10 bar to selectively retain CO_2, N_2, O_2, etc. inside the pores of the adsorbent (Bauer et al. 2013). CH_4 flows through the column unretained and can be collected from the top by decreasing the pressure. The sequence of the aforesaid steps is repeated in a cyclic manner. Commercial upgrading plants operate four, six or nine adsorber columns in parallel within this sequence. The regeneration of adsorbent heavily loaded with CO_2 gas is a stepwise process (Grande 2011). This cyclic sequence of adsorption and regeneration is known as Skarstrom cycle and usually lasts for 2–10 min (Grande 2011). As this cycle consists of four phases as described below, a common design for PSA units includes four columns. One of the columns is always engaged in adsorption while the other three are in different phases of regeneration. To reduce the loss of methane from the process the columns are interconnected so that the exiting desorbed gas flowing from one column during blowdown is used to pressurize another column in a pressure equalization phase, which also reduces the energy consumption of the process. Typical adsorption pressures and temperatures are in the range of 3–8 bar and 50–60 °C, and regeneration pressure is around 100–200 mbar (Grande and Rodrigues 2007). The four phases of the PSA cycle (Bauer et al. 2013) are discussed below:

1. *Adsorption*: During the adsorption phase, biogas is fed from the bottom at a pressure of 6–8 bar into one of the adsorbers after removal of hydrogen sulphide and water vapour. When passing through the vessel, CO_2 and/or O_2 and/or N_2 are adsorbed selectively by the media and the gas exits as methane. Before the adsorbent material is completely saturated biogas goes to another ready vessel that has already been regenerated to achieve continuous operation.
2. *Depressurization*: In this step, a stepwise depressurization of the adsorber vessel to atmospheric pressure and finally to near vacuum conditions is performed. Initially the

Table 7 Equilibrium and kinetic selectivity of adsorbents for CO_2 and CH_4 at 100 kPa

Adsorbent	Absorbent name	Type	CO_2/CH_4 equilibrium selectivity	CO_2/CH_4 kinetic selectivity	Reference
Activated carbon (AC)	PCB, Calgon Corp.	Equilibrium	3.29	–	Ritter and Yang (1987)
Zeolite 5A	5A (Sinopec)	Equilibrium	5.19	3.6	Saha et al. (2010)
Zeolite 13X	13X (Sinopec)	Equilibrium	8.92	4.5	Bao et al. (2011b)
Metal-organic frameworks (MOF)	Mg-MOF-74	Equilibrium	8.5	3.8	Bao et al. (2011b)
Activated carbon/carbon molecular sieves (AC/CMS)	CORK-DC-0	Kinetic	4.76	8.9	Cansado et al. (2010)
Metal-organic frameworks (MOF)	Cu-MOF	Kinetic	1.86	9.7	Bao et al. (2011a)

pressure of 6–8 bar is first released to approx. 3–4 bar by pressure communication with column 4, which was previously degassed by a slight vacuum and then finally the pressure is then reduced to atmospheric pressure.

3. *Regeneration/purge*: In this step, the column is evacuated to almost atmospheric pressure (0.1 bar) or by putting it under vacuum (VSA). The desorbed gas consists predominantly of not only CO_2 but also some CH_4. In order to reduce the amount of CO_2 in the desorbed gas, a purge step is performed in which some of the purified CH_4 is recycled to displace CO_2 from the CH_4 product end. During regeneration, the off gas composition changes with depressurization. Concentration of released CH_4 in off gas is high at high pressures and at low pressures, the bulk of CO_2 is specially desorbed. Therefore, off gas of the initial phase of decompression with high concentration of CH_4 is piped back to the raw biogas inlet in order to reduce the CH_4 loss. Off gas obtained from the later steps of regeneration is rich in CO_2 which could be directed to the next stage of adsorption to the off gas treatment unit or could be vented to the atmosphere (if CH_4 loss is low). The exiting gas from the CO_2 saturated column is led to the adjacent previously regenerated adsorption column. This is the pressurization step of this column while the previous saturated column is stepwise depressurized to almost atmospheric pressures. Off gas, a mixture of CO_2/CH_4 with high CH_4 content is released and recycled back to the inlet of PSA system in order to reduce energy consumption. The saturated column is finally washed with upgraded biogas to complete the regeneration of the adsorbent material
4. *Pressure Buildup:* Since the purge is also performed at low pressure, in order to restart a new cycle, the pressure should be increased. Before the adsorption phase starts again, the adsorber vessel is re-pressurized stepwise to the final adsorption pressure. After a pressure balance with an adsorber that has been in adsorption mode before, the final pressure build-up is achieved with feed gas.

The prerequisite of this process is to remove H_2S, moisture and siloxanes contents of biogas before the process which adds to the capital costs, because these components irreversibly harm the adsorbent material. Since PSA is a dry technology, it does not involve additional costs of water or solvent make-up or heat for regeneration of adsorbent as required in water scrubbing and chemical scrubbing respectively. Although PSA is a complex task, it has the advantage of equipment compactness; therefore, small, compact and modular units can be easily fabricated for small-scale applications. The schematic diagram of pressure swing absorption is shown in Fig. 8.

CH_4 loss, energy requirements and cost economics

Capital costs in PSA decrease from 2700 € per Nm^3/h for plants having treatment capacities of 600 Nm^3/h to 1500 € per Nm^3/h for plants of 2000 Nm^3/h capacity (Bauer et al. 2013; Cucchiella and D'Adamo 2016). Electricity requirements for compression of biogas and biogas dehydration are in the range of 0.24–0.6 kWh/Nm^3 (Pertl et al. 2010). However, a recent survey estimates electricity requirement of 0.25–0.3 kWh/Nm^3 which includes off gas treatments using catalytic oxidizers. PSA is a complex process, since process control, yield and purity of the product are difficult to maintain as compared to other upgrading technologies. Moreover, selection of optimal design and operating parameters is a difficult task due to highly complex and tough design procedure of transport phenomena of adsorbate in adsorption column and extreme computational requirements to reach the steady cyclic state between the sequences. Additionally, the number and arrangement of adsorption columns and cycle sequences can also affect the performance of PSA. Unfortunately, a major drawback of PSA is low CH_4 recovery especially in comparison to other biogas upgrading technologies like amine scrubbing, since a substantial amount of CH_4 is lost with the off gas (Khan et al. 2017). CH_4 recovery of 85–90% is usually obtained and an off gas with a CH_4 content of about 15–20% is often produced (Patterson et al. 2011). Because of this high CH_4 content in the off gas, it cannot be vent into the atmosphere, but requires further treatment (Augelletti et al. 2017).

Cryogenic separation of CO_2

Basis of operation

Cryogenic technology is popular for treating landfill gas, particularly for the removal of contaminants such as CO_2 and N_2. The process is based on the difference in condensation and distillation properties of CH_4, CO_2 and other impurities for selective separation (Goffeng 2013). At 1 atm, the boiling point of CH_4 is − 161.5 °C which is quite low in comparison to the boiling point of CO_2 which is − 78.2 °C. This facilitates separation of CO_2 from CH_4 by liquefaction bars (Jonsson and Westman 2011). The essential pre-requirement of the process is cleaning of raw biogas, i.e. removal of hydrogen sulphide, moisture and siloxanes from biogas in order to avoid freezing and clogging of pipes. The cryogenic process is performed through a series of successive reduction in temperature separating liquefied CH_4 from CO_2 and other components of biogas in order to obtain liquefied biomethane similar to liquefied natural gas (LNG). The process operates at a very low temperature of − 170 °C and high pressures of 80 bar (Jonsson and Westman 2011).

The initial step is drying of biogas followed by compression to 80 bar and stepwise reduction in temperature to −

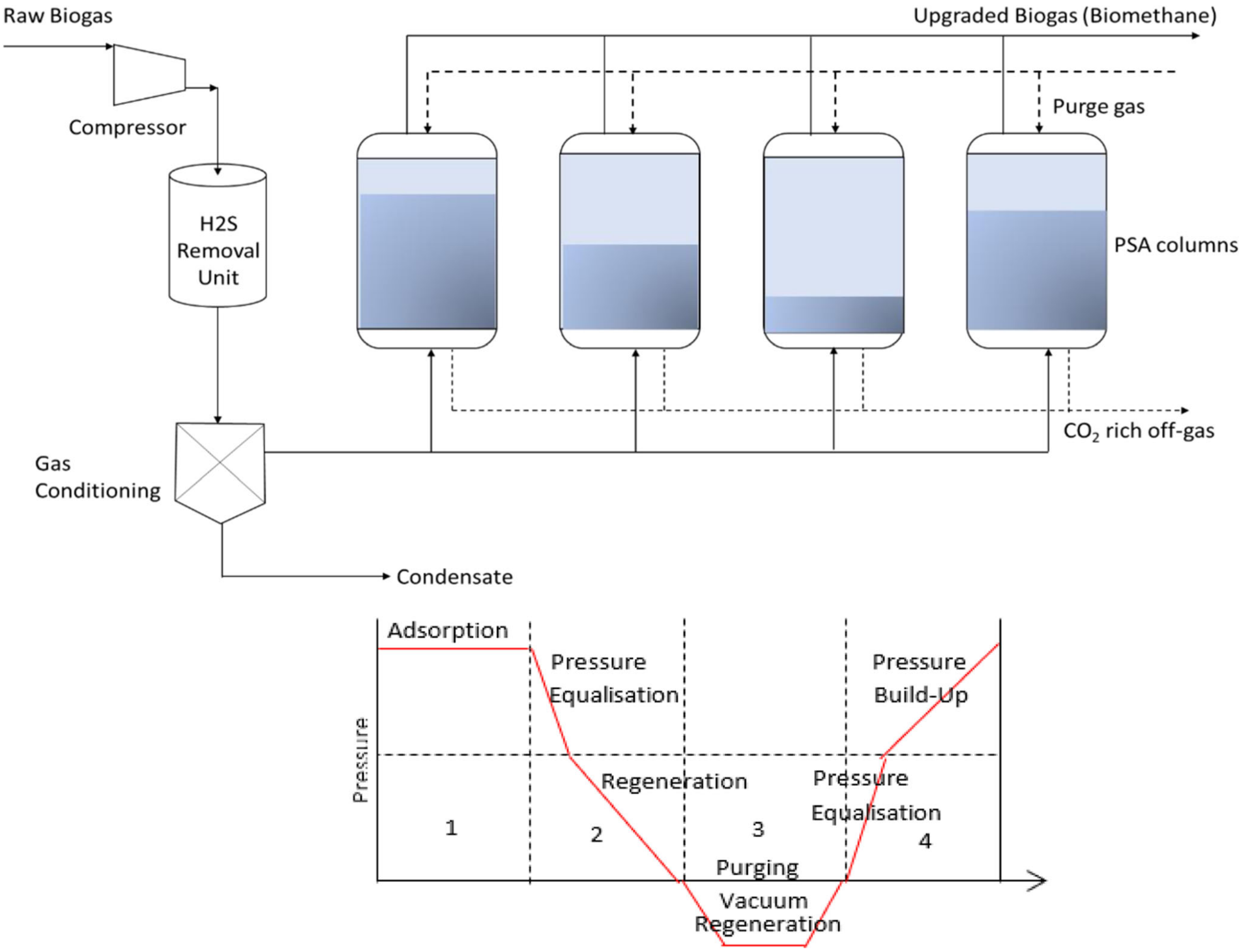


Fig. 8 Process flow diagram of biogas upgrading by pressure swing adsorption process

110 °C (Yousef et al. 2016). Accordingly, CO_2 and other impurities are steadily removed from biogas as per their condensation points in order to recover almost pure biomethane (> 97%) (Persson 2003; de Hullu et al. 2008; Bauer et al. 2013). Water, H_2S, siloxanes, halogens, etc. must be removed prior to the process in order to avoid operational problems like clogging of pipes or heat exchangers. These operating requirements of the process are maintained by using equipments in linearly connected compressors and heat exchangers (Yousef et al. 2016). The most significant part of cryogenic process is low temperature requirement. Lower temperatures result in high removal efficiency of CO_2 from biogas. Different purities can be achieved depending on the temperature of the process (Andriani et al. 2014; Khan et al. 2017). To achieve low temperatures, two cooling options are available; direct and indirect cooling. In indirect cooling, liquid nitrogen is used as cooling agent. This type of method is not advisable for large scales because running cost would be very high. Direct cooling accommodates combination of compressor, heat exchanger and expansion devises as used in refrigeration systems. So for better operational conditions, combination of direct and indirect cooling is used in biogas upgrading process.

Initially, raw biogas is compressed to 17–26 bar and cooled to − 26 °C using the first heat exchanger (Bauer et al. 2013). This facilitates removal of hydrogen sulphide, sulphur dioxide, halogens and siloxanes. The first step of cooling is followed by a cascade of compressors and heat exchangers which further decreases its temperature to − 55 °C where maximum CO_2 is liquefied and finally to − 85 °C as refining step where the remaining CO_2 solidifies (de Hullu et al. 2008; Yousef et al. 2016). Finally, the distillation column separates CH_4 from CO_2. The main advantage of cryogenic separation is the recovery of highly pure biomethane with almost negligible CH_4 loss. This mode of upgrading can provide biomethane with above 97% purity and CH_4 loss lower than 2%. The process flow of cryogenic separation process is shown in Fig. 9.

Cryogenic method has various potential or expected benefits like no requirement of chemicals, production of pure CO_2

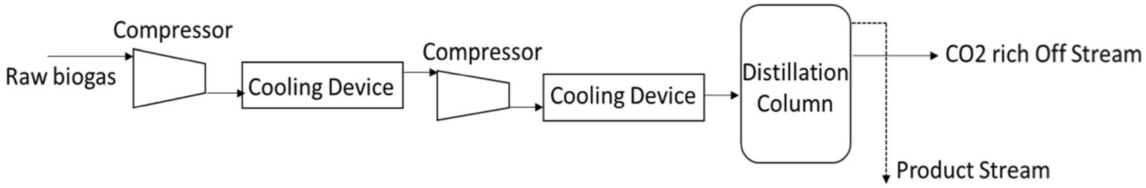


Fig. 9 Process flow diagram of cryogenic separation of biogas (removal of CO_2)

as secondary product and production of LBG. The main drawback of technology is its complexity due to the use of a number of equipments like compressors, turbines, heat exchangers and distillation column (Bauer et al. 2013). This increases the capital cost of the process which increases the final cost of biomethane production. The high energy requirements, investment and operational costs, practical problems of clogging and freezing due to high concentration of solid CO_2 or other impurities limit its extensive widespread implementation.

CH_4 loss, energy requirements and cost economics

Even with the promising results, this process is still under development with few plants operating in the United States, Sweden and the Netherlands. Still, this technology is emerging and has only 0.4% share in the biogas upgrading market (Persson 2003; UNIDO 2017). Due to limited information about these plants, reliable data for investment and operating costs is not available. Hence, an accurate determination of its technical parameters becomes difficult. Still, an estimation for investment and operating costs of cryogenic upgrading plants was done by de Hullu et al. (2008) and found to be 0.4 € Nm^3. There is also a huge ambiguity on energy assessments for this process, with values ranging from 0.42 to 1 kWh/Nm^3 (Muñoz et al. 2015).

Membrane separation

Types of membranes

The membrane-based gas separation has become a significant method in gas purification market since last 40 years (Basu et al. 2010). Recently, this technology has emerged as an attractive process for biogas upgradation. It is based on the fundamental rule of selective permeation of gas components through a semi-permeable membrane. Membrane acts as a permeable barrier that allows specific gaseous constituents to permeate according to the size of different gas molecules with different permeabilities through the membrane. It is also driven by driving forces such as the differences in concentration, pressure, temperature and electric charges of different gases. Membranes employed for biogas upgrading enable preferential permeation of CO_2, H_2O, O_2 and H_2S while retaining CH_4 and N_2, with CO_2/CH_4 selectivity factors of up to 1000/1 (Scholz et al. 2013a).

There are basically three types of membranes used for gas separation, polymeric, inorganic and mixed matrix membranes (MMMs). Polymeric membranes are the most commonly used membranes commercially. These are made from organic materials such as polysulphone (PSf), polyimide (PI), polycarbonate (PC), polydimethylsiloxane (PDMS) and cellulose acetate (CA) (Basu et al. 2010; Chen et al. 2015). These membranes exhibit high selective permeability, exceptional mechanical and thermal strength; have simple and cheap fabrication procedure; and are easily scalable. Among the various polymeric membranes, CA and PI are preferred for biogas upgradation. CA membrane is the first polymeric membrane commercialized for biogas purification. It is comparatively cheap owing to the availability of cellulose in abundance. However, it also possesses quite a few limitations like susceptibility to plasticization ($P_{plasticization} = 8$ bar) because of the presence of its –OH rich functional group which easily dissolves CO_2 within the membrane (Scholz et al. 2013a; Zhang et al. 2013). PI is a crystal-like material with high permeability and selectivity as well as high mechanical/thermal stability. Matrimid® is a commercially available PI with a strong polymer backbone. This property makes it a rigid and mechanically and thermally stable to withstand harsh working environment. In spite of its availability in abundance, it is not cheap and also vulnerable to plasticization ($P_{plasticization} = 17$ bar) (Basu et al. 2010). As compared to the conventional polymeric membranes, inorganic membranes offer more benefits in terms of high mechanical strength, thermal and chemical stability. Inorganic membranes provide permeability and selectivity, beyond the Robeson upper bound. Inorganic membranes are classified as zeolites, activated carbon, silica, carbon nanotubes (CNT), and metal-organic framework (MOF). However, the most critical factor in the stringent fabrication process of inorganic membranes is the development of defect-free inorganic membranes due to their brittle structure. In spite of superior gas separation property, carbon molecular sieves and zeolites are difficult to form continuous and defect free membranes because of their rigid porous structure. The limitations of polymeric and inorganic membranes led to the development of MMMs (Basu et al. 2010; Chen et al. 2015). These are amalgamated membranes comprising of polymeric materials in the form of a continuous phase with inorganic particles as a dispersed phase. The discrete spread of inorganic filler into polymer base not only results in better performance of membranes but also increases its tensile strength and thermal stability. For example, zeolite acts as a filler membrane which further discriminates CH_4 from CO_2. MMMs are expected to perform better as compared to individual membranes because these are fused membranes with combined benefits of both polymeric and inorganic materials. High process ability and reasonable processing cost of base polymeric membranes along with better separation performance of inorganic particles are merged properties in MMMs'. Table 8 summarizes the CO_2/CH_4 separation performance some membranes in terms of ideal separation factor '$\alpha = (P_{CO2}/P_{CH4})$'.

The membranes to be employed for the biogas upgradation process should be strong enough to resist harsh process conditions such as high pressure and temperature and should be chemically resistant to the significant amounts of H_2S and H_2O present in the biogas. All the membranes discussed above possess their own specific features and advantages. However, each membrane has limitations. A comparative summary between different types of membranes for CO_2 and CH_4 separation from gas mixtures is presented in Table 9 below.

Basis of operation

Usually, two models are used in membrane separation process; solution–diffusion and pore-flow model (Scholz et al. 2013a). In solution–diffusion model, firstly, the permeate dissolves and then it diffuses through the membrane due to concentration difference and pressure driven convective flow. Solution–diffusion model is normally used for gas separation in polymeric membranes. During this process, CH_4 retains on the inlet side while CO_2, H_2S, H_2O and O_2 pass through the pores of the membrane to the permeate side as shown in Fig. 10. Pressurized biogas at 20–40 bar in gas–gas systems (although some commercial units also operate in the 6–20 bar range) result in CH4 rich retentate and a CO_2 rich permeate with traces of CH_4 and H_2S. A major disadvantage of this technique is the low CH_4 recovery because CH_4 also passes through the pores under pressure. Due to low CH_4 recovery, biogas is upgraded to maximum 92% CH_4 in single stage systems (Zhang et al. 2013; Chen et al. 2015). In order to achieve high purity biomethane (above 95% CH_4), larger size or multi (two or three) stages of membranes are employed for upgradation. Therefore, a trade-off is required between high purity biomethane and low CH_4 loss. Gas–gas units are manufactured under different configurations: single membrane module or multiple membrane modules with internal recirculation of permeates for CH_4 recovery. In case of multiple modules connected in series, recirculation of only the permeated gas from the last module is done. Chen et al. (2015) reported that multi stage modules improve CH_4 recovery from 80 to 99.5%. Furthermore, lower investment and operating costs with high CH_4 purity and recovery of biomethane in comparison to single membrane are the advantages of multi stage membrane process (Chmielewski et al. 2013).

Table 8 Permeability and selectivity of polymer membranes for gas separation

Classification	Type	CO_2/CH_4 selectivity (α)	Reference
Polymeric	Cellulose acetate (CA) Ethyl cellulose (EC)	30.0 1.39	Basu et al. 2010
	Polycarbonate (PC)	32.5	
	Polydimethylsiloxane (PDMS)	3.38	
	Polyimide (PI)	42.8	
	Polymethylpentene (PMP)	5.75	
	Poly(*p*-phenylene oxide) (PPO)	6.89	
	Polysulphones (PSF)	22.4	
MMM	SWNT-PSf (10% SWNT)	18.4	
	Silica nanotubes- Psf (10% np)	24.5	
	Cu-BPY-HFS-PI (30 wt)	27.5	
Carrier facilitated transport membranes	PVAm on PSf support	700–1100	Kim et al. 2004
	VSA-SA on PSf support	46.8	Wang et al. 2006
	DMAEMA-AA on PSf support	255	Shen et al. 2006
	PVAm/PEG blend	63	Yi et al. 2006
Inorganic	SAPO-34 zeolite (on porous stainless steel tube)	120	Li et al. 2006
	Silicalite-1 (on porous alumina disk) B-ZSM-5	2.25 8.19	Othman et al. 2009
	Na-ZSM-5	6.29	

Table 9 Comparative summary between different types of membranes (Basu et al. 2010; Zhang et al. 2013; Chen et al. 2015)

Membrane classification	Membrane type	Energy requirement	Permeability–selectivity	Chemical requirement	Cost
Polymer	Gas permeation	oooo	oooo	N	oooo
	Carrier	oo	ooo	N	oo
	Hollow fibre membrane contactor	o	ooooo	Y	o
Inorganic	Inorganic	ooooo	ooooo	N	ooooo
Mixed (hybrid)	Mixed matrix membrane	ooo	ooo	N	ooo

From ‘o’ to ‘ooooo’—parameter value from low to very high, N—not required, Y—required

Recently, gas–liquid absorption membrane process for biogas upgradation is also being developed. A microporous hydrophobic membrane provides a partition between gases flowing in one direction and liquid flowing counter currently from the other side while gases diffuse through the membrane (Dindore et al. 2004). In this method, CO_2 and H_2S gas molecules diffuse through the membrane and get absorbed into the liquid on the other side. Gas is slightly pressurized to near atmospheric pressure to prevent the liquid to flow towards the gas side. The major advantage of this process is low construction cost due to process operation at low pressures and high selectivity. Alkanolamines or alkali aqueous solutions are used as CO_2 liquid absorbents (Dindore et al. 2004). Gas liquid membrane systems employing amine solution, is very

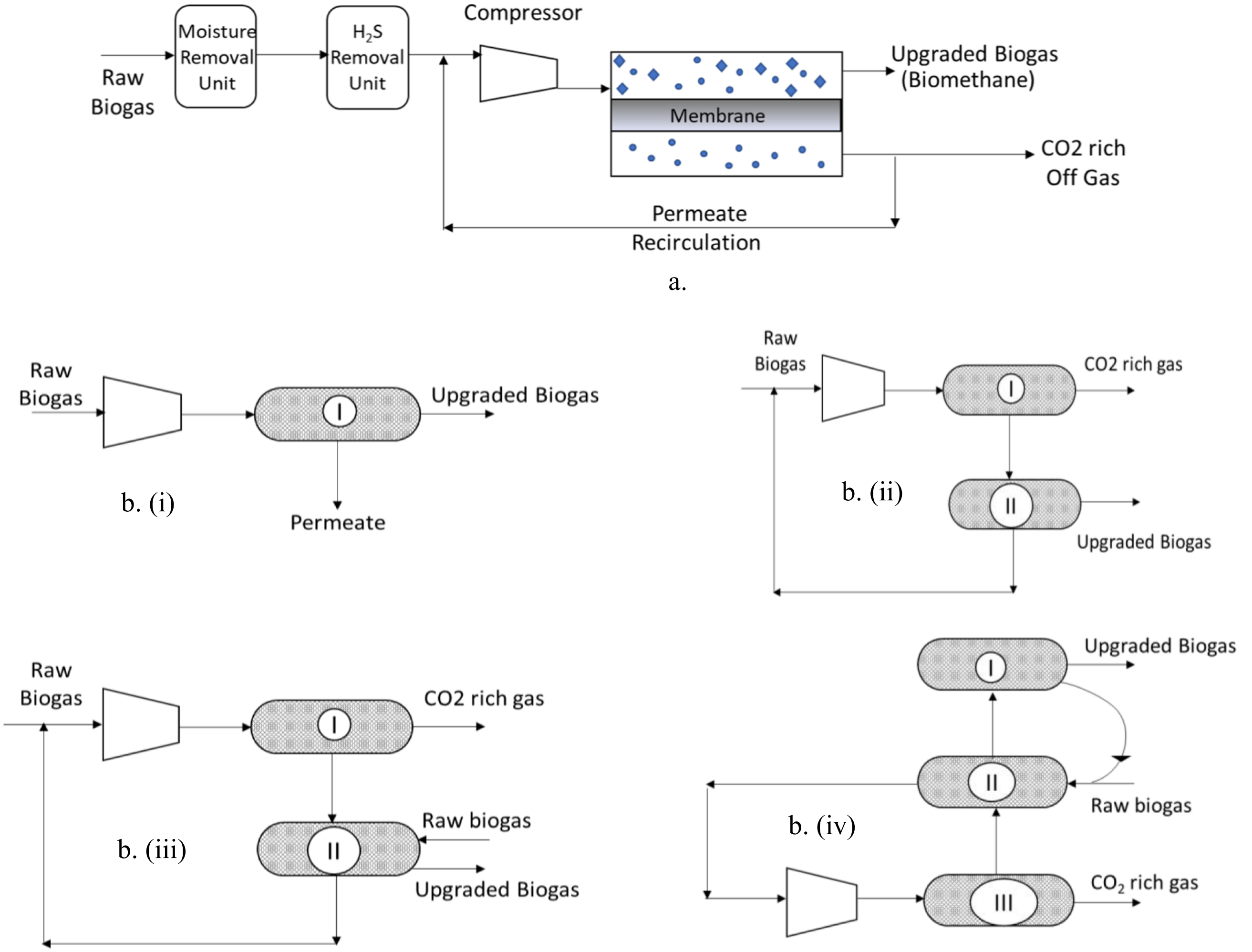


Fig. 10 (a) Process flow diagram of membrane separation process, (b) (i) single stage configuration, (ii) two-stage configuration with a recirculation loop, (iii) two-stage configuration with sweep and (v) three-stage configuration with sweep

efficient for upgrading biogas to biomethane (96% CH_4) in a single step. The regeneration of amine is done by heating, thereby releasing pure CO_2 as off gas which can be sold for industrial applications. Another major advantage of membrane technology is that by applying sufficient driving force for permeation, H_2S, H_2O, and siloxanes permeate faster than CO_2 through the membrane, facilitating removal of these components present in biogas simultaneously (Adewole et al. 2013). However, biogas pre-treatment is highly recommended prior to membrane separation to avoid deterioration, clogging of the membrane and to prolong the membrane life.

CH_4 loss, energy requirements and cost economics

Membrane separation is a developed and commercially available technology, either in high-pressure gas–gas modules or in low-pressure gas–liquid modules but with only 10% market share in biogas upgrading market (Thrän et al. 2014). Membrane manufacturers and process developers guarantee biomethane with 96–98% CH_4 purity in gas–liquid or multiple-stage gas–gas units. With single-pass gas–gas modules, only 92–94% CH_4 purity of biomethane is achievable with off gas permeates having 10–25% of CH_4 concentration (Patterson et al. 2011; Chen et al. 2015). The investment costs of membrane modules from 2500 to 6000 € per Nm^3/h for capacities 100 to 400 Nm^3/h respectively. For plants above 1000 Nm^3/h capacity investment cost remains constant at 2000 € per Nm^3/h (Chen et al. 2015). The operating costs mainly involve mainly involve expenses due to membrane replacement which usually have a lifetime of 5–10 years, pressurization cost of biogas which consumes energy in the range of 0.2–0.38 kWh/Nm^3 and cost for pre-treatment of biogas. Maintenance costs of membrane-based upgrading units incur slightly higher maintenance cost in the range of 3–4% of the initial investment costs (Muñoz et al. 2015). Membrane separation technology has attracted great attention due to its energy efficiency, simple process design, ease of scale-up and module construction, as well as safety of operation, without use of hazardous chemicals. It is comparatively a cheap process with low operating and capital costs. The demand for energy is less due to simple and compact membrane modules.

Emerging technologies for biogas upgradation

Recent developments in biogas upgrading technology include biological and hybrid technologies. These methods, although promising and present better performance, are still under development. Both traditional and emerging biogas upgrading technologies are continuously being improved for better performance, enhanced upgrading efficiency and low cost so that the technology gets a wider implementation worldwide.

Biological biogas upgrading technologies

Compared to the biogas upgrading technologies such as water scrubbing, PSA and membrane separation which are highly energy intensive, biological biogas upgradation involves the application of microbes for conversion of CO_2 and H_2 into methane (Rachbauer et al. 2016). There are two metabolic pathways involved in biological biogas upgrading (Fig. 9). One involves the role of hydrogenotrophic methanogens involved in direct conversion of CO_2 to CH_4. The same conversion can be carried out by a catalytic chemical reaction called the Sabatier process. However, biological methanation has numerous advantages over chemical processes such as requirement of moderate temperatures compared to chemical process along with a higher resistance to gas contaminations, like H_2S, organic acids and NH_4 (Götz et al. 2016). The second metabolic pathway is an indirect biogas upgrading involving the homoacetogenic bacteria which first convert CO_2 to acetate through Wood–Ljungdahl pathway, which is then converted to methane by the acetoclastic methanogens (Angelidaki et al. 2018).

Efficient biogas upgradation depends on the hydrogenotrophic methanogen population and there are numerous strategies for increasing their abundance, such as bioaugmentation with pure microbial cultures or enrichment with hydrogenotrophic methanogens endogenously. Assessment of microbial community during biogas upgrading has revealed that the hydrogenotrophic methanogens belonging to genera *Methanobacterium*, *Methanoculleus*, *Methanomicrobium* and *Methanothermobacter* are more abundant compared to the acetoclastic methanogens such as *Methanosarcina* (Agneessens et al. 2017; Mulat et al. 2017).

Types of biological biogas upgrading technologies

The biological biogas upgrading process is of two types: (a) in situ biogas upgradation which involves the addition of H_2 inside the liquid phase of a biogas reactor and subsequently the production of CH_4 by the coupling of endogenous CO_2 with the supplied H_2 and (b) ex situ biogas upgradation which involves the addition of CO_2 (biogas, syngas, etc.) as well as H_2 from external sources into the liquid phase of a reactor having the hydrogenotrophic microbes, resulting in their conversion to CH_4. Table 3 summarizes recent research in the field of in situ and ex situ biological biogas upgradation technologies.

In situ biogas upgradation Though an advantage of in situ biogas upgrading is reduction in the cost due to the use of the existing digester, major technical challenges faced in case of in situ upgradation technology include (a) increased pH above 8.5 due to the removal of the key buffering agent, i.e. bicarbonate, thereby inhibiting the process of methanogenesis

(Fig. 11); (b) gas–liquid mass transfer of H_2; and (c) high H_2 injection in the reactor inhibits the anaerobic digestion and results in acidification due to accumulation of electron acceptors, i.e. volatile fatty acids (VFAs), ethanol (Liu and Whitman 2008; Luo et al. 2012; Tirunehe and Norddahl 2016). Also, process optimization becomes more complex as H_2 not only regulates methanogenesis but may possibly also influence upstream processes. Under normal conditions, oxidation of VFAs is endergonic in nature and is viable only if the partial pressure of H_2 is kept low by means of hydrogenotrophic methanogens (Dolfing et al. 2008; Schmidt and Ahring 1993). However, addition of H_2 increases the H_2 partial pressure rapidly leading to inhibition of VFA oxidation, which can lead to a complete process failure. Additionally, homoacetogens may be stimulated resulting in the production of acetate and in case its production and consumption rates are not balanced, then also, the process will be inhibited. Due to these reasons, in situ biogas upgrading is restricted to a few lab-scale studies only (Luo and Angelidaki 2013; Luo et al. 2012; Wang et al. 2013) and more R&D is needed to understand the effect of optimum and excess supply of H_2 on the complex bio-chemical processes of methanogenesis, homoacetogenesis and VFA oxidation for successful process optimization.

Ex situ biogas upgradation To overcome these challenges and to avoid the inhibition of core biogas production, the concept of ex situ process came into existence. In the ex situ method, CO_2 and H_2 are supplied externally in a separate reactor containing enriched mixed or pure hydrogenotrophic methanogenic archaea cultures that utilizes CO_2 as carbon source and H_2 as reducing agent for the production of CH_4 (Aryal et al. 2018). Here, the source of CO_2 can be biogas, syngas and flue gas and H_2 can be produced by hydrolysis of water using renewable electricity sources, i.e. wind mills and solar cells. The major benefits associated with the ex situ process are it can hold high volume of influent gas with reduced retention time, waste CO_2 from other sources such as flue gas and syngas can also be utilized, biomass independent and biochemically simpler process ensure the stability of existing biogas plant as the process occurs in separate reactor (Angelidaki et al. 2018). The major factors that govern the biological hydrogen methanation are partial pressure of H2, biomass growth, temperature of the bioreactor, reactor design and gas–liquid mass transfer rate (Lecker et al. 2017). Here the limitation of gas–liquid mass transfer of H_2 can be addressed by the use of different types of reactors such as continuous stirred tank reactor (CSTR), fixed-bed reactors, anaerobic trickle-bed reactors (ATBR), series upflow reactors in series and bubble column reactor (Kougias et al. 2017; Lecker et al. 2017). Kougias et al. (2017) studied the ex situ biogas upgrading using three different bioreactor configurations and obtained 98% enriched methane in bubble column and series upflow reactors due to enhanced gas recirculation. Furthermore, 16S rRNA–based microbial community analysis of the anaerobic digestion process identified the presence of novel uncultured phylotypes during H_2-aided methanogenesis. Methanothermobacter thermautotrophicus was found to be the dominant archaeal community on the surface of bubble column reactor. In ex situ biological hydrogen methanation the methane evolution rate (MER) is higher, i.e. 0.37 and 688.6 L/Lreac/day than in situ, i.e. 0.08 to 0.39 L/Lreac/day (Wang et al. 2013; Luo and Angelidaki 2013; Nishimura et al. 1992; Luo et al. 2012). A methane enrichment of 95.4% was achieved in CSTR operated in thermophilic condition using methanogenic mixed culture at 800 rpm (Luo and Angelidaki 2013). ATBR operated with bound methanogenic microbes in continuous process showed 98% CH_4 enrichment by liquid recirculation under mesophilic condition (Burkhardt et al. 2015). ATBR operated under thermophilic condition reported 98% of CH_4 concentration operated under thermophilic condition (Strübing et al. 2017). In another study, 96% CH_4 production was achieved when biogas (from pilot-scale biogas plant) and H_2 (from electrolysis) was injected directly into the ATBR with immobilized hydrogenotrophic culture (Rachbauer et al. 2016). Electrochaea, an ex situ biological CH_4 upgrading commercial plant, was established in Avedøre, Denmark (Bailera et al. 2017). The energy for electrolysis of water was provided by excess wind power. The plant produces 90–95% CH_4 concentration which was further upgraded via membrane cleaning unit (Aryal et al. 2018).

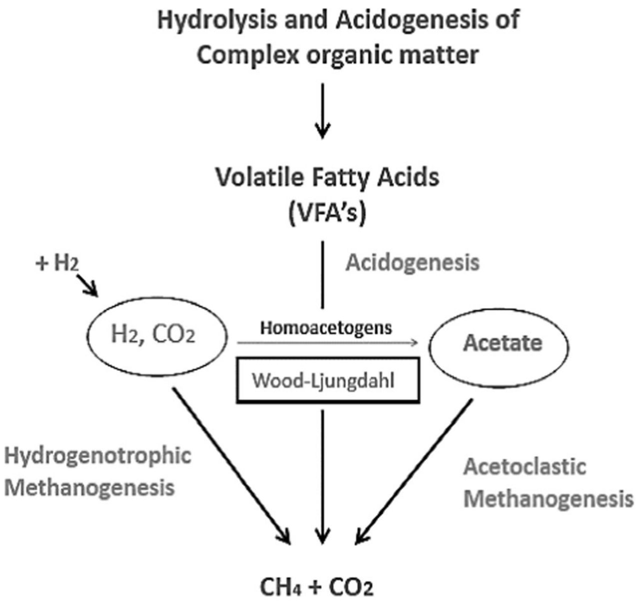


Fig. 11 Bacteria mediated metabolic pathways for hydrogen assisted methanogenesis

Hybrid technologies

Each biogas upgrading technology has its own strengths and weaknesses. The limitations can be overcome by integrating different technologies to form a hybrid method (Sahota et al.

2018). For example, integrating membrane gas permeation with water scrubbing, amine absorption or cryogenic separation to develop hybrid process not only merges the advantages of both but also improves the performance and efficiency of biogas upgradation. Scholz et al. (2013b) studied seven different configurations of hybrid membrane processes for biogas upgradation. It was reported that membranes combined with water scrubbing and cryogenic method reduce the upgrading costs and energy intensiveness of conventional individual technologies. Recently, Pentair commercialized hybrid technology with combined membrane and cryogenic technology. Song et al. (2017) similarly reported that temperature–membrane–cryogenic process consumed less energy than individual technologies. Pinghai et al. (2012) merged temperature swing adsorption with membrane process for processing biogas from wastewater treatment plant. It gave a yield of 97% CH_4 purity biomethane and also reduced CH_4 loss by recycling the off gas into the membrane process. Recently, Corbellini et al. (2018) studied hybrid biological upgrading which integrates in situ and ex situ biogas upgrading technologies, in which the initial phase involves in situ process capturing a part of the CO_2 and upgrading the biogas to 80–90% CH_4, which is then followed by ex situ process, where the enriched biogas is further upgraded to a CH_4 content greater than 95%. Improving the overall stability of the system was found to be the major challenge associated with scaling up of the hybrid upgrade system. In particular, monitoring and controlling the concentration of VFAs is the most important as its accumulation negatively influences the CH_4 production rate. Thus, more hybrid technologies need to be developed for improving the techno-economics of biogas upgradation (Table 10.

Perspectives for future direction

Process optimization for efficient biogas upgradation

Optimization of process and design parameters of water scrubbing columns for high CH_4 recovery, reduction in capital and operating costs and energy consumption of biogas upgrading plant is an active area of research (Budzianowski et al. 2017; Rotunno et al. 2017). Additionally, research on the development of novel packing materials which can enhance mass transfer between gas and liquid and relatively low-pressure drop is being focussed. Operational process parameters like pressure, flow rate and temperature of the gas should be optimized in order to reduce the large quantities of water required, cost for biogas compression and water pumping (Rasi et al. 2008; Chandra et al. 2012). Efficient methods of water regeneration and recycling are also an area worth exploring.

Chemical absorption techniques need to be optimized for efficient implementation for biogas upgrading. Efforts should be focused on the energy consumption for regeneration, solvent degradation and environmental impact of chemical scrubbing. The feasibility of using blends of amines (primary secondary, tertiary and sterically hindered) for biogas upgrading should be further explored. Caustic solvents provide high CO_2 loading capacity than amines but major improvements are required to lower the energy consumption during the regeneration. The research should also be focussed on converting spent caustic solutions into value added products rather than regenerating.

Research and development in PSA is mainly focused on improving the technology with low-energy use, increasing adsorbent efficiency and minimizing CH_4 losses (Augelletti et al. 2017). Development of advanced and efficient adsorbent materials is one of the most significant area of study for refining PSA technology; thus, extensive research on the development of novel adsorbents like carbonaceous adsorbents, zeolites, graphene and carbon nanotubes, metal-organic framework (MOFs) and zeolitic imidazolate frameworks (ZIFs) is being carried out (Tagliabue et al. 2009; Zhou et al. 2017). Further, research should also be focussed upon making PSA process control simple and easy. Research should also be directed towards making PSA systems for making compact and modular units for small-scale applications.

Cryogenic upgrading is an upcoming biogas upgrading technology. Though it produces biomethane in liquid form, its implementation is not widespread due to complex operational process and high energy requirements (Yousef et al. 2016). More R&D is required for reducing the cost associated with indirect cooling in cryogenic separation. Research on development of energy efficient compressors, heat exchangers and expansion devices should be focussed for reduced operational cost. Also, effect of combining direct and indirect cooling methods for cryogenic separation should be explored further.

Membrane technology is being emerged as a significant technology with high market demand. Due to its economic and environmentally benign characteristics, it can replace conventional biogas upgrading processes in the future. However, research should be directed towards easy operation with low-energy requirements and high CH_4 recovery using multistage system for biogas upgrading (Vrbova and Ciahotný 2017). Intensive research is required to synthesize new membrane materials for better performance. However, future research developments should focus on the improved aptitude of membrane material with other biogas components than CO_2 apart from high selectivity and permeability. Moreover, use of membrane technology in biogas cleaning for H_2S and moisture removal should also be focussed upon.

Table 10 Comparison of different in situ and ex situ biogas upgrading technologies

Type	Reactor type	Feedstock	Temperature (°C)	Retention time	CH_4 (%)	Findings	Reference
In situ	Batch	Maize	52	–	89.4	The results showed that excess H_2 addition results in stimulating the homo-acetogens and inhibition of methanogenesis. Thus, it is important to regulate the H_2 addition rate and gas retention time to the CO_2 production rate, H_2-uptake rate and growth of hydrogenotrophic methanogens for obtaining higher CH_4 content without the build-up of acetate and other VFAs.	Mulat et al. (2017)
In situ	Batch	Sludge from wastewater treatment plant	35 and 55	15 days	96	Gas recycling at a rate of 100 L/L/day under thermophilic condition was found to be the best option for 96% H_2 conversion to CH_4 within 15 days.	Yun et al. (2017)
In situ	CSTR	Biogas sludge	38	20 days	100	Pulse H_2 injections were found to be effective in increasing H_2 uptake rate as well as specific hydrogenotrophic methanogens.	Agneessens et al. (2017)
In situ	Continuous	Chicken manure	–	10 days	60–70	Higher effluent recirculation rate (200%–400%) resulted in higher methane enrichment.	Boontawee and Koonaphapdee-lert (2016)
In situ	UASB	Potato starch wastewater	55	5–20 d	82	Use of porous inert devices, such as ceramic sponge was found to improve H_2 distribution. Also, gas recirculation and chamber configuration were reported to maximize CH_4 production from CO_2.	Bassani et al. (2016)
Ex situ	Membrane bioreactor	Anaerobic sludge	55 ± 1	–	–	Gas sparging through the ceramic MBR showed a high capacity of H_2mass transfer.	Alfaro et al. (2018)
Ex situ	CSTR, 2 upflow reactors, bubble column reactor (batch and continuous)	Digested slurry from biogas plant	52 ± 1	6–18 h	79–98	Different reactor configurations were tested for ex situ biogas upgrading and enhancement. Maximum (> 98%) methane content in the output gas of upflow reactors in series or bubble column reactors was observed. Also, it was reported that increasing gas recirculation rate improved the efficiency of biogas upgrading.	Kougias et al. (2017)
Ex situ	UASB continuous	Digested slurry from biogas plant	55 ± 1	4–15 h	89.5–96.3	Higher gas recirculation rate and pore size of the diffuser improved gas–liquid contact.	Bassani et al. (2017)
Ex situ	Trickle bed	Mixed anaerobic culture	37 ± 2	3.5 h	96	A mesophilic trickle-bed reactor with an immobilized hydrogenotrophic microbial culture resulted in > 96% CO_2 conversion with above 96%CH_4 concentrations and less than0.1% residual H_2. The gas quality showed compliance with the grid standards without the need for further CO_2 removal.	Rachbauer et al. (2016)

Methane loss minimization from biogas upgradation plants

A major challenge in most of the upgrading plants is CH_4 loss through the off gas. PSA and membrane separation techniques have high amounts of methane in the off gas. Removal of $CH_4$from off gas can be done by either flaring oxidation (combustion), thermal oxidation, catalytic oxidation, thermal catalytic oxidation or regenerative thermal oxidation (Petersson and Wellinger 2009; VUT 2015; Jonerholm and Lundborg 2012). The off gas can be mixed with raw biogas and fed to an existing combined heat and power (CHP) or upgrading plant for heat production. Recently, Wu et al. (2017) used solid digestate as immobilized material for methane-oxidizing bacteria (MOB) in bio-filter to eliminate the CH_4 in off gas by producing active carbon from solid digestate. However, these methods for off gas treatments are complex, involve sophisticated design and sizing of the system or require separate gas treatment facilities. Apart from being expensive, these methods do not recover CH_4 but instead oxidize it to other products like active carbon or CO_2 and H_2O. Research is required to develop off gas treatment techniques which are simple, cheap and do not require separate source of energy for operation.

Recently, adoption of flash vessel in water scrubbing biogas upgrading systems is becoming the most preferred method for CH_4 loss recovery. In water scrubbing biogas upgrading system, flash vessel is installed after the packed-bed scrubber. The flash tank is fed with pressurized water which does not require extra power for water pumping (Patterson et al. 2011). Several reports state that the CH_4-rich flash gas obtained from the top of the flash vessel is recovered and recirculated back into the input of raw biogas compressor which is then injected into scrubbing column. However, this affects the composition of the biogas entering the column as the flash gas is mixed with the raw biogas. Gas recirculation also raises the power requirements (energy intensity of the system) because operating parameters like pressure, gas and water flow rate (more scrubbing water would be required) need to be optimized for upgrading to biomethane. Therefore, extensive experimental investigations should be done to study and examine the effects of flash gas recirculation on energy requirements and optimization of the operating parameters.

Emerging novel technologies for biogas upgradation

Biological conversion of biogas to biomethane is being explored using various species. However, as they are still under development and most available information has been obtained in laboratory-scale or pilot tests, more work needs to be done to improve its productivity. More efforts are needed to bridge the knowledge gap between such tests and large-scale operations. Research should be focussed on gas-to-liquid mass transfer and novel reactor design which is a limiting step for biological approaches.

Some innovative technologies such as hybrid technology, hydrate separation, supersonic and industrial lung are also emerging for biogas upgradation. These technologies provide enormous potential in respect to feasibility and technological simplicity with high efficiency. Although evaluated at laboratory and pilot level still commercial scale optimization and testing are required of these technologies to demonstrate full potential for biogas upgrading. Even though these approaches are capable to provide better performance as compared to well-established technologies already operating at different scales of biomethane production, more efforts are required to bridge the gap between pilot level and industrial scale.

A comparative assessment of the upgradation technologies led to the opinion that the limitations of individual biogas upgradation technology can be overcome by integrating them into hybrid technologies. Hybrid method is an interesting alternative to overcome the challenges of different technologies. It results in reduced operating costs, low-energy requirement and high CO_2 separation efficiency. For example, integrating membrane gas permeation with water scrubbing, amine absorption or cryogenic separation to develop hybrid process improves the efficiency of biogas upgradation (Scholz et al. 2013a, 2013b). More research on hybrid technologies is required for improving the techno-economic dimension of biogas upgradation.

An industrial lung, also known as ecological lung, is a biotechnologically hybridized process. Carbonic anhydrase enzyme is used to enhance and catalyses breakdown of carbon dioxide formed from cell metabolism. This technology is patented and marketed by CO_2 Solutions, Inc. based in Quebec (Ong et al. 2014). The carbonic anhydrase bioengineered by the company is 10 million times more thermally and chemically resistant than the ones naturally occurring. Lab-scale experiments with carbonic anhydrase in water showed that biogas could be purified up to 95–99% methane content with CO_2 content less than 1% (Allegue and Hinge 2012). However, more research is required to enhance the limited enzyme lifespan and reduce the cost of enzyme production. Further, exploration is needed to study the utilization of carbonic anhydrase with different solvents to improve CO_2 absorption rates and simultaneously reduce energy consumption.

Gas hydrate technology is based on selective separation of target gaseous component between the hydrate phase and the gaseous phase. Gas hydrates have been successfully developed and used to separate CO_2 from contaminated natural gas. Hydrate formation requires huge energy consumption due to high pressure requirement of the process. This limitation has called for more research on this technology for separation of CO_2 and other contaminants from biogas (Sahota et al. 2018).

Supersonic process for CO_2 separation from biogas is a recently developed novel technology. The process consists of series of expansion, cyclonic gas/liquid separation and re-compression of gas in a compact convergent–divergent tubular device in the shape of a nozzle (Sahota el al. 2018). Expansion of biogas to supersonic velocity leads to decrease in temperature and pressure. This causes formation of condensed water droplets and hydrocarbons. By using a cyclonic separator, the droplets centrifuge to the wall due to high vorticity swirl which splits the liquids from the gas. Zhang et al. (2006) used this technology to condense and separate water and hydrocarbons from natural gas. Even though this technology is simple, reliable, not susceptible to fouling or poisoning and has significantly lower life cycle costs compared to conventional adsorption-based systems, still it is the most expensive. Hence, more research is required to utilize this technology for making it cost-effective for biogas upgradation.

Development of efficient adsorbents

For adsorption, absorption and membrane-based biogas upgrading, low operating and maintenance costs and maximum separation efficiency are dependent upon the material being used in the process. Upgradation of biogas by sorbent materials through CO_2 adsorption requires further research on the development of new and alternative materials. High sorption and affinity of the material and separation competence as sorbents for the removal of H_2S, CO_2 and other biogas impurities is the need of the hour (Tagliabue et al. 2009; Zhou et al. 2017). Additionally, high chemical and thermal stability for the lifetime of the process are the needed in the material. New alternative materials are required to be explored in separation (membrane) and sorption (sorbents) technologies for biogas upgrading (Wu et al. 2015). Research should also be focussed on developing sorbents from wastes for removal of H_2S, CO_2 and other biogas impurities. Starr et al. (2012, 2014) reported novel biogas upgrading technologies based on wastes rich in calcium from municipal solid waste incinerators (MSWI) like bottom ash and air pollution control residues which separate and store CO_2 from biogas. The major challenge in the development of these new materials and processes for biogas upgradation is to drive them from experimental to industrial settings with high efficiency and low costs.

Alternative biogas utilization pathways

Biogas can be used as fuel for stoves, boilers, internal engines, vehicles and fuel cells, or it can be injected into natural gas grids (Sun et al. 2015; Budzianowski 2016) (Fig. 12). Inappropriate quality of biogas and biomethane can lead to unnecessary costs. Precise quality of biogas and biomethane can satisfy the specific requirement of the particular application. The requirements on gas quality are not similar for different applications. Therefore, integration of gas upgrading and its utilization in applications requiring different qualities of gas are urgently required.

R&D avenues for innovative and efficient strategies for management and valorization of biogas and biomethane are highly desirable. Research and development are required in exploitation of CH_4 and CO_2 of biogas as potential raw materials for innovative applications and ways for power production and value added chemical production (Sun et al. 2015; Khan et al. 2017). Production of ethanol and higher alcohols from biogas and biomethane is gaining attention. Still, equipment and kits for direct conversion of CH_4 to ethanol and higher alcohols are limited, whereas indirect conversion with syngas production and catalytic conversion is being extensively studied. Possible pathways to fully utilize the energy of biogas in different utilization options are also needed to be explored. Utilization of biogas in fuel cells is also gaining importance, however, connection between overall efficiency of fuel cells and CH_4 purity should be further explored. Methane (external) reforming is a well-established technology

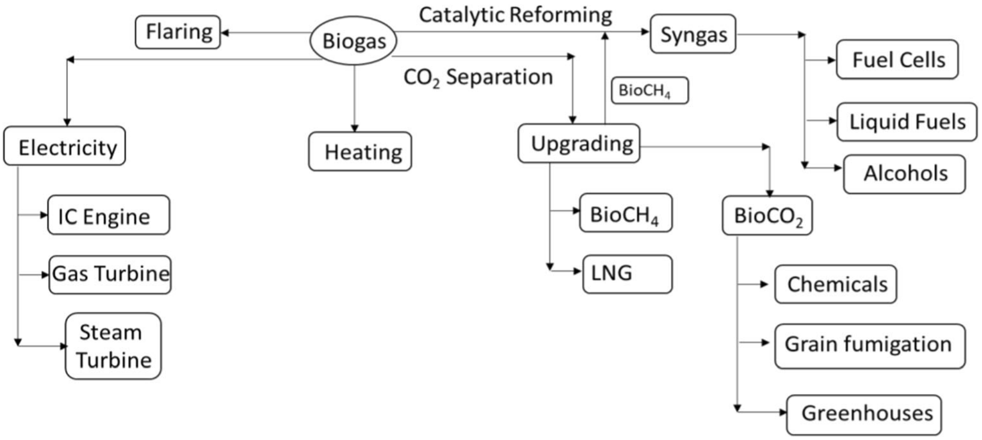


Fig. 12 Schematic representation of the possible routes for biogas utilization

for synthesis gas ($H_2 + CO$) or H_2 production. Any quality of biogas/biomethane can be a suitable feed to produce syngas via catalytic reforming. Research should be focussed on dry reforming, steam reforming and auto-thermal for utilization of biogas/biomethane for producing syngas which can be further exploited in production of H_2-rich feed for used fuel cells or in converting to liquid fuels like gasoline, kerosene and alcohols (Awe et. al 2017, Yentekakis and Goula 2017).

Bio-CO_2 as a promising by-product

A major advantage of biogas upgrading technology is the CO_2 rich off gas obtained from the upgrading plant. This off gas stream is usually emitted into the atmosphere as a waste product, causing a detrimental effect to the environment. Instead of releasing, CO_2 can be used as a valuable green product after processing. BioCO_2 can be sold as an additional commercial product by the biogas producer (Sun et al. 2015). It could be utilized for chemical production (calcium carbonate, potassium carbonate, etc.), algae cultivation and welding purposes. BioCO_2 can be used to produce dry-ice for refrigeration of dairy products like milk, curd and cheese in rural areas. It can be also used to enhance crop production in greenhouses. BioCO_2 is an excellent alternative to synthetic CO_2 and chemicals being used as fumigants for pest control. It is absolutely safe, cost effective, non-hazardous and does not produce harmful residues in grain storages in comparison to chemicals used for long-term storage of grains like methyl bromide and phosphine. Although chemical fumigants like methyl bromide and phosphine are very effective in pest control, these are highly toxic for humans, spur environmental side effects like thinning of ozone layer and contaminate soil and water ways. BioCO_2 produced from biogas is of biogenic origin. Its recovery from biogas and utilization in different applications makes the complete process carbon negative (CO_2 fixed during photosynthesis in biomass–biogas production–biogas upgradation–bioCO_2 recovery–utilization). More research attention should be paid to the separation of CO_2 as a potential by-product, since there is not much information is available about the quality, purification and applications of CO_2 rich off gas.

Improving the cost economics of upgradation plants

Upgradation cost depends mainly on the scale of biogas upgradation. The specific investment costs for all the technologies are nearly equal for large-scale biogas upgrading units; however, it increases significantly for small-scale systems. This is because, for small-scale plants, pipes and valves, sensors, control systems, analysis equipments are nearly same as required for a plant with larger capacity. Therefore, the overall economy of biogas upgrading depends upon the capacity of the plant. There is a need for reducing the costs of small-scale plants by development of simple, efficient materials and practical approaches.

Implementation of support policies

An important issue for the future development and wider implementation of biogas technology market calls for the development of soft policies, subsidies and governmental support. Currently, biogas production is only emerging rapidly in countries with reliable, convenient regulatory environment, lucrative feed-in-tariff, support policies and governmental support. The development of biogas market requires proper policy interventions to enable more research and development and its commercial implementation (Mittal et al. 2018). Moreover, providing incentives for schematized collection, segregation and transport of organic wastes to biogas plants, establishment of training centres for creating future skilled personnel for this sector in emerging markets should also be looked upon.

Increased awareness, technical knowledge and support

There is widespread availability of organic wastes worldwide, but one barrier in the promotion of this technology is the lack of expertise and strategies for collection, segregation and transportation of biodegradable waste. Supply chain management needs to be streamlined. If proper systems are developed for waste management and feeding into digesters, then projects can become viable for implementation of biogas upgrading plants. There is a need of spreading awareness about the role of this technology for waste management and energy security. The main bottlenecks in financing of biogas plants are the lack of knowledge about biogas projects in general from the side of the decision-makers. Biogas upgrading is a scattered market with only few established players at national and international levels. There is a limited technical expertise in biogas upgrading technology. Experienced and skilled workforce is lacking. This is also a major technology barrier for its widespread dissemination. Also, there is lack of human resource training programmes for project developers on technical knowledge and economics of biogas upgrading systems.

Formulation of standards on biogas/biomethane utilization

Standards for biogas and biomethane quality for end use applications are crucial for its widespread adaption. A gas standard is a technical requirement which defines the quality and composition of gas, as in our case biomethane. The standards for upgraded biogas ensure that biogas can be technically and safely be used for natural gas based applications such as injection or transported through the natural gas grid or utilized in vehicles (Allegue and Hinge 2012). Permission procedures for upgraded biogas (biomethane) injection into the gas grid are considerably rationalized as soon as gas quality requirements are satisfied, which helps and motivates biomethane producers and local stakeholders to implement such projects. There are no international technical standards for utilization of upgraded biogas but some countries like Germany, Sweden and California have established national standards and procedures for its application as an alternate to natural gas (Persson et al. 2006). In India, standards for use of biomethane in stationary engines and in vehicles were formulated and published recently in the year 2013 by the bureau of Indian standards (BIS 2015). For widespread implementation and adaptation of this technology, formulation of international and national standards for biogas and biomethane is required.

Promotion of biogas fertilizer

Biogas digested slurry is a nutrient rich material with the potential to replace inorganic fertilizers and raw manure. The digested slurry constitutes good quality manure free from weeds, pathogens and contaminants like heavy metals or infectious microorganisms (Bonten et al. 2014). Large quantities of macro- and micronutrients like nitrogen, potassium and phosphorus are preserved during anaerobic digestion of organic wastes. Therefore, the nutrients are recycled by using the biogas digested slurry as a bio-fertilizer. The nitrogen present in the bio-fertilizer is in the ammoniacal form which can be easily absorbed by the soil for crops (Drosg et al. 2015). It is an organic fertilizer and should be better promoted and used instead of artificial fertilizers. However, there are no legal provisions for inclusion of biogas digested slurry in place of chemical or artificial fertilizers. This is also a major barrier in the promotion of this technology in the market. Biogas slurry improves the cost economics of the biogas production and upgrading plant. Therefore, supportive schemes and policies should be in place for promotion of biogas slurry in place of chemical fertilizer.

Conclusions

Biomethane is a promising renewable energy option as a substitute of natural gas for grid and vehicular applications. It can be easily compressed to increase its utility as compressed natural gas and can directly be fed to transportation vehicles. The upgrading technologies which are commercially available in the market are water scrubbing, pressure swing adsorption, amine scrubbing, membrane process and cryogenic separation. Some advanced upgradation technologies like biological and hybrid methods are also emerging as promising biogas upgrading processes in the commercial marked but are yet not popularized and still at pilot level. The technological improvements along with economical consideration in biogas upgrading processes are likely to be continued in future along with regulations for its utilization in different applications. The comprehensive analysis of the existing and emerging biogas upgrading technologies deliberates that future research should be directed towards process optimization, CH_4 loss minimization, development of novel technologies, efficient adsorbents for biogas upgradation and augmented utilization pathways for biogas, bioCH4, bioCO_2 and biofertilizer. It was also understood that for increased and widespread promotion of this technology, cost economics of upgradation plants needs to be improved with substantial subsides, policies and governmental support. With increased awareness, technical knowledge and support this technology can be dispersed worldwide for waste management, energy security and climate change mitigation.

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