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Progress and perspectives in converting biogas to transportation fuels

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ABSTRACT

The discovery of abundant natural gas resources has greatly increased the study of using methane as a feedstock to produce transportation fuels. Biogas (primarily containing methane and CO₂), which is generated from waste biomass via anaerobic digestion or landfills, is regarded as a renewable source of methane, and has the potential to achieve sustainable production of transportation fuels. Since biogas also contains a significant amount of impurities (e.g., H₂S, NH₃, and siloxane), a cleaning procedure is generally required prior to conversion to transportation fuels. Physical approaches, mainly compression and liquefaction, have been commercially applied to upgrade biogas to bio-compressed natural gas (CNG) and liquefied biogas (LBG). For chemical approaches, catalytic reforming is the dominant method for converting methane to syngas, followed by Fischer–Tropsch synthesis (FTS) or fermentation of syngas to a variety of alcohols (e.g., methanol, ethanol, and butanol) and liquid hydrocarbon fuels (e.g., gasoline, diesel, and jet fuels). High purity hydrogen, a clean fuel, can also be produced via reforming. Methanol can be produced by direct oxidation of methane, while interest in the biological conversion of methane to methanol has grown recently due to its mild operating conditions, high conversion efficiency, and potential for using raw biogas. The derived methanol can be further converted to gasoline via a methanol to gasoline (MTG) process. This paper provides a comprehensive review of major research progress on technologies for converting biogas/methane into transportation fuels, and discusses the principles, kinetics, operating conditions, and performance of each technology. Efficient direct conversion of biogas into ethanol and higher alcohol fuels (e.g. butanol), which is envisaged to be the focus of research pursuits in the near future, is also discussed, with emphasis on the development of methane-utilizing microbes through genetic engineering.

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Abbreviations: AD, anaerobic digestion; AOB, ammonia oxidizing bacteria; ATR, autothermal reforming; CBG, compressed biogas; CFC, chlorofluorocarbons; CNG, compressed natural gas; CHP, combined heat and power; COE, crude oil equivalents; ctl, coal-to-liquid; DEA, diethanolamine; DGE, diesel gallon equivalent; FTS, Fischer Tropsch synthesis; GGE, gasoline gallon equivalent; GHG, greenhouse gas; GTL, gas-to-liquid; HAS, higher alcohols synthesis; IEA, International Energy Agency; LBG, liquefied bio-gas; LPG, liquid petroleum gas; LNG, liquid natural gas; MDEA, methyldiethanolamine; MDH, methanol dehydrogenase; MEA, monoethanolamine; MMO, methane monooxygenase; MTG, methane-to-gasoline; NADH, nicotinamide adenine dinucleotide hydrogen; OFMSW, organic fraction of municipal solid waste; POM, partial oxidation of methane; POR, partial oxidative reforming; PSA, pressure swing adsorption; PWS, pressurized water scrubbing; TSA, temperature swing adsorption; WGS, water gas shift

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1. Introduction

Concerns about depletion of fossil fuels, energy security, and emission of greenhouse gas (GHG) have prompted renewable energy studies. Biogas, generated from anaerobic digesters or landfills via biological degradation of organic compounds, is considered a renewable energy carrier. Production of biogas via anaerobic digestion (AD) involves a series of biochemical processes, primarily comprised of four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Organic materials, such as food processing wastes, lignocellulosic biomass, and animal manure, which contain carbohydrates, fats and proteins, are commonly used as feedstocks. These feedstocks are usually available at a low cost or may even generate a tipping fee, thus making biogas production economically favorable. According to an AgSTAR report, a 1 MW AD facility can produce approximately 3 million kWh of electricity per year, which is enough to supply power to more than 200 homes [1]. Another study evaluated energy crops for biogas production in the EU-25 (the 25 Member States of the European Union). It showed that 320 million tonnes of crude oil equivalents (COE) could be produced with crop rotations that integrate the production of food, feed, raw materials (e.g. oils, fats, organic acids), which would provide up to 96% of the total energy demand of cars and trucks in the EU-25 [2]. In China, biogas production from small-scale biogas digesters has increased from approximately $1.8 \times 10^9 \text{ m}^3$ in 1996 to $1.0 \times 10^{10} \text{ m}^3$ in 2007 (equivalent to $1.1 \times 10^{11} \text{ kWh}$ electricity), while biogas production from medium- and large-scale biogas projects has increased from approximately $1.2 \times 10^{11} \text{ m}^3$ in 1996 to $6.0 \times 10^{12} \text{ m}^3$ in 2007 (equivalent to $6.3 \times 10^{13} \text{ kWh}$ electricity) [3]. Given the tremendous amount of organic wastes from agriculture and food processing, there is growing interest worldwide in employing AD as a waste treatment method as well as an energy production technology.

A variety of feedstocks have been used for AD. At mesophilic conditions (35–40 °C), one tonne dry feedstock can produce 13–635 m^3 of CH_4 gas, depending mainly on the composition of the feedstock [4–8]. Municipal wastes usually have higher CH_4 yields than lignocellulosic biomass such as yard trimmings. For instance, one tonne of dry organic fraction of municipal solid waste (OFMSW) showed a high CH_4 yield of 635 m^3 [5], which is

equivalent to $2.39 \times 10^{10} \text{ J}$ energy or 751 l gasoline. Assuming fuel consumption is 10.6 km/L (25 mile/gallon) for a passenger car, energy produced from one dry tonne of OFMSW would allow a passenger car to travel 7963 km. To date, efforts have been made to improve the CH_4 yield during anaerobic digestion. Feedstock selection, process design and operation, digestion enhancement, and co-digestion with multiple substrates have been extensively studied, and several reviews are available [9–13].

Currently, biogas is primarily used for: (1) burning biogas in a combined heat and power (CHP) unit for heat and electricity generation; (2) upgrading biogas for natural gas pipeline injection; and (3) converting purified biogas to compressed biogas (CBG) or liquid biogas (LBG) for a variety of fuel applications (Fig. 1). CBG is considered to be the same as compressed natural gas (CNG), and is often referred to as Bio-CNG. Heat and electricity production systems are usually adopted for on-site usage of biogas. Purified biogas is almost the same as natural gas in terms of heating value; therefore, injection of clean biogas into a natural gas pipeline becomes an option. Biogas was used as a transportation fuel in Germany in the 1930s and the interest was renewed in the 1990s. Nowadays, biogas is provided as a transportation fuel in gas filling stations in Europe, especially Germany and Sweden, either as 100% methane (CBG100) or blended with natural gas (e.g. CBG10 and CBG50) [14]. Using biogas as a transportation fuel has the advantage of generating low GHG emissions compared to conventional fossil fuels. Vehicles using CNG/Bio-CNG generate approximately 8–22 g $\text{CO}_{2\text{eq}}$ per MJ, which is over 80% lower than those using petroleum based fuels [15]. Lower particulate matter (e.g. metals and soot) emissions are another advantage. Use of LBG is also growing. In 2005, a commercial LBG filling station, which used landfill gas, was opened in Los Angeles, California. Commercial LBG filling stations are also available in China and a few European countries.

Besides Bio-CNG and LBG, biogas may be converted to other transportation fuels (Fig. 1). Clean biogas can go through a catalytic reforming process, from which syngas or high purity H_2 can be obtained. H_2 is a clean transportation fuel, and syngas can be used as a substrate for alcohol production. Previously, studies mainly focused on the reforming of CH_4 , while recent studies reported that both CH_4 and CO_2 can be converted to syngas via dry reforming or steam reforming, thus enabling direct use of biogas

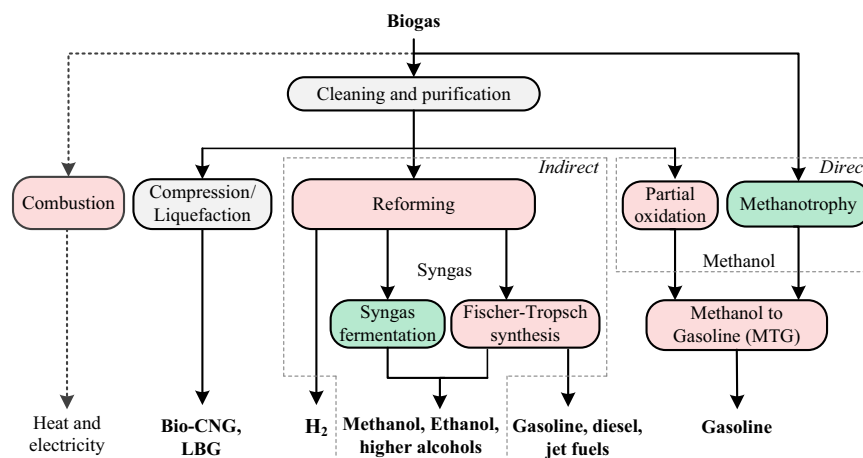


Fig. 1. Route-map of biogas cleaning and conversion to transportation fuels. The two dashed areas show direct and indirect approaches for methanol production.

without removing CO_2 [16]. Syngas can be used as a substrate for fermentation or Fischer–Tropsch synthesis (FTS) to produce ethanol and higher alcohols that have been used as fuel blends. Methanol can be produced via methanotrophy of biogas or partial oxidation of methane (POM). A specific group of microorganisms, methanotrophs, are able to use CH_4 as the single carbon and energy source to produce methanol. The POM is a thermal catalytic process. Although methanol has been tested as a transportation fuel, its toxicity is a concern. Therefore, the methanol-to-gasoline (MTG) process is often employed to further upgrade methanol to gasoline as a transportation fuel. The FTS and MTG processes have already been reviewed previously [17,18], therefore, are not major focuses of this study.

One challenge for biogas applications is the complex composition of biogas. CH_4 and CO_2 are the two major components in raw biogas, accompanied by many other unfavorable impurities such as N_2 , O_2 , H_2 , H_2S , and NH_3 . These impurities can cause problems such as corrosion, toxicity, and reduction of heating value. Therefore, biogas applications have varied requirements for its composition. For instance, when biogas is used for heat and electricity production, only vapor and H_2S removal is required. However, most of the impurities need to be removed for transportation fuels and pipeline injection applications [19]. Biogas cleaning is usually considered the first step for biogas applications, and is also an energy demanding process. A variety of physical and chemical biogas cleaning methods have been developed; however, choosing the appropriate method(s) is site-specific and application dependent. Commonly used methods are pressurized water scrubbing, pressure swing adsorption, membrane permeation, and absorption with amine [20]. Most of these methods are derived from traditional air pollution control and natural gas treatment technologies, and are capable of removing single or multiple impurities from raw biogas.

This review covers biogas cleaning and conversion technologies for transportation fuel production. Major technologies that have been commercially applied or are currently in the research stage are included, with an emphasis on their working principle, conditions, performance, advantages, disadvantages, and cost. Possible future research directions are also envisaged.

2. Biogas cleaning

The composition of biogas varies from site to site, depending on the type of feedstock and also the applied digestion technology. In general, biogas has two major components, CH_4 and CO_2 , and also contains impurities such as H_2S , N_2 , and NH_3 (Table 1). The biogas

Table 1

Typical composition of biogas and natural gas, adapted from [20,22].

Character	Unit	AD biogas	Landfill biogas	Natural gas
CH_4	vol%	53–70	30–65	81–89
CO_2	vol%	30–50	25–47	0.67–1
N_2	vol%	2–6	< 1–17	0.28–14
O_2	vol%	0–5	< 1–3	0
H_2	vol%	NA	0–3	NA
Higher hydrocarbons	vol%	NA	NA	3.5–9.4
H_2S	ppm	0–2000	30–500	0–2.9
NH_3	ppm	< 100	0–5	NA
Total chlorines	mg/N m^3	< 0.25	0.3–225	NA
Siloxane	$\mu\text{g/g-dry}$	< 0.08–0.5	< 0.3–36	NA

generated from anaerobic digesters is very similar to that produced from landfills but with a slightly higher CH_4 content. However, unlike natural gas which contains very low CO_2 (0.67–1%), CO_2 in biogas can range from 25% to 50%. High CO_2 content decreases biogas heating value (Table 2). Biogas also has higher contents of N_2 , O_2 , H_2S , and NH_3 , but much lower hydrocarbons (other than CH_4) compared to natural gas. Besides that, halogen emissions can result from burning biogas, and are attributed to the digestion of wastes containing halogenated hydrocarbons [21]. The halogen concentration is usually higher in landfill biogas than in AD biogas. Chlorine compounds (especially chlorofluorocarbons) are the most abundant halogen compounds, followed by bromine and fluorine containing compounds. In addition, a trace amount of siloxanes usually can be found in biogas. Siloxanes are compounds containing Si–O–Si bonds. The most commonly found siloxanes in biogas are the linear compounds, which are designated with the letter L (L2–L5), and cyclic compounds, which are designated with the letter D (D3–D6). Water and dust can also be found in biogas. The possible sources and negative impacts of these impurities are summarized in Table 2.

When biogas is used for heat and electricity production via a combined heat and power (CHP) unit, only water and H_2S removal is required. However, using biogas for pipeline injection and transportation fuel conversion has strict requirements on its composition. According to U.S. pipeline specifications, natural gas pipeline injection requires purified biogas that contains CO_2 , water, and H_2S at less than 3%, 112 mg/m^3 , and 4 ppm, respectively [26]. Bio-CNG conversion requires purified biogas with higher than 97% CH_4 . For liquefied biomethane production, biogas has to be purified to contain less than 25 ppm, 4 ppm, and 1 ppm of CO_2 , H_2S , and H_2O , respectively, to prevent dry ice formation and corrosion [4]. Converting biogas to syngas using the dry reforming

Table 2
Possible sources and negative impacts of biogas impurities, adapted from [20,23–25].

Impurities	Possible sources	Possible impact
CO ₂	Hydrocarbons	Low calorific value
O ₂	Air	Explosive with high O ₂ concentration in biogas
H ₂ S	Proteins and other sulphur containing compounds, such as manure	Corrosive to steel reactors and instruments; toxic at > 50 ppm; formation of SO ₂ and H ₂ SO ₄
NH ₃	Proteins, such as food wastes	Toxic to anaerobic bacteria; corrosive in water; formation of nitrous oxide when burns
Siloxanes	Personal hygiene products, cosmetics, detergents, pharmaceuticals, and lubricants	Formation of SiO ₂ and microcrystalline quartz; deposition on engine surfaces
Halogens	Halogenated hydrocarbons, such as discarded refrigerants, plastic foams, aerosols, and paints	Toxic and forms polyhalogenated dioxins and furans; corrosive to combustion engines
Water	Hydrocarbons and proteins	Corrosion; clogging in pipes; absorption/accumulation of other contaminants
Dusts	Metals, plastics, and aerosols	Clogging

Table 3
Plant number and averaged methane purity using different biogas cleaning technologies^a.

Method	Plant number	Ave. CH ₄ purity (%) ^b
Water scrubbing	107	96.1
Pressure swing adsorption	55	95.8
Chemical absorption	53	94.6
Membrane permeation	22	90.3
Genosorb [®] scrubbing	12	96 ^c
Cryogenic method	1	88

^a Calculated based on data from the IEA energy database [29].

^b If a range was shown in the original database, the lower limit was adopted for calculation.

^c Data are available for only two plants.

method actually needs both CO₂ and CH₄ as inputs, so CO₂ removal is not necessary. Therefore, the need for biogas cleaning is application dependent.

Most biogas cleaning methods are derived from conventional gas separation technologies and many of them have been successfully applied for natural gas purification [27]. Commonly used methods are pressurized water scrubbing, pressure swing adsorption, absorption using amine or other organic compounds, membrane permeation, Genosorb[®] scrubbing, and a cryogenic approach. Currently, there are about 80 commercial scale biogas cleaning plants in operation in Europe, which generate clean biogas that is equivalent to 200 MW electricity or 170 million m³ of natural gas [28]. Worldwide, there are at least 249 commercial scale biogas cleaning plants. The selected cleaning technologies in these plants are summarized in Table 3, together with their averaged CH₄ purity.

2.1. Pressurized water scrubbing

Pressurized water scrubbing (PWS) is the most commonly used biogas cleaning method (Table 3). It takes advantage of the higher water solubility of CO₂ and H₂S compared to CH₄, thereby separating both CO₂ and H₂S simultaneously from biogas with a high efficiency [30]. A schematic diagram of this method is shown in Fig. 2. To enhance the absorption of CO₂ and H₂S, biogas is usually compressed to 900–1200 kPa and a high surface area packing media is used. Inside the scrubber, biogas flows counter-currently to water that is sprayed from the top of scrubber, and the absorption primarily occurs on the surface of the packing media. Cleaned biogas can contain > 96% CH₄ after drying [31]. The liquid effluent contains a high concentration of CO₂ and a low concentration of CH₄. CH₄ is recycled in the flash tank where pressure is lowered to 200–400 kPa. Finally, water is regenerated in the

stripper at near atmospheric pressure with air blown into the stripper. The advantages of this method include no need for chemicals and simultaneous removal of CO₂, H₂S, and other water soluble impurities, e.g. NH₃ and dust. However, the challenge of this method is the high water demand.

Current studies on PWS mainly focus on applying high pressure, reducing water usage, and optimizing water pH [32]. Water pH affects absorption of H₂S. Solubility of H₂S decreases with reducing pH, while high pH leads to precipitation of sulfate and carbonate ions. Therefore, a neutral pH is often preferred for PWS devices. At high pressure, solubility of gases increases, which reduces water demand in the scrubber. Also, the washing water is oversaturated in the stripper where the pressure is reduced to 100 kPa, which facilitates water regeneration. Recently, a pilot scale PWS test was carried out by Lantela et al, in which a high pressure of 2000 kPa and a relatively low pH of 4.6 were used [33]. Their results show that a closed water recycle can be achieved, with the highest CH₄ purity of 90.2% during the 64 day trial (326 total hours). In addition, siloxanes and halogenated compounds were reduced by 16.6% and 90.1%, respectively. Although this test was not operated continuously, it shows a possible strategy to reduce water usage.

2.2. Pressure swing adsorption

Pressure swing adsorption (PSA) uses the adsorbent's differences in gas adsorption rates to capture preferred gases (e.g. CO₂, O₂, and N₂) at a high pressure, and then releases the adsorbates at a low pressure to regenerate the adsorbent for a subsequent adsorption cycle. Commonly used adsorbents are zeolite, carbon molecular sieve, silica gel, and activated carbon, due to their low cost, large specific area and pore volume, and excellent thermal stability [34]. These adsorbents are designed to have a specific pore size thus enabling selective adsorption of molecules that are smaller than the designed pore size. The molecular size of CH₄, CO₂, O₂, and N₂ are 4.0, 2.8, 2.8, and 3.0 Å, respectively, at standard conditions. Therefore, an adsorbent with a pore size of 3.7 Å is able to capture CO₂, O₂, and N₂, but not CH₄, thereby cleaning the biogas. This method was first employed in 1989 for CH₄ enrichment from biogas when Pande and Fabiani [35] used a natural zeolite to purify simulated biogas. Since then, the PSA method has been used extensively for biogas cleaning. The PSA adsorption and desorption process usually includes four steps as shown in Fig. 3. In the pressurized vessel (700–800 kPa, step 1, Fig. 3), CO₂ and other small-size gases are adsorbed, while the enriched CH₄ leaves from the top of the vessel. When the adsorbent is saturated by adsorbates, the biogas flows to another vessel. It usually needs four or more vessels operating at the same time to create a continuous operation, which reduces the energy needed for gas

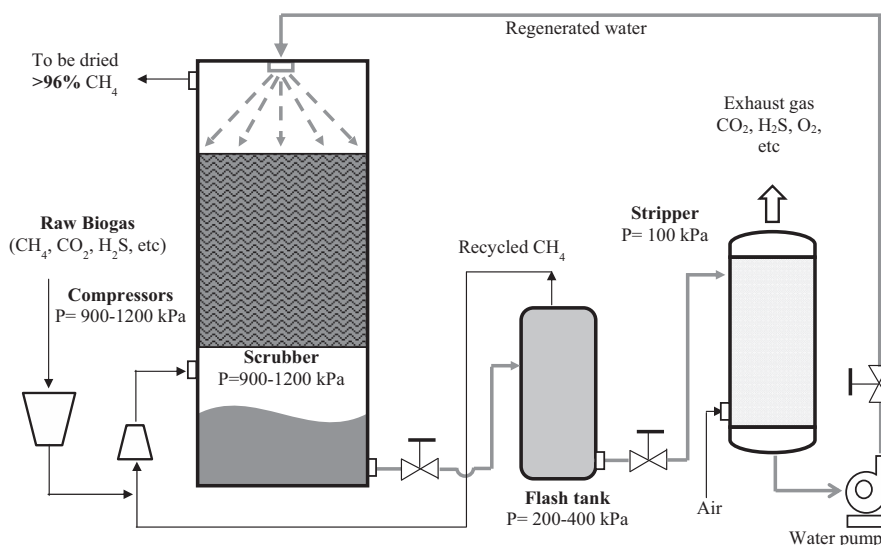


Fig. 2. Schematic diagram of pressurized water scrubbing.

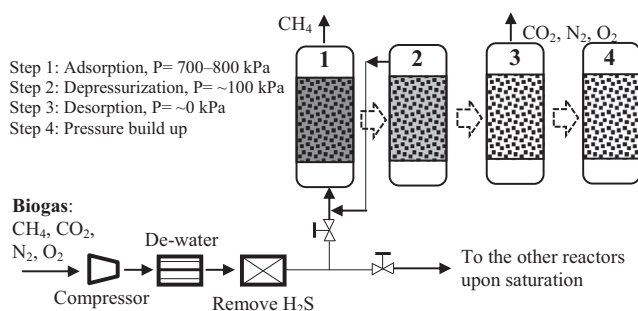


Fig. 3. Schematic diagram of PSA process.

compression. When a vessel becomes saturated, it goes through a depressurization step in which the pressure is reduced to around atmospheric condition (~ 100 kPa, step 2). Gas released in this step contains both impurities and methane, and is recycled through the desorption vessel. The pressure of the vessel is then further decreased to near vacuum (~ 0 kPa, step 3), which de-adsorbs captured impurities, regenerating the adsorbents. The gas that leaves the vessel in this step mainly consists of CO_2 , N_2 and O_2 . The pressure is built up in step 4 for a subsequent cleaning cycle.

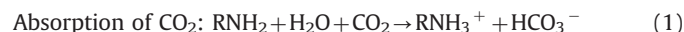
The major concern of the PSA system is its toxicity and overloading of adsorbents. Sticky gases, such as H_2S and NH_3 , may irreversibly attach to many adsorbents and reduce their available surface area for adsorption, while water competes with other adsorbates for adsorption spots [36]. Previous studies noted that H_2S accumulation to 1.39 mg/g-adsorbent can cause biogas breakthrough in a natural zeolite PSA system [37], and H_2S higher than 46 mg/g-adsorbent can completely saturate activated carbon [38]. Therefore, H_2S and water need to be removed from biogas before the PSA cleaning process (Fig. 3).

Research efforts to identify advanced PSA adsorbents have focused on selectivity, capacity, and regenerability. Cavenati et al. [39] examined the adsorption ability of a carbon molecular sieve for biogas cleaning ($\text{CH}_4/\text{CO}_2=55/45$, volume basis) at 303 K and 320 kPa, and showed that CH_4 purity higher than 96% can be obtained with a recovery rate of 75%. Besides molecular sieves, there is also interest in using natural zeolite. Alonso-Vicario et al. [40] showed that its CO_2 adsorption capacity could be as high as 173.9 mg/g-natural zeolite, which was twice the adsorption capacity of a synthetic molecular sieve tested in that same study. Their testing condition was 700 kPa and 25 °C, with a biogas feeding

velocity of 1 cm/s (composition: $\text{CH}_4/\text{CO}_2/\text{H}_2\text{S}=59.95/39.95/0.10$). Zeolites and carbon molecular sieves can also be used simultaneously in a PSA system. As biogas diffusion is relatively fast in zeolites but is slow in carbon molecular sieves, a two-stage PSA system was tested using zeolites as the first adsorbent and a carbon molecular sieve as the second adsorbent in order to provide sufficient contact time between the gas and the adsorbent [41]. By combining these two systems, a CH_4 purity of over 98% was achieved. To date, regenerability of adsorbents has rarely been examined. In the same studies carried out by Alonso-Vicario et al., H_2S and CO_2 saturated zeolites were successfully regenerated at a high temperature of 280 °C, atmospheric pressure, and a N_2 flash velocity of 0.46 cm/s [40]. The cost for regeneration has not been evaluated.

2.3. Amine absorption

Amine solvent has a high absorption selectivity of CO_2 ; therefore, is often used to separate CO_2 from gas streams. Amine absorption technology was originally developed for separating CO_2 from coal-fired power plant flue gas in the early 1980s [42], and later was adopted as a biogas cleaning technology. Commonly used solvents are alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA) or methyldiethanolamine (MDEA), among which MEA is the most widely employed solvent for low pressure absorption [43]. These solvents not only enhance CO_2 absorption capacity but also reduce corrosion problems. The reactions during adsorption and desorption processes are shown below.



where R is an organic component. For example, R is $-(\text{CH}_2)_2\text{OH}$ for MEA. The above reactions are mainly governed by temperature and pressure. Low temperature and high pressure favor absorption, while high temperature and low pressure promote desorption.

A schematic diagram of amine absorption and desorption is shown in Fig. 4. Biogas is usually compressed at 600–700 kPa before feeding into the absorption reactor. In the absorption phase, CO_2 and some H_2S gas dissolve into the solvent, while high-purity CH_4 gas leaves the reactor. The CO_2 -rich solvent is then transferred to the regeneration reactor. To accelerate desorption, high temperature (115–125 °C) and relatively low pressure (140–170 kPa)

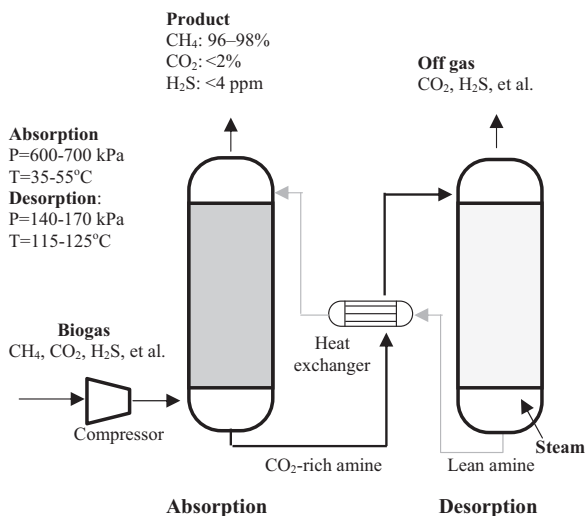


Fig. 4. Schematic diagram of amine absorption and desorption.

are usually employed. After desorption, a high-purity CO_2 product can be collected and the CO_2 -lean solvent is returned to the absorption reactor. Due to the high temperature in the regeneration reactor and low temperature in the absorption reactor, a heat exchanger is usually used to increase the temperature of the CO_2 -rich solvent before it enters the regeneration reactor and also to reduce the temperature of the lean solvent leaving the reactor. A cooler may be needed in some cases to further decrease the temperature of the CO_2 -lean solvent prior to entering the absorption reactor. The cleaned biogas usually contains high purity CH_4 (96–98%). Also, due to the fact that amine solvents have a much higher solubility of CO_2 over CH_4 , CH_4 loss can be very low during this process [22]. Therefore, amine absorption is preferred where strict environmental regulations on CH_4 emissions are applied.

A primary hurdle for the application of the amine-based biogas cleaning method is its intensive demand for energy and amine solvents, given that desorption requires a high temperature of 115–125 °C and the MEA price is about \$1–1.5 per kg. Studies have been carried out to decrease the regeneration temperature and to improve the absorption efficiency [44–46]. For instance, lipophilic amine solvents and amine amino acid salts were used to replace MEA and successfully decreased regeneration temperature to around 80 °C [44,47]. Bidart [48] attempted to add functionalized ionic liquids, such as 1-butyl-3-methylimidazolium bromide and 1-propylamine-3-methylimidazolium bromide, to amine solvents and slightly improved CO_2 absorption efficiency. However, no large scale application using these novel solvents/additives has been carried out yet, mainly due to stability concerns. Other related challenges are the possible corrosion caused by H_2S and the accumulation of water if the desorption temperature is significantly decreased.

2.4. Membrane permeation

The design principle of membrane permeation is that under a certain pressure, gases with high permeability (e.g. small molecular size and low affinity) can be transported through the membrane while gases with low permeability are retained. As shown in Fig. 5, high permeable impurities, such as CO_2 , O_2 , and H_2O , pass through the membrane as permeate, while low permeable CH_4 is retained and can be collected at the end of the hollow column [49,50].

Using membranes for biogas treatment began in the early 1980s when Kimura and Walmet [51] made polymer membranes and used them to separate a synthetic mixture of CH_4 and CO_2 .

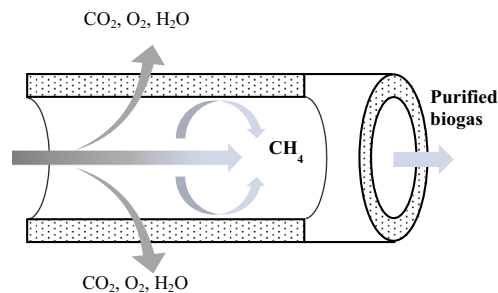


Fig. 5. Schematic diagram of membrane permeation.

After decades of development, the membrane permeation method is now known for its safety, scale-up flexibility, simplicity of operation and maintenance, and no requirement for hazardous chemicals. General criteria for evaluating membrane separation are selectivity, pressure drop, CH_4 loss, and membrane life span. In 1983, a cellulose acetate spiral-wound membrane was used to treat biogas [52]. During the 18 month trial, 96.5% CH_4 content was obtained. Inspired by this study, Rohr and Wimmerstedt [53] compared the performance of a polysulphone membrane and a cellulose acetate membrane on purifying biogas generated from a sewage plant, and noted that the permeability of CH_4 and CO_2 of both membranes was generally increased with temperature, which led to decreased separation efficiency. Stern et al. [54] utilized membranes made from “glassy” polymers, such as cellulose acetate and polyimides, to separate biogas generated from a municipal wastewater treatment plant, and showed that CH_4 content higher than 90% can be obtained, while organic impurities may poison the membrane. Based on this result, pretreating biogas to remove organic impurities prior to membrane separation is generally recommended. Along with the development of bioenergy in recent years, interest in large-scale membrane separation projects has been increasing [55–57]. One of the earliest industrial-scale biogas cleaning projects using membrane separation was built in 2007 [58], and currently, there are at least 22 membrane separation plants in operation with an average CH_4 purity of 90.3%, which is slightly lower than the PWS, PSA, and amine absorption methods (Table 3).

To further improve the membrane method, a few numerical studies have been carried out. Makaruk et al. [59] simulated the performance of a hybrid membrane system with a combination of rubbery and glassy membranes to simultaneously remove both H_2S and CO_2 , and noted that this hybrid system significantly improved H_2S separation efficiency with acceptable CO_2 removal and CH_4 recovery. Molino et al. [60] also numerically demonstrated the feasibility of integrating an AD plant with an on-site polymeric membrane purification system, in which hollow fiber membranes were used to remove CO_2 , H_2 , and N_2 from biogas.

Membranes can also be used for removal of other impurities, such as water vapor and N_2 . Membranes usually have a very good water permeability, and the $\text{H}_2\text{O}/\text{CH}_4$ selectivity can be as high as 500, thus making membranes a good choice for biogas dehydration [61]. CH_4 is more condensable than N_2 , and the selectivity of CH_4/N_2 can achieve 5 or even higher [62]; therefore, membranes becomes a feasible method for N_2 separation, although, in some cases, multistage systems may be required. With regard to H_2S removal, very high separation efficiency (decreased from 3400 ppm to 40 ppm) was observed in a previous study treating biogas with high levels of H_2S [63].

2.5. Other methods

Other biogas cleaning methods include temperature swing adsorption (TSA), cryogenic process, Genosorb[®] scrubber, and

Table 4
Technical advantages and disadvantages of biogas cleaning methods.

Purifying methods	Advantages	Disadvantages
Pressurized water scrubbing	Removes CO ₂ , NH ₃ and dust; high CH ₄ purity; low CH ₄ loss; needs no special chemicals or equipment	High water demand, H ₂ S removal efficiency may be low
Pressure swing adsorption	Removes CO ₂ , N ₂ and O ₂ ; low power demand; low level of emissions	H ₂ S and water removal is needed before PSA; needs to periodically regenerate adsorbent
Amine absorption	Very low methane loss; produces high quality CO ₂ , and almost complete H ₂ S removal	High energy demands; amines are expensive; corrosion at high temperatures; produces waste chemicals
Membrane	Compact and light in weight; easy operation and maintenance; low energy requirements	Relatively low CH ₄ purity and high loss rate; membrane can be expensive
Temperature swing adsorption	Needs no special chemicals	High energy demands; low CH ₄ purity
Cryogenic method	Produces CO ₂ as by product	High energy demands; high capital cost
Genosorb	Removes H ₂ S efficiently	Not designed for CO ₂ removal
Biofiltration	Removes NH ₃ , H ₂ S, and particles; low cost	Does not remove CO ₂ , may generate N ₂ O

biofilters. Similar to the amine absorption technology, TSA was also originally developed for post combustion CO₂ capture [64]. It is a combination of adsorption at a low temperature level (40 °C) and desorption at a high temperature level (120 °C). Shao et al. [65] reported that pipeline quality CH₄ (> 97% purity) can be obtained using a hybrid membrane–TSA system. However, there is no publicly available report about using TSA alone for biogas cleaning. Cryogenic technology takes advantage of the different boiling points of gases (CO₂: –78.5 °C, CH₄: –161 °C) by progressively cooling the raw biogas under pressure and, consequently, obtaining high purity CH₄. High purity CO₂ is produced as a valuable byproduct [30]. This method is also used for liquefied biogas production, which will be introduced in detail in Section 4. Genosorb[®] scrubber is an absorption method particularly designed for H₂S removal [66]. Genosorb[®] is a mixture of polyethylene glycol dimethyl ethers (CH₃O(CH₂–CH₂O)_nCH₃) with *n* mainly between 4 and 10. Although biofiltration has not been used for industrial-scale biogas cleaning, it could be a feasible technology to remove NH₃ and H₂S in biogas [67]. A typical gas phase biofilter is a bioreactor that is filled with organic or inorganic packing materials [68]. Microorganisms grow on the surface of the packing media and are able to consume NH₃ or H₂S. NH₃ is absorbed and then oxidized into nitrite and nitrate, while H₂S can be oxidized to sulfite or sulfate. Biofilters are known for effectively treating gas emissions with a large volume but relatively low concentrations of contaminants [68,69]; therefore, it could be a feasible technology for biogas generated in AD and landfills. In addition to these after-treatment methods, it may be possible to reduce impurities by adjusting the AD operating conditions. Peu et al. [70] added a sulfate reduction inhibitor, potassium molybdate, into an AD system. Although this method only temporarily reduced H₂S emissions, it has the potential to be improved. Similarly, micro-aeration, a method that can enhance hydrolysis during AD [71], is likely to reduce the generation of H₂S by oxidizing it into either sulfite or sulfate.

Selection of a biogas cleaning method varies from site to site, and depends on the required biogas quality; the availability of water, chemicals, and equipment; and markets and regulations for products and byproducts. A summary of the technical advantages and disadvantages of these methods is shown in Table 4 [25,30,72–74]. Given the complex composition of biogas, it is important to prioritize the targeted impurities to facilitate selection of cleaning methods. Pressurized water scrubbing and pressure swing adsorption are able to remove multiple impurities, e.g. CO₂ and NH₃, simultaneously, but are not very effective in reducing H₂S. In contrast, scrubbing using Genosorb[®] can remove H₂S efficiently. A combination of two methods is also used in some cases, especially for the membrane separation method, which is easy to install and operate but has a relatively low CH₄ purification

capacity. Biofilters also need to be combined with other methods as they can remove NH₃ and H₂S, but not CO₂. For amine absorption and cryogenic methods, both produce high-quality CO₂ as a byproduct, but also require high energy inputs for operation. Therefore, combination with another method, such as pressure swing adsorption, may improve the energy efficiency.

The capital and operating costs of biogas cleaning methods have been reviewed previously [20]. The costs are dependent on the selected method, quality of raw biogas, desired quality, and more importantly, the capacity of the plant. Typical capital costs are US \$1.6–2.0 million for a plant treating 1000 N m³/h of raw gas and US \$0.7–1.1 million for a plant treating 250 N m³/h of raw gas. Estimated operating costs are US \$0.59, \$0.34, \$0.23, \$0.18, and \$0.16 per N m³ methane for cryogenic, PSA, amine absorption, water scrubbing, and membrane permeation method, respectively [32]. If H₂S removal is included, the operating cost for the amine absorption and membrane permeation methods could be increased to US \$0.38 and \$0.30 per N m³ of methane, respectively [32].

3. Bio-CNG

Compressed natural gas (CNG) is recognized as an alternative to conventional transport fuels (e.g. gasoline and diesel). Due to the high octane number (> 110) of natural gas, the compression ratio of engines can be increased resulting in higher thermal efficiency. Another advantage of using CNG is the reduction of vehicle emissions. As natural gas has the smallest C/H ratio among all hydrocarbon fuels, the carbon based emissions (CO, CO₂, and HC) decrease significantly [75]. A modeling study showed that the well-to-wheel GHG emissions dropped from approximately 93 g/MJ for gasoline/diesel to about 74 g/MJ for fossil natural gas [76]. CNG is also a lead free fuel. Nowadays, there are approximately 8.7 million CNG vehicles concentrated in Argentina, Pakistan, Brazil, India, Russia, Iran, and Italy [77]. In some countries, such as Italy and Argentina, the CNG vehicle fleets represent between 10% and 20% of the total fleets [78]. In the U.S., there are approximately 1000 public and private CNG stations compared to 120,000 gasoline stations, and CNG stations are envisaged to grow quickly [79].

Cleaned (> 97% CH₄ purity) biogas can be compressed to produce Bio-CNG, which is very similar to regular CNG. Bio-CNG is also known as compressed biomethane. Chandra et al. [80] compared the performance of a constant speed internal combustion engine using CNG and Bio-CNG, and noted that their engine performances were similar in terms of brake power output, specific gas consumption, and thermal efficiency. Another study carried out by Subramanian et al. [81] also showed no significant

difference in vehicle fuel economy and emissions of CNG and Bio-CNG. As biogas is produced from renewable sources or wastes, its lifecycle GHG emissions have been shown to be 80% less compared to gasoline [75].

3.1. Production, storage and distribution

Conversion of biogas into Bio-CNG requires removal of impurities using the methods introduced in Section 2. Cleaned biogas should contain more than 97% CH₄ and less than 2% O₂. Bio-CNG is then produced by compressing (20–25 MPa) clean biogas to less than 1 percent of the volume it occupies at standard atmospheric pressure. A typical Bio-CNG station usually is composed of an impurity separation unit, a multi-stage compressor, and a high pressure storage tank, following the steps shown in Fig. 6. Storage of Bio-CNG or regular CNG is critical as it affects vehicle filling time, filling completeness, and energy consumption [82]. There are two commonly applied storage systems in industry: buffer storage and cascade storage. The buffer storage system maintains the pressure of CNG in the range of 20.5–25 MPa, and provides CNG with a maximum pressure of 20 MPa to a vehicle's on-board cylinders. In this case, all filling station reservoirs are connected and maintained at the same pressure. The cascade storage system is typically composed of three reservoirs with low, medium, and high pressure, respectively, and filling CNG to on-board cylinders takes three steps. The vehicle's on-board cylinders are firstly connected to the low-pressure reservoir. As the pressure in the

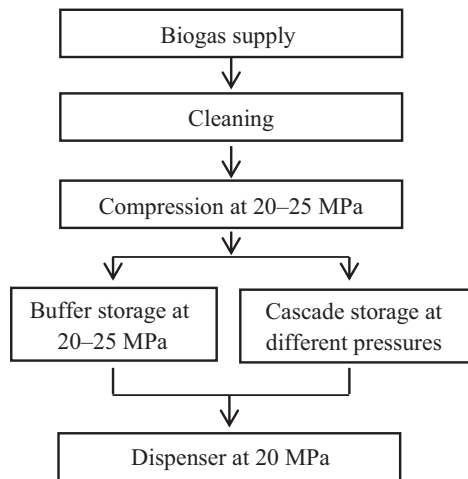


Fig. 6. Bio-CNG production, storage, and distribution.

reservoir declines and that in the on-board cylinder increases, the gas flow rate decreases. When the flow rate has declined to a pre-set level, the system switches to the medium-pressure reservoir, then finally to the high-pressure reservoir to complete the filling. Oppositely, when refilling the reservoirs, the high-pressure reservoir is prioritized, and then followed by the medium and low reservoirs. This method ensures that the high-pressure reservoir (used to complete the fill) is maintained at a maximum pressure all times, ensuring that vehicles are always supplied with the maximum amount of gas. Compared to the buffer storage system, the cascade system consumes about 50% less energy but charges 20% less biogas and takes three times longer to fill [83]. Therefore, the cascade system is preferred for filling fleet vehicles that usually takes hours (time-fill), while the buffer system meets the needs for fast-fill that can be completed within five minutes.

3.2. Industrial practices

Given its low cost and environmental benefits, upgrading biogas to Bio-CNG has gained extensive attention. Currently, there are more than a dozen industrial plants in operation and at least one plant is in the design phase (Table 5). The number of biogas plants with Bio-CNG stations is expected to increase quickly in the near future.

In Austria, the first Bio-CNG fueling station has been operating since it was built in 2008 [100]. This station uses a membrane separation method to clean biogas and then compresses it to Bio-CNG. The plant has a capacity of 25 kg/h and can supply up to 200 CNG cars assuming an annual road performance of 15,000 km. In the U.S., at least 11 Bio-CNG stations are in operation. A typical example is the one located in Fair Oaks, Indiana [85,93]. This dairy farm has 11,000 cows which produce 1.9 million liters of liquid wastes every day. Biogas is generated from anaerobic digesters using these wastes as feedstock, and then is purified and compressed into Bio-CNG. In 2012, this station produced Bio-CNG equivalent to 5.6 million liters of diesel. The produced Bio-CNG fuels 42 long-haul milk trucks which deliver over 1 million liters of milk per day. In India, a pilot test of biogas conversion into Bio-CNG was carried out in 2006. Vijay et al. [97] purified biogas using a scrubbing method that reduced CO₂ concentration to less than 2%. A set of ultra-fine filters were used to remove water vapor. The CH₄ enriched biogas was then compressed at 20 MPa using a three-stage compressor to produce Bio-CNG. The final product was stored in a 0.5 m³ vessel. One vessel of Bio-CNG (9.3 kg) was able to fuel a three cylinder vehicle for 60.6 km. Another study carried out by Nema and Bhuchner [101] reported that 100,000 N m³/day

Table 5

Current industrial projects that convert biogas to Bio-CNG.

Plant site	Energy yield (10 ⁹ J day ⁻¹)	Vehicles fueled	Biogas source	Waste treated (Mg day ⁻¹)	Location	Starting year	Reference
Biogas plant	–	200	–	–	Austria	2008	[84]
Fair Oaks dairy	913	42	AD	242 ^a	USA	2011	[85]
Columbus bioenergy digester	433	25+	AD	224	USA	2012	[86,87]
Zanesville bioenergy digester	216	–	AD	–	USA	2012	[88]
Cleveland bioenergy digester	216	–	AD	106	USA	2012	[89]
Janesville wastewater plant	144	40+ by 2022	AD	75,000 m ³ /day	USA	2011	[90]
Riverview land preserve	54–66	2	Landfill	–	USA	2013	[91]
Sacramento waste digester	54	–	AD	22.7	USA	2013	[92]
Rodefild landfill	30	25–30	Landfill	–	USA	2011	[93,94]
St. Landry parish landfill	25	15+	Landfill	–	USA	2012	[93,95]
Rumpke landfill	–	10	Landfill	–	USA	2011	[93]
Hilarides dairy farm	9–14	2	AD	220 ^a	USA	2009	[96]
Biogas plant	–	1	–	–	India	2006	[97]
NextGen Bio-CNG	–	–	AD	–	India	2012	[98]
Des Moines WWTF	93–132	In design phase	–	–	USA	–	[90]

^a Assuming a daily wet manure production of 22 kg day⁻¹ head⁻¹ [99].

biogas, which is equivalent to 309.5 m³/day Bio-CNG, was produced using organic wastes generated in New Delhi, India. The first large scale Bio-CNG station in India was constructed in 2012 and uses biogas generated from anaerobic digesters [98]. Details about this project have not been released yet. In Thailand, Papong et al. [102] investigated the energy and environmental impacts of Bio-CNG during its life cycle, including digestion, cleaning, compression, distribution, refueling, and combustion. Cassava starch wastewater was used as the AD feedstock. Based on their estimations, a positive energy gain was expected and the global warming potential of Bio-CNG was shown to be 20% lower than that of fossil-based CNG. The biogas production and cleaning were found to be the two major contributors of global warming potential of Bio-CNG. Converting biogas into Bio-CNG has also been considered in Algeria [103] and Iceland [104]. Based on these practices, a process model was developed by Rapport et al. [105] to predict mass and energy balance from full scale anaerobic digesters. The proposed model is based on a system that is composed of five 786 m³ reactors (one bio-gasification reactor and four hydrolysis reactors) that can treat 104 tonne/day of food and green waste (50:50, volatile solids basis). Based on this model, if all biogas is used for Bio-CNG conversion, this system can produce 8.84×10^3 m³ Bio-CNG every day, and is financially viable.

The capital cost of a CNG station varies with its capacity and compression method. A typical CNG station using a buffer system with a capacity of supplying 52–216 vehicles could cost US \$675,000, while a station using a cascade system with a capacity of supplying 103–432 vehicles could cost one million US dollars [106]. Operating costs of CNG stations are also dependent on station capacity. A case study in North Carolina estimated the operating and maintenance costs for a 21 buses scheme and a 75 buses scheme, showed cost of US \$0.33 and \$0.13 per diesel gallon equivalent (DGE, 1 gallon is equal to 3.78 L), or US \$0.08 and \$0.03 per liter gasoline equivalent (based on energy balance), respectively [107]. In West Virginia, an economic analysis for a truck (Ram 2500) showed that the lifecycle costs of CNG and gasoline were US \$1.35 and \$3.25 per gasoline gallon equivalent (GGE), or US \$0.36 and \$0.86 per liter gasoline equivalent, respectively [108]. In Lafayette, Indiana, CNG was compared to diesel and hybrid diesel-electric as a potential option for bus fuel replacement; results showed that CNG had the lowest cost among the three options in a life span of 15 years, along with the benefits of reducing greenhouse gas and particulate emissions [109].

Currently, CNG is primarily used in passenger cars or light/medium duty trucks, as the energy density of CNG is much lower than gasoline. Also, the vehicle on-board cylinders take a relatively large space, which also limits the application of CNG as a transportation fuel. More efforts will be needed in the future to improve the availability of Bio-CNG and the compatibility of CNG to other power sources. Besides working on biogas cleaning and compression technologies, logistical studies are needed, especially for biogas plants located in remote rural areas. In particular, storage of Bio-CNG is an important topic that includes concerns about filling efficiency, cost, and safety. In general, converting biogas to Bio-CNG could be a good choice for on-farm anaerobic digesters, as it significantly reduces the volume for transportation, although the relatively small scale of farm digesters may present a challenge for biogas conversion.

4. Liquefied biogas

LBG is a liquid fuel and a valuable product as it is more than 600 times more space efficient compared to biogas in its gas phase at atmospheric pressure, or around 3 times more space efficient compared to Bio-CNG. Therefore, converting biogas to LBG

Table 6

Current projects that convert biogas into LBG, summarized from [19].

Starting point	Energy cost MJ m ⁻³ biogas	Scale LBG/day	Method
Raw biogas	5.40	9.5–37.8 m ³	Cryogenic
Raw biogas	4.82	–	Cryogenic
Raw biogas	2.88	–	Cryogenic
Clean biogas	0.54	–	Cryogenic
Clean biogas	2.27	> 4.5 Mg	Liquefaction
Clean biogas	1.55	4.5–45 Mg	Liquefaction

facilitates transporting biogas produced in remote locations to where it is needed. LBG is generally recognized to be the same as liquid natural gas (LNG) in terms of CH₄ content and heating value. The quality of LBG depends on the biogas cleaning process. Global LNG production is expected to be 320 million tonnes and 450 million tonnes in 2015 and 2020, respectively [110]. According to BP's statistical review, about 30% of the international natural gas trade movement was made in the form of LNG in 2011–2012 [111]. Therefore, natural gas liquefaction technologies have been well established, and similar technologies can be used for LBG production. LNG and LBG have been widely used as a vehicle fuel in many countries, especially in China, Russia, Japan, South Korea, Spain, and the U.S. [112–114]. Due to its high energy density, LNG/LBG is considered as a substitute for diesel fuel for heavy duty vehicles.

To produce LBG, biomethane (cleaned biogas) undergoes a liquefaction process that converts the biomethane to a cryogenic liquid at a temperature lower than –161 °C, but higher than –196 °C [115]. Commonly used LBG production methods include cryogenic technology, liquefaction, and pressure letdown [19]. As the biomethane goes through a dramatic temperature drop, LBG production requires a high energy input. However, given the low cost of biogas, converting biogas to LBG can still be economically favorable. A few industrial projects, as shown in Table 6, have been established in recent years. The energy demand for converting raw biogas to LBG (2.88–5.40 MJ m⁻³) is much higher than that required for converting clean biogas to LBG (0.54–2.27 MJ m⁻³), and the cryogenic method is generally preferred for liquefying raw biogas (Table 6).

4.1. Cryogenic technology

Cryogenic technology takes advantage of the different condensation temperatures of gases to purify biogas and produces LBG. Typically, CO₂ can be separated from biogas by lowering the temperature to –78.5 °C at which CO₂ is condensed; then, as the temperature is further decreased to –161 °C, CH₄ is condensed into LBG. The condensation temperature of N₂ at atmospheric pressure is –196 °C. This method does not need chemical additions and provides high-purity CO₂ as a byproduct. A typical cryogenic process, which is shown in Fig. 7 [116], is composed of four steps: moisture removal, H₂S and siloxane removal, CO₂ condensation, and CH₄ condensation. In step 1, water vapor is partially condensed at 6 °C; most heavy organic components that are dissolved in water also leave the gas stream in this step. The gas is then compressed at 2.5–3.5 MPa. In step 2, siloxane and the remaining water vapor are condensed at –25 °C; a H₂S filter, named Sulfur Oxidation and Siloxane Adsorption (SOXSIAR) filter, is used to oxidize H₂S to element sulfur and then filter both element sulfur and siloxanes. In step 3, CO₂ is frozen and separated from the gas stream at –78.5 °C; the liquid CO₂ leaving this step has a high purity and thus can be used as a refrigerant or other valuable byproduct. In step 4, the remaining biogas is liquefied at around –190 °C so that CH₄ is condensed into LBG. The produced

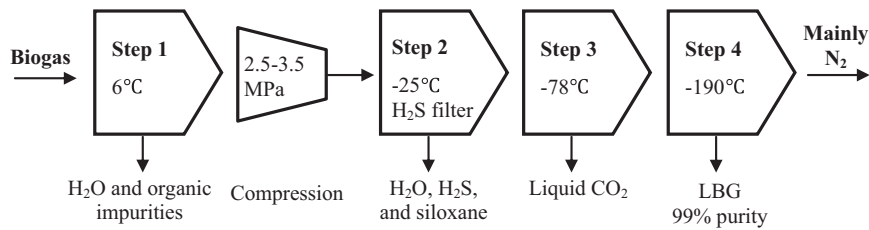


Fig. 7. Schematic diagram of the cryogenic process.

LBG usually contains more than 99% CH₄. The remaining gas stream is mainly N₂.

4.2. Pressure letdown

The pressure letdown method has been recently developed in the U.S. and Sweden. It takes advantage of the high pressure of the natural gas grid to produce LNG and LBG. The natural gas grid is usually operated at 6–8 MPa. When the high-pressure gas enters a pressure letdown station, it is firstly dried through an adsorption system to remove water. Often, methanol is injected into the gas stream and bonds to water molecules. The water–methanol mixture can be separated from the gas stream via condensation. After drying, the gas is split into a large stream that is used for expansion and a small stream that is used for liquefaction. The large stream is fed to an expansion turbine where the pressure is reduced to a lower level. Energy extracted from the expansion is recovered using an electric generator, and the temperature reduction caused by the expansion is used to cool down the small stream using a heat exchanger. The large stream leaving the heat exchanger has a pressure of about 0.4 MPa and is injected into a distribution network for end use. The small stream is fed to the second adsorption system to remove CO₂. After that, it is cooled sufficiently in a second heat exchanger to produce hydrocarbon vapor and LNG. Solid CO₂ can be formed during the cooling process and is separated from the CH₄ stream using a separation tank, a hydro cyclone, and a final filter [117]. This process can tolerate a CO₂ content of 2.5% [19].

Small-scale pressure letdown plants can balance the availability of natural gas or biogas during high and low demand periods, and also provide stored LNG or LBG to communities without access to the natural gas grid. One pressure letdown station has been built and operated since 2003 in Sacramento, California by the Idaho National Laboratory [118]. This station was designed to liquefy 10–20% of the gas entering the plant, which can produce up to 114,000 l liquids per day [119]. The plant needs only a minor power supply as it is mainly powered by the energy created through the pressure reduction. In Sweden, the natural gas pipeline is normally operated with a pressure of 5.5–6.5 MPa, and its pressure can be dropped to 1.0 or even 0.4 MPa for LNG production [19].

4.3. Biogas liquefaction

Small-scale liquefaction is a conventional method to produce LBG. It transfers heat in biogas to refrigerants within a cryogenic heat changer so that biogas is condensed into LBG. As this method does not separate impurities step by step as described in the cryogenic processes, it has a strict requirement on the inlet biogas, which should contain < 25 ppm CO₂, < 4 ppm H₂S, and < 1 ppm H₂O, in order to prevent built-up of dry ice or corrosion of downstream equipment [120]. This method can be identified as closed-loop or open-loop, depending on whether the applied refrigerant is external or is part of the gas stream. N₂ or a mixture of N₂ and hydrocarbons are commonly used as the refrigerant [19].

This method has been applied in a pilot-scale plant in Sweden in 2003, which produces 1400 N m³ LNG per day [120].

The major concern for LBG production is the high energy demand; therefore, academic and industrial stakeholders are looking for methods to improve the energy efficiency. For cascade systems, such as cryogenic technology, the energy demand depends on the temperature and duration of each step, and is also affected by the composition of biogas. For the liquefaction system, which includes no impurity separation, energy demand is mainly required for the cooling process and biogas cleaning process. The pressure letdown station is slightly more complicated compared to the other two systems as it involves an expansion unit, two adsorption units, and two heat exchangers. A case study in Italy showed that among all the on-site liquefaction technologies, pressure letdown could be the best option [121].

An economic analysis of various methods producing LBG/LNG was carried out by TIAX for the America's Natural Gas Alliance in 2013 [122]. The cryogenic method (categorized as a gas separation method in this report) was shown to have an estimated liquefaction cost of US \$0.15 per gallon LNG, or equivalently, US \$0.06 per liter gasoline. With regard to the pressure letdown method, the station built in Sacramento, California was used as an example, which showed an estimated capital cost of US \$110–170 per liter LNG per day and a low operating cost of US \$0.05 per gallon LNG [123], or equivalently, US \$0.02 per liter gasoline. The low operating cost was due to the energy provided by the pressure release from natural gas pipeline. With regard to the small scale liquefaction station, its capital cost was estimated to be about the same as pressure letdown plants, but its operating cost was much higher at US \$0.31 per gallon LNG, or equivalently, US \$0.13 per liter gasoline. If both biogas cleaning and liquefaction are considered, the costs will be even higher. The Altamont plant, built by the Linde and Waste Management joint venture at the Altamont landfill east of the San Francisco Bay Area, is one typical biogas-to-LBG project [122]. This plant has a capacity of 13,000 gallon, or 49,000 l, per day. It costs US \$15.5 million to build and has an operating cost of US \$0.58 per gallon LNG, or equivalently, US \$0.23 per liter gasoline.

5. Syngas/hydrogen

Syngas is a fuel gas mixture consisting primarily of H₂, CO, and a small amount of CO₂. Syngas is a highly valuable raw material for the petrochemical industry as it plays an important role in large scale gas-to-liquid (GTL) processes [124]. Typically, syngas can be converted into methanol and dimethyl ether in catalytic processes, upgraded to higher alcohols in fermentation, or used in the Fischer–Tropsch synthesis (FTS) to produce gasoline and diesel [125]. As shown in Fig. 1, syngas synthesis is critical for indirectly converting biogas into transportation fuels. Syngas can be produced from biogas via reforming, e.g. dry, steam, or partial oxidative reforming, or from a combination of two or three of these reforming methods. By manipulating the reforming process, the ratio of H₂/CO in syngas can be optimized, and high purity H₂

Table 7
Converting biogas into syngas via dry reforming.

Input CH ₄ /CO ₂	Catalyst or plasma	Temp. (°C)	Output H ₂ /CO	CH ₄ conversion (%)	CO ₂ conversion (%)	Carbon formation (mg/g-catalyst)	Source
0.5	Ce–Gd–O	800	1.07	50	88	–	[133]
0.8	Rh–Al	700	1.00	42	–	–	[134]
1	Mg–Al–Ni–La	700	0.76	80	82	–	[135]
1	Ni–Al	700	~0.67	19	31	–	[136]
1	Ni–Pb–Al	700	~0.88	60	78	–	[136]
1	Ni–Pb–1P–Al	700	~0.77	55	71	–	[136]
1	Ni	700	1.0	54	66	41	[137]
1	Co	700	1.0	75	67–80	20–268	[137]
1	Ni–Co	700	1.0	56–71	83	290	[137]
1	Pt–Ru	700	< 0.5	90	48	–	[138]
1	La–Ni–Mg–Al–O	750	0.95	0.90	0.92	–	[139]
1	Ni	750	–	32	36	3.6% of inlet C	[140]
1	Ce–Gd–O	800	0.96	68	72	–	[133]
1	Pt–Al	900	–	–	–	22% of inlet C	[141]
1	Ni–La–Al	950	–	99	90	–	[142]
1.5	Plasma	100	1.40	81	76	–	[143]
1.5	Ni–Al	750	0.90	49	81	–	[144]
1.5	Ni–Mg–Al	750	0.86	59	70	–	[144]
1.5	Ni–La–Mg–Al	750	0.95	61	70	–	[144]
1.5	Rh–Ni–Mg–Al	750	1.00	58	85	–	[144]
1.5	Rh–Ni–La–Mg–Al	750	1.06	50	94	–	[144]
1.5	Rh–Ni	800	1.00	65	100	–	[145]
1.5	Ni–Al	850	0.55	72	96	180	[146]
1.5	Ni–Ce–Al	850	0.65	73	97	170	[146]
1.5	Ni–Ce–Al	850	1.30	71	97	168	[146]
2	Ce–Gd–O	800	0.84	66	46	–	[133]
2.1	Ni	750	–	21	29	3.6% of inlet C	[140]

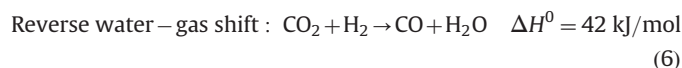
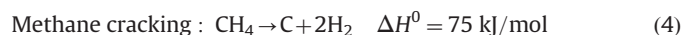
gas can be produced as a clean transportation fuel. Steam reforming is employed for commercial production of H₂ [126].

5.1. Dry reforming

Dry reforming is a highly endothermic reaction that catalytically converts two stable molecules, CH₄ and CO₂, into syngas, a highly reactive product, at 700–900 °C (Eq. (3)). This method was proposed in the 1920s and has attracted extensive attention thereafter. Biogas generated from AD can be a suitable source for this application as it contains both CH₄ and CO₂ with a molar ratio of about 1–1.5, which is favorable for dry reforming [16].



Dry reforming is usually accompanied by several side reactions, especially the CH₄ cracking, Boudouard reaction, and reverse water–gas shift reaction (Eqs. (4)–(6)). The CH₄ cracking and Boudouard reaction produces carbon, which can deposit on the surface of catalysts and thus reduce their selectivity toward syngas. The Boudouard reaction is exothermic and is favored at relatively low temperatures (250–350 °C), while the CH₄ cracking reaction is more likely to occur at high temperatures (600–800 °C). Therefore, it is very challenging to avoid carbon formation and deposition in the dry reforming reaction, especially with a CH₄/CO₂ ratio higher than 1 [127]. The reverse water–gas shift reaction is endothermic and is preferred in CO₂-rich environments. This side reaction produces H₂O and decreases the H₂/CO ratio to a value slightly less than 1 at 400–800 °C. At temperatures higher than 900 °C, CH₄ and CO₂ can be completely converted to syngas with a H₂/CO ratio of about 1, which is ideal for many Fischer–Tropsch processes.



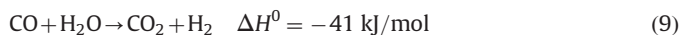
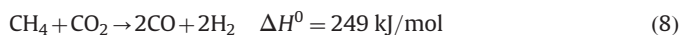
Catalysts are commonly used for lowering the activation energy of the dry reforming reaction and increasing selectivity toward syngas. Numerous studies have focused on using both noble and non-noble metal catalysts [127–129]. Non-noble metal catalysts such as nickel (Ni) are attractive due to their low costs compared to noble metal catalysts, but they are less effective because they also promote the Boudouard and/or methane cracking reactions. In contrast, noble metal catalysts, such as Pt, Pd, Rh, Ru and Ir, are less sensitive to carbon deposition than Ni based catalysts, probably due to their lower carbon solubility [130], but they are usually too expensive for industrial applications. More recently, non-thermal plasma was applied for biogas dry reformation. One advantage of the plasma method is the reduction of the carbon deposition, as the radicals induce chemical reactions at a low temperature of about 100 °C. Tu and Whitehead observed a synergistic effect of plasma and Ni/γ-Al₂O₃ catalyst in dry reforming that showed no serious carbon deposition and a CH₄ conversion of 56.4% and a H₂ yield of 17.5% [131]. Some cobalt nanocatalysts, e.g. Ni–Co/Al₂O₃, may also suppress carbon formation, as cobalt can control the size of active sites [132].

Table 7 summarizes representative studies of dry reforming of biogas to syngas. A CH₄/CO₂ ratio of 1–1.5 was commonly used with a few exceptions. Except the plasma study, all the metal catalyst based studies were conducted at 700–950 °C. The CH₄ and CO₂ conversion rates and H₂/CO ratio in the products varied, largely depending on the temperature and applied catalysts. Although the carbon formation was quantified in only a few reports, all these studies demonstrated serious carbon formation and deposition problems.

5.2. Steam reforming

Steam reforming is widely used in industry to produce H₂-enriched gases. Worldwide, 80–85% of H₂ is produced via steam

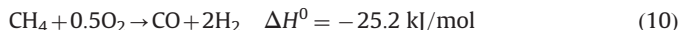
reforming [126]. Due to its high heating value and low environmental impact, hydrogen has received wide interest for fuel applications. It can be reacted with oxygen to generate electricity in a fuel cell or burned in an internal combustion engine to provide power for vehicles. Cleaned biogas with 60% CH₄ and 40% CO₂ can be used as a feedstock as well as a heat source to boil water into steam. The reforming reactions are shown in Eqs. (7) and (8) [147,148], and very often, are followed with a water gas shift (WGS) reaction as shown in Eq. (9) to maximize H₂ production. Steam reforming reactions are endothermic reactions and occur at a high temperature of 700–1000 °C, while the WGS reaction normally happens at a relatively low temperature of 150–400 °C. To enhance H₂ production, the WGS reaction temperature can be lowered or excess steam can be added. In a previous study, in which the WGS reaction was carried out at both high (250–450 °C) and low temperature (150–250 °C) with Cu/Fe/Cr and Cu/Zn catalysts, respectively, the final product contained 68% H₂ and only 0.2% CO (equivalent to CO conversion of > 99%) [147]; while in another study that used biogas that contained a 1.5:1 mixture of CH₄ and CO₂, a final H₂ concentration of 60–70% and CO concentration of lower than 10 ppm were attained by adding extra steam [149]. One concern in steam reforming of biogas is the presence of H₂S which may cause catalyst deactivation due to sulfur poisoning. As noted, biogas containing 20–108 ppm H₂S caused sulfur formation in the temperature range of 873–1200 K [150]. Therefore, biogas desulfurization is needed for hydrogen/syngas production via the steam reforming process. An economic and ecological analysis of biogas steam reforming was conducted by Braga et al, who showed that the H₂ production cost was 0.27 USD/kWh with a payback period of 8 years and an ecological efficiency of 94.95% [151].



Similar to dry reforming, catalysts play an important role in steam reforming. Ni and Rh/Ni based catalysts are usually selected for steam reforming [152–154], while Cu/Fe/Cr and Cu/Zn based catalysts are often used for the WGS reaction [147]. Carbon formation during steam reforming is less of a concern compared to dry reforming, however, it is not negligible. Using biogas alone as the input may cause carbon formation. Therefore, extra oxidizing agents (CO₂, air, and steam) can be added to reduce carbon formation [154,155]. As noted, excess steam addition successfully inhibited carbon formation and achieved almost complete CH₄ conversion of > 98% [147]. To obtain high purity H₂ gas, a purification process will be needed to separate H₂ from the steam reforming products.

5.3. Partial oxidative reforming

Partial oxidative reforming (POR) refers to partial oxidization of CH₄ using oxygen or air to produce syngas (Eq. (10)). POR is an exothermic reaction and therefore can be combined with dry reforming or steam reforming to provide heat. The combination of steam reforming and POR is known as autothermal reforming (ATR), which is also commonly used for H₂ production [156]. POR is the dominant process at temperatures lower than 600 °C [157], while dry or steam reforming dominates at temperatures higher than 600 °C. In industrial practices, these three reforming processes can occur simultaneously in one reactor, named tri-reforming, producing syngas with a desirable H₂/CO ratio by manipulating the amounts of reforming reagents [158,159].



Considerable efforts have been made to examine the performance of POR. Both non-noble metal (e.g. Ni, Co) catalysts and noble metal (e.g. Rh, Ru) catalysts have been employed. Noble metals have been shown to be more active and less sensitive to coke formation, while non-noble metal catalysts were more economically favorable. The recent studies have used a micro-reactor and plasma for biogas POR. For instance, Izquierdo et al. [154] used a micro-reactor for biogas POR (60% CH₄ and 40% CO₂), and noted that both the productivity and the turnover frequency (moles of converted CH₄ per mole of active metal and per second, respectively) in the micro-reactor was about one order of magnitude higher than those achieved in a conventional fixed bed reactor; while the plasma-shade reactor was shown to have several significant advantages, including high feed flexibility and sulfur tolerance, long durability, and fast response. Increasing the O₂/CH₄ ratio was also found to enhance syngas production and reduce energy demand in biogas POR [160].

Currently, industrial syngas/hydrogen production uses natural gas or coal as the feedstock, while syngas production from biogas has been extensively studied in lab scale tests. Cleaned biogas that contains CH₄ and CO₂ can be directly used for dry reforming, steam reforming, and autothermal reforming, while purified biomethane can be used for POR. Biogas impurities such as H₂S and NH₃ can compete with CH₄/CO₂/H₂O for catalyst active sites and sulfur formation may deactivate catalysts. Therefore, economically favorable catalysts that tolerate biogas impurities and carbon deposition are needed for large-scale syngas/hydrogen production. Plasma may be a promising approach to reduce carbon deposition, while its challenges are cost and scalability. Steam reforming and autothermal reforming are widely used for hydrogen production, while dry reforming and partial oxidative reforming provide starting materials for Fischer–Tropsch synthesis. Technical advantages and disadvantages of these reforming methods are summarized in Table 8.

Economic analysis of reforming mainly focuses on hydrogen production via steam reforming of methane. For a typical facility

Table 8
Comparison of different methane reforming methods.

Methods	Advantages	Disadvantages
Dry reforming	Can use both CH ₄ and CO ₂ in biogas; high conversion efficiency.	Carbon formation; moderate selectivity; side reaction consumes hydrogen; high operating temperature and energy demand; catalyst can be expensive.
Steam reforming	Produces high-purity hydrogen fuel; low carbon formation; widely used for hydrogen production.	Needs to remove H ₂ S and add oxidizing agents; high operating temperature and energy demand; catalyst can be expensive.
Partial oxidative reforming	High energy efficiency; relatively low operating temperature; can be combined with other reforming methods.	May completely oxidize methane to CO ₂ and H ₂ O; limited industrial application.
Autothermal reforming	Produces high-purity hydrogen fuel; high energy efficiency; can use both CH ₄ and CO ₂ in biogas.	Complex process control; needs multiple catalysts; relatively unstable.

providing 120,500 kg hydrogen per day using natural gas as the feedstock, the direct capital cost could be about US \$30 million and the production cost (includes capital, operating, and maintenance cost) could achieve US \$0.83 per kg of hydrogen, or equivalently US \$0.22 per liter gasoline [161]. If biogas was employed as the feedstock, with a payback period of 8 years and at a small scale, the hydrogen production cost would be increased to US \$0.27 per kWh, or equivalently US \$2.39 per liter gasoline [151]. When dry reforming was combined with steam reforming of methane, its cost was up to 10% higher than the sole steam reforming system, but it had a lower carbon footprint [162].

6. Methanol for gasoline production

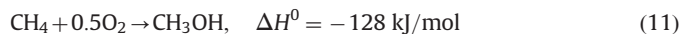
Methanol can be used as a transportation fuel and also can be upgraded to gasoline via the methanol-to-gasoline (MTG) process. Methanol was proposed as a transportation fuel or fuel blend after the first oil crisis in 1973. Thereafter, several programs were carried out to produce methanol and to manufacture vehicles using methanol, mostly in California and New York. Vehicles using 85% methanol with 15% additives of choice (M85) have been tested by several major auto companies. In China, M5, M10, M15, M85, and M100 are produced and sold in markets, especially in the Province of Shanxi. In 2007, official consumption of M15 in China was 530,000 tonnes [163]. Compared to gasoline, methanol is highly toxic, but can reduce emissions of CO₂, hydrocarbons, and NO_x. The MTG process, which was first invented by Mobil Oil in the 1970s [164], converted methanol to gasoline over ZSM-5 catalysts. Optimization of the MTG process and ZSM-5 catalysts has been extensively studied and a few reviews are available [18,165,166]. Therefore, the present review only focuses on methanol production from biogas.

Currently, methanol is primarily produced from fossil fuels, while methanol produced from biomass, often known as bio-methanol, has increased in recent years. About 200,000 tonnes of bio-methanol was produced in 2012 and the global production capacity of bio-methanol is projected to be over 1 million tonnes in the next few years [167]. Most facilities produce bio-methanol via biomass gasification followed by catalytic conversion of syngas to methanol. Life cycle analysis showed that bio-methanol can reduce greenhouse gas emissions by 25–40% compared to methanol produced from fossil fuels [167]. Biogas can also be converted into methanol via either direct or indirect approaches. Direct conversion methods include partial oxidation of methane, photo-catalytic conversion, and biological conversion, while the indirect conversion method involves biogas reforming to syngas and subsequent conversion to methanol via FTS.

6.1. Partial oxidation of methane

Partial oxidation of methane (POM) to methanol, as shown in Eq. (11), is probably the most commonly used method for methanol production. The POM process was first reported in 1931 [168], and has been extensively studied thereafter. The mechanism, reaction efficiency, and selectivity were reviewed in the 90s [169,170], and the applied catalysts were summarized recently [171]. In general, this reaction is carried out with catalysts at a very high pressure of 0.5–15 MPa to achieve a sufficiently high yield of the target products [172]. In recent years, conversion at atmospheric pressure but extremely high (700–750 °C) temperature has been tested with successful outcomes [173]. One example is the study carried out by Benlounes et al. [173] who employed hetero-poly-compound catalysts (NH₄)₆HSiMo₁₁FeO₄₀, (NH₄)₄PMo₁₁FeO₃₉, and H₄PMo₁₁VO₄₀, and noted that the methanol selectivity reached up to 31.34%. Another recent study of POM used non-thermal plasma

as it can be conducted under ambient conditions [191]. This method was shown to be very attractive and results were comparable to catalytic POM. CH₄ conversion of 30% and methanol selectivity of up to 40% were reported by Nozaki et al. [174,175] who worked on a flow-type, micro-scale, non-equilibrium plasma reactor. The major concern of the non-thermal plasma method is the scalability as these tests were operated in very small (< 2 mm inner diameter) reactors.



6.2. Photo-catalytic conversion

Photo-catalytic conversion of CH₄ to methanol uses photo-generated hydroxyl radicals to react with CH₄ to generate methyl radicals (CH₃•), which in turn react with an additional water molecule to produce methanol and hydrogen. Providing sufficient hydroxyl radicals is the key for methanol production. Early studies used 185 nm and 254 nm photons for the generation of hydroxyl radicals with a UV light source, e.g. mercury lamp. One example is from a study that at atmospheric pressure and a temperature of 90 °C, CH₄ was converted to methanol (70%), formic acid (11%), and ethanol (5%) [176]. Later, generation of hydroxyl radicals using 355 nm UV light over a semiconductor photocatalyst was examined by Gondal et al. [177,178], at room temperature. Their maximum conversion selectivity of CH₄ to methanol was 29%, 21%, and 20% using WO₃, TiO₂, and NiO, respectively. More recently, Hameed et al. [179] showed that impregnation of WO₃ with silver (Ag) can enhance the absorption of photons and increase the lifetime of excited states, thus improving the conversion efficiency. To avoid using UV light, Taylor et al. [180–182] developed a new method that employs visual light to generate hydroxyl radicals. A semiconductor photocatalyst, LaWO₃, was applied. The reactions involved in this method are shown in Eqs. (12)–(17) [180]. His results showed that at 1 MPa and 94 °C, the photocatalytic reaction produced 1.7 g methanol per g catalyst - per h in the steady-state mode and 43 g methanol per g catalyst - per h when hydrogen peroxide solution was added.



6.3. Biological conversion

Biological conversion of CH₄ to methanol is another promising approach. In nature, there are two groups of bacteria that can activate the stable C–H bond of CH₄ under ambient conditions. One is ammonia-oxidizing bacteria (AOB), which utilize ammonia as an energy source and partially oxidize CH₄ to methanol [183]. However, AOB generally produce only a small amount of methanol, since they are sensitive to ammonia and methanol. The other group is methanotrophic bacteria which are able to use CH₄ as their sole source of carbon and energy [184]. Most methanotrophic bacteria are obligate strains that only use one-carbon substrates, while some are facultative strains that can grow on one-carbon and multi-carbon substrates.

All methanotrophic bacteria use methane monooxygenase (MMO) to activate and convert CH₄ into methanol. In general, there are two types of MMOs, i.e. soluble MMO (sMMO) [185] and

Table 9
Biological production of methanol from methane.

Bacteria	Medium	MDH inhibitors	T (°C)/pH	Methanol productivity ^a (g/g-dry cell/h)	CH ₄ conversion (%)	Source
<i>Consortium</i>	phosphate buffer +NMS	N/A	30/7.0	N/A	58	[194]
<i>Consortium</i>	NMS	NaCl	30/7.0	N/A	80	[194]
<i>Consortium</i>	NMS	NH ₄ Cl	30/7.0	N/A	80	[194]
<i>Consortium</i>	NMS	EDTA	30/7.0	N/A	43	[194]
<i>Consortium</i>	NMS	NaCl	30/7.0	0.139	N/A	[194]
<i>Ms. trichosporium</i>	phosphate buffer+Formate	MgCl ₂	35/6.4	0.085	27	[195]
<i>Ms. trichosporium</i>	phosphate buffer+formate	Cyclopropanol	30/7.0	0.0051 ^b	71	[196]
<i>Ms. trichosporium</i>	phosphate buffer+formate	Cyclopropanol	25/7.0	0.049	61	[192]
<i>Ms. trichosporium</i>	phosphate buffer	MgCl ₂	32/7.0	1.39 × 10 ⁻⁶	N/D	[197]
<i>Ms. trichosporium</i>	phosphate buffe+formate	NaCl	30/7.0	0.011	N/D	[198]
<i>Ms. trichosporium</i>	phosphate buffer+formate	NaCl/EDTA	25/7.0	0.046	N/D	[199]
<i>Ms. trichosporium</i>	Phosphate buffer+formate	Phosphate/MgCl ₂	30/7.0	0.002	> 60	[200]
<i>Ms. trichosporium</i>	Phosphate buffer+ formate	Phosphate	30/7.0	0.19	N/D	[201]
Unknown	NMS+vitamins	N/A	N/A	0.069–0.138	N/D	[189]

^a Methanol production data were calculated from original publications.

^b Based on wet weight of cell.

particular MMO (pMMO) [186,187]. The sMMO is often found in bacterial cytoplasm in copper-deficient environments, while pMMO, a membrane protein, is found in copper-saturated environments. The structure and function of the sMMO and pMMO have been reviewed by Park and Lee [171]. One major difference between the two MMOs is that Cu can enhance the activity of pMMO, but is inhibitory to sMMO. NADH is usually added as an electron donor for the methanol production reaction as shown in Eq. (18). Since NADH is expensive, a much cheaper alternative, H₂O₂, can be used as a source of both oxygen and electrons for the reaction with similar conversion results to that using NADH [188].



Purified MMO is normally not stable and requires electron donors for the catalysis of CH₄ oxidation [171]. Alternatively, whole cells of methanotrophic bacteria can be used to accumulate methanol by manipulating culture conditions [189]. Under normal conditions, methanotrophic bacteria will convert the methanol into formaldehyde using methanol dehydrogenase (MDH) (Eq. (19)), and eventually convert formaldehyde into biomass or CO₂ with other enzymes. In order to accumulate methanol, MDH inhibitors such as EDTA [190], MgCl₂ [191], high concentration salts [191], and cyclopropane-derived reagents [192] were added to the reaction system. When MDH is inhibited, additional electron donors (such as formate) are needed to maintain cell vitality.

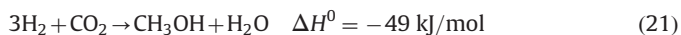
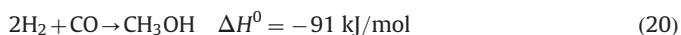


The conditions and performance of biological conversion of CH₄ to methanol with methanotrophic bacteria are shown in Table 9. *Methylosinus trichosporium* OB3b was the most commonly employed strain, while the other bacteria were rarely tested. The biological conversion was usually conducted in mineral media prepared in phosphate buffer (12.9–20 mM, pH 6.4–7.0) with MDH inhibitors and formate. Production rates of 1.39 × 10⁻⁶–0.19 g methanol per g-dry cell per h, and CH₄ conversion rates of 27–80% were reported. Compared to thermal catalytic methods, biological conversion has several advantages, such as being operated under mild conditions and achieving higher conversion efficiency. Furthermore, methanotrophic bacteria can adapt to various environments, e.g. lake sediments, deep oceans, wetland, and landfills, due to their biological diversity. For example, Criddle et al. [193] reported that one methanotrophic bacterium, *Methylocystus parvus* OBBP, was able to utilize dirty biogas without

costly purification, and Corder et al. isolated two methanotrophs from anaerobic digester effluent but without further identification [189]. However, low methanol productivity is a major concern for biological methods.

6.4. Indirect conversion

Indirect conversion of biogas to methanol involves the first step of biogas reforming and the second step of methanol synthesis. The second step is governed by two exothermic reactions as shown in Eqs. (20) and (21). The liquid-phase methanol synthesis process (LPMeOH) is a typical conversion process developed by the Eastman Chemical Company [202]. In this process, methanol is produced with a finely powdered Cu/Zn/Al₂O₃ catalyst dispersed in an inert liquid. The slurry-phase of reactants promote heat transfer, thus creating an isothermal environment in the conversion reactor [203]. This process is capable of using CO-rich syngas for methanol production. Trickle bed reactors, which have also been used for methanol production, co-currently flow feed gas and the solvent over a bed of catalyst to facilitate heat dissipation. This system showed a higher methanol yield and syngas conversion rate compared to fixed bed or slurry reactors [204]. More recently in industry, a multi-slit integrated micro-packed bed reactor-heat exchanger was used for methanol synthesis at 8 MPa and 523 K, and showed near equilibrium conversion at a low contact time of about 470 ms-g/ml [205]. Besides Cu/ZnO/Al₂O₃, a variety of other catalysts such as Cu/ZrO₂, ZrO₂/CuZnO, Pd/CeO₂, Mo(CO)₆, and Ni/Mo have also been tested [206–209]. Due to the development of conversion methods, the cost for methanol production from biogas has been decreased from 4.47–5.38 USD/liter in 1991 to 1.55–2.01 USD/liter in 2006 [163].



Given the dramatic differences among the above mentioned conversion methods, comparison of these methods is difficult. The indirect method involves two steps, while all the others need only one step. Except for the biological conversion method, the methods require a careful selection of catalysts. To date, the indirect method and partial oxidation method have been commercially used in industry, while the photo-catalytic method and biological conversion have been studied at bench scale. Table 10 shows both the advantages and disadvantages of these four methods.

Table 10
Advantages and disadvantages of four methods that convert methane to methanol.

Conversion methods	Advantages	Disadvantages
Partial oxidation	High methane conversion rate, high reaction rate	High pressure requirement, catalyst can be expensive
Photo-catalytic	Low energy input; uses visual light; high selectivity	Low conversion rate, low reaction rate
Biological	Low energy input, high selectivity	Low productivity, chemical instability of enzyme, high cost associated with enzyme usage
Indirect	High selectivity, high productivity	High energy input

Industrial natural gas based methanol usually costs 100–200 EUR per tonne, or US \$0.13–0.27 per kg [167]. A case study analyzed the cost of an integrated methanol and electricity plant with a capacity of producing 1.7 million tonne of methanol per year [210]. Its capital cost was estimated to be US \$1.25 billion and the operating cost was US \$0.20 per kg methanol; with that, a payback period of less than 5 years was expected. Another study showed that the capital costs of a methanol plant producing 10,000 tonne of methanol per day were comparable by using either partial oxidation method or indirect method [211]. As the MTG process is not included in this review, the overall economic evaluation of gasoline production from biogas will not be addressed.

7. Ethanol and higher alcohols

Using biogas or biomethane for ethanol and higher alcohols production is of increasing interest, due to their high energy density and low carbon and particulate matter emissions. Ethanol/bioethanol blends, e.g. E85, have been widely used, are provided by most gas stations in the U.S., and their feasibility has been reviewed previously [212]. Currently, no vehicle is known to be approved by the manufacturer for use with 100% butanol, but BP and Dupont have engaged in a joint venture to produce and promote butanol fuel. E85B (85% ethanol and 15% butanol) has been proposed so that existing E85 internal combustion engines can run on 100% renewable fuels. To-date, availability of direct conversion of CH₄ to ethanol and higher alcohols is still limited, while indirect conversion with syngas as the intermediate has been extensively researched. To-date, commercial production of ethanol from biogas was only tested by a few start-up companies, and the production cost was reported to be US \$1.25–2.35 per gallon, or equivalently, US \$0.50–0.94 per liter gasoline [213].

7.1. Direct approaches

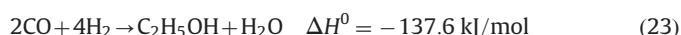
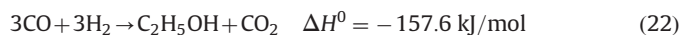
In 1996, Exxon patented a technology that can directly convert CH₄ into ethanol and methanol via a catalytic approach [214]. This method involved the reaction of CH₄ with an acidic (pH=1–3) aqueous solution of an electron acceptor, e.g. Fe₂(SO₄)₃ or Fe(CIO₄)₃, to produce mixtures of ethanol and methanol. Noble metal catalysts, such as platinum or palladium, having a diameter of at least 10 nm, were preferred. The reaction occurred at a temperature of 60–100 °C. Details about utilization of this method have not been released. No direct approach for butanol production from biogas/biomethane has been reported.

7.2. Indirect approaches

Indirect approaches usually involve the first step of biogas reforming to syngas and the second step of converting syngas to higher alcohols. There are biological and catalytic approaches to carry out the second step.

7.2.1. Syngas fermentation

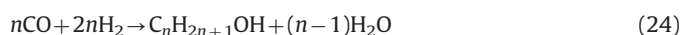
Syngas-fermenting microorganisms use the acetyl-CoA pathway to produce ethanol, acetic acid, butanol, and butyrate from syngas. Commonly used microorganisms are *Clostridium ljungdahlii*, *Clostridium carboxidivorans*, *Clostridium autoethanogenum*, *Clostridium ragsdalei*, *Eubacterium limosum*, and *Alkalibaculum bacchi* [215–218]. H₂ serves as an electron source while CO provides both electron and carbon for the conversion via hydrogenase and carbon monoxide dehydrogenase enzymes, respectively. The overall reactions are shown in Eqs. (22) and (23), and depend on the H₂/CO ratio [219]. Ethanol and butanol production via syngas fermentation is very attractive due to the high specificity of biocatalysts, operation at ambient conditions, and no concerns of metal poisoning. To date, the maximum ethanol yield was found to be 48 g/L-reactor, while most other studies showed a yield of lower than 12 g/L [220]. With regard to n-propanol and n-butanol, their maximum yields were 6 g/L and 1.11 g/L, respectively [218].



The major concerns in syngas fermentation for alcohol synthesis are the gas-to-liquid mass transfer limitation and low yield of higher alcohols [220]. A hollow fiber membrane reactor and trickle-bed reactor have been designed to enhance mass transfer. In a hollow fiber membrane reactor, cells grow onto membranes either by forming a biofilm on the flat surface of the membrane or by coating the surface pores to increase their direct contact area with the gas. In a trickle-bed reactor, gas and liquid flow counter-currently in the reactor, with fermenting cells growing on the surface of packing media to enlarge the contact surface area [218,221,222]. The low yield can also partially be attributed to the inhibitory effects of impurities in syngas such as NH₃, NO, and H₂S. For instance, NH₃ can be rapidly converted into ammonium and inhibit hydrogenase activity and cell growth [223], and NO higher than 40 ppm also becomes a non-competitive inhibitor of hydrogenase activity [224]. A previous review has covered the related inhibitory effects [225]. One possible strategy to resolve the inhibition issue is to culture mixed fermenting microorganisms that tolerate the impurities.

7.2.2. Catalytic conversion

Catalytic conversion of syngas offers a promising route for ethanol and higher alcohol synthesis (HAS). The overall stoichiometric reaction is summarized in Eq. (24), and is usually operated at a high pressure of about 20 MPa and a temperature of 300–400 °C. To-date, at least one patent has been claimed for the alcohol production process from syngas [226], and the National Renewable Energy Laboratory and The Dow Chemical Company recently worked on the process design and economic evaluation for ethanol production from biomass [227]; however, no industrial application has been reported yet



To obtain decent productivity, novel catalyst design is critical. The catalysts should have sufficiently active sites, catalytic stability in syngas, and high selectivity towards ethanol and higher alcohols. The main problem in catalytic conversion lies in the fact that the catalysts need to be efficient in breaking the C–O bond to convert long chain intermediates $C_xH_y\cdot$, and hydrogenating $C_xH_y\cdot$, $CO\cdot$ intermediates into alcohols, but not too strong, as high hydrogenation activity leads to termination into C_xH_y [228]. The catalysts for HAS from syngas can be divided into four categories: modified methanol synthesis catalysts (e.g., alkali-doped Cu/Zn/ Al_2O_3), modified Mo-based catalysts, noble metal catalysts (e.g., Rh, Pd), and modified FTS catalysts (e.g., Fe, Ni, Co–Cu) [229]. Modified methanol synthesis catalysts exhibit the highest selectivity and activity for alcohol production in terms of CO conversion; however, methanol is the predominant alcohol product and the selectivity of higher alcohols is limited. Modified Mo-based catalysts are employed at relatively high temperature (200–320 °C) and high pressure (1.6–9.7 MPa) for HAS, and can have an alcohol selectivity of 25–71% [229]. Noble metal catalysts, such as Rh-based catalysts, show excellent catalytic performance for HAS, especially high selectivity towards ethanol at operating temperatures of 150–250 °C and pressures of 0.1–2.5 MPa [228]; however, they are too expensive for commercialization. Therefore, it is urgent to develop comparable but less expensive alternatives. Modified FTS catalysts, such as Cu–Co and Cu–Fe based catalysts [230,231], are one of the most promising candidates for HAS from syngas because of their relatively low costs and high activities for HAS. The modified FTS catalysts were also shown to be able to tolerate sulfur containing compounds, such as H_2S [232].

8. Perspectives

Among all the transportation fuels that can be produced from biogas, Bio-CNG and LBG have been commercially produced via biogas compression and liquefaction, respectively. Hydrogen and syngas also have been commercially produced via reforming of natural gas, while biogas based reforming is emerging. With regard to methanol production, partial oxidation of methane and an indirect approach have been commercialized, while the biological approach has been extensively studied and the photocatalytic approach is of interest to a few research groups. For ethanol and higher alcohols production, direct conversion of CH_4 to ethanol and indirect catalytic conversion have been patented, but there are no publicly available reports about the commercialization of these methods. Syngas fermentation for ethanol production is being commercialized by a few start-up companies such as LanzaTech Inc. and Coskata Inc. In the near future, the market shares of Bio-CNG and LBG are expected to increase rapidly as the technologies have been well established and they are economically and environmentally favorable, while converting biogas to methanol, ethanol, and higher alcohols is envisaged to be main research pursuits, given the current progress and their potential as transportation fuels.

Several challenges, including CH_4 activation barriers, low mass transfer efficiency, and poor end product selectivity, need to be resolved to produce alcohols from biogas or biomethane. CH_4 activation using catalytic methods is efficient but can be costly, while biological approaches may be promising as they usually require no expensive metal catalysts and can be carried out at mild conditions. A potential approach is to genetically engineer microorganisms to enable breaking the C–H bond with or without sunlight. Biological conversion of biogas to methanol has been studied for years using various species, however, more work needs to be done to improve its productivity [233]. Gas-to-liquid mass transfer is a limiting step for biological approaches; therefore,

novel reactor design is needed. Besides the trickling-bed reactor, an entirely new, ultra-thin, stacked plate bioreactor was recently proposed by a research group at Oregon State University [234]. As alcohols are generally toxic to microbes, an efficient alcohol extraction procedure is also needed. End product selectivity is a challenge for both catalytic and biological approaches, especially for producing higher alcohols. For catalytic approaches, modified FTS catalysts would be a major component of the solution as they have relatively high conversion selectivity and productivity with an affordable price, while biological approaches will most likely rely on developing highly selective reaction promoters and inhibitors.

To improve energy efficiency and productivity, there is growing interest in direct conversion of biogas or CH_4 to alcohols, especially via biological approaches. In recent years, the U.S. Department of Energy ARPA-E program has awarded a few related cutting-edge research projects [234]. For instance, researchers from the University of Delaware proposed to engineer microbes to directly produce methanol from CH_4 and then convert methanol to butanol. In this process, CO_2 will be recaptured and reused in the proposed metabolic pathway so that no CO_2 emissions will be generated [235]. Researchers from the Massachusetts Institute of Technology aimed to integrate CH_4 activation and fuel synthesis into one step and use nitrate instead of oxygen to oxidize CH_4 to increase the conversion energy efficiency [234,236]. If successful, these studies will greatly advance the biogas based transportation fuel production technologies.

It is anticipated that further development of these technologies will not only provide environmentally friendly transportation fuels but also reduce the cost for waste management. All of the biogas based transportation fuels have much lower greenhouse gas and particulate matter emissions during their life cycle when compared to traditional fossil fuels. As biogas is generated from wastes, upgrading biogas to transportation fuels will increase its value and improve the economic feasibility of AD as a waste management method. Therefore, converting biogas to transportation fuels is promising and is a necessary component of solutions for future energy and environment.

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