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A Review of Biogas Utilisation, Purification and Upgrading Technologies

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Abstract Biogas is a valuable renewable energy and also a secondary energy carrier produced from biodegradable organic materials via anaerobic digestion. It can be used as a fuel or as starting material for the production of chemicals, hydrogen and/or synthesis gas etc. The main constituents of biogas are methane (CH_4) and carbon dioxide (CO_2), with various quantities of contaminants, such as ammonia (NH_3), water vapour (H_2O), hydrogen sulfide (H_2S), methyl siloxanes, nitrogen (N_2), oxygen (O_2), halogenated volatile organic compounds (VOCs), carbon monoxide (CO) and hydrocarbons. These contaminants presence and quantities depend largely on the biogas source, which could be anaerobic digestion of many substrates and landfill decompositions. The removal of these contaminants especially H_2S and CO_2 will significantly improve the quality of the biogas for its further uses. In parallel, biogas upgrading market is facing challenges in term of operating costs and energy consumption. The selection of appropriate technology depends on the specific biogas requirements, site specific, local circumstances and is case sensitive. This paper reviews the present state-of-the-art of biogas cleaning and upgrading technologies, including its composition, upgrading efficiency, methane recovery and loss. In addition, biogas production, utilization and the corresponding requirements on gas quality for grid injection and vehicle usage are investigated. Based on the results of comparisons of various technologies, recommendations are made on further research on the appropriate low cost technologies, especially using solid waste as low cost materials for biogas purification and upgrading.

Introduction

Biogas is a renewable energy resource that can be an alternative solution for the world insatiable energy demands and at the same time help in reducing waste and the greenhouse gases (GHG) emissions. It is also regarded as carbon neutral because the carbon in biogas comes from organic matter (feedstocks) that captured this carbon from atmospheric CO_2 over relative short timescale.

Biogas is produced from the methanation of biomass and organic wastes from sewage sludge anaerobic digestion, commercial composting, landfills, biomass gasification (thermos-chemical production process), animal farm manure anaerobic co-digestion with energy crops, agro-food industry digestion facilities in both mesophilic (35 °C) and thermophilic (55 °C) conditions. These activities produced biogas that is rich in methane (CH_4), with higher heating value range from 15 to 30 MJ/Nm^3 [1, 2]. Raw biogases from anaerobic degradation of sewage sludge, livestock manure, and agro-industrial bio-waste are generally composed of methane (55–70%), and carbon dioxide (30–45%). Other gases (contaminants) present are nitrogen (0–15%), oxygen (0–3%), water (1–5%), hydrocarbons (0–200 mg m^{-3}), hydrogen sulfide (0–10,000 ppm$_v$), ammonia (0–100 ppm$_v$), and siloxanes (0–41 mg Si m^{-3})

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[3, 4]. Biogas produced from landfills is some complex mixtures, which composed of methane (35–65%), carbon dioxide (15–40%), hydrogen (0–3%), carbon monoxide (0–3%), nitrogen (5–40%), oxygen (0–5%), water (1–5%), halogenated hydrocarbons (20–200 ppm_v Cl^-/F^-), hydrogen sulfide (0–100 ppm_v), ammonia (0–5 ppm_v), volatile organic compound (0–4500 mg/m^3), and siloxanes (0–50 mg Si m^{-3}) [3, 5–7]. Typical compositions of different types of biogas which are comparable with natural gas and the possible impact of the contaminants are shown in Table 1.

Carbon dioxide (CO_2) is a recalcitrant gas that reduces the density and decreases the calorific value of the biogas, but it is not toxic and corrosive like H_2S. This last one is harmful to the environment and corrosive to the metallic parts of engines, pumps, compressors, gas storage tanks, valves and reduce the lifespan of process equipment [7, 8]. Contaminative components in biogas have to be removed before any eventual utilization. Basically there are two steps involved in biogas treatment; cleaning (removal of harmful and toxic compounds such as H_2S, N_2, O_2, Si, H, VOCs, CO, and NH_3), and upgrading (adjustment of CO_2 content, to increase the calorific value of the biogas to optimal level). Biomethane is the final product which composed of CH_4 (95–99%) and CO_2 (1–5%), with little or no trace of H_2S [9]. Many biogas upgrading technologies has been developed in recent years, and their main differences are related to the nature of the operation. These include; physical, chemical, and biological, their efficiency and operational conditions, investment and maintenance costs. These technologies are still highly energy and chemical intensive, which has prompted the rapid development of biogas upgrading based on biotechnologies, because of their superior economic and environmental sustainability [10]. Therefore, as biogas upgrading market and technologies are rapidly evolving, there is need for frequent evaluation of these state-of-the-art technologies. This paper reviews the current available technologies for the removal of biogas contaminants, with special focus on H_2S, CO_2, H_2O, O_2, N_2, and siloxanes removal. The potentials and limitations of these technologies are also highlighted. In addition, new novel research by the authors on the valorization of calcium carbonate-based solid wastes, for removing the contaminants from the biogas stream, was also discussed.

Table 1 Parameters and composition of gases from different origins, impurities and their consequences [1, 12, 33]

Parameters	Unit	Biogas from AD	Landfill gas	North Sea natural gas	Dutch natural gas	Impact on biogas utilization
	MJ/Nm^3	23	16	40	31.6	
Lower heating value	KWh/Nm^3	6.5	4.4	11	8.8	
	MJ/kg	20	12.3	47	38	
Density	Kg/Nm^3	1.1	1.3	0.84	0.8	
Relative density	–	0.9	1.1	0.63	0.6	
Wobbe index, upper	MJ/Nm^3	27	18	55	43.7	
Methane number	–	>135	>130	73	–	
Methane (CH_4)	Vol%	60–70	35–65	85–92	80–90	
Heavy hydrocarbons	Vol%	0	0	9	9	
Water vapour (H_2O)	Vol%	1–5	1–5	–	–	Corrosion in compressors, gas storage tanks and engines due to reaction with H_2S, NH_3, CO_2 to form acids
Hydrogen	Vol%	0	0	0	–	
Carbon dioxide	Vol%	30–40	15–40	0.2–1.5	0.2–1.5	Decreasing calorific value, anti-knock properties of engines and corrosion
Nitrogen, range	Vol%	0–0.5	15	0.3–1.0	14	Decreasing calorific value, anti-knock properties of engines and corrosion
Oxygen	Vol%	0	1	–	–	Corrosion, fooling in cavern storage, risk of explosion
Hydrogen sulphide	Ppm	0–4000	0–100	1.1–5.9	–	Corrosion, catalytic converter poison, emission and health hazards. SO_2, SO_3 are form
Ammonia (NH_3)	Ppm	100	5	0	–	Emission, anti-knock properties of engines and corrosion when dissolved
Total chlorine as Cl^-	Mg/Mm^3	0–5	20–200	–	–	Corrosion in engines

Recall of Biogas Production and Utilization

Due to its increased usage of biogas in many ways, such as production of heat and steam, electricity production and co-generation, vehicle fuel, feedstock for the production of bio-based chemicals and substrate in fuel cells, starting reactants in chemical processes, substitute for natural gas for domestic and industrial use, and gas grid injections [1], biogas production shows an increased trend in recent years. This is driven in Europe mainly by feed-in-tariffs, offered by different countries. This has led to the increase in biogas production plants in Europe from 17,240 with total installed electricity generating capacity of 8,339 MW at the end of 2014, a 18% increase compared to 2013. Germany leads the growth rate with 10,786 plants, followed by Italy with 1,491, UK 813, and France 733 [11]. The total amount of electricity produced from biogas is 63.3 TWh, enough for annual consumption of 14.6 million European. The major part of EU-27 renewable energy target (25%) by 2020 will be met by bioenergy [12]. According to Pike [13], the global power generation capacity will more than double in biogas production over the next decade, from 14.5 gigawatts (GW) in 2012 to 29.5 GW in 2022. Biogas can be deployed on both integrated and distributed basis, to meet demands in heat, power, and transportation markets and at the same time address a range of environmental issues.

It should be noted that the final use of biogas is determined by its composition, the upgrading process required, national framework such as tax systems, subsidies, availability of heat and gas grids. Different countries have different defined standard and specifications for utilization as vehicle fuel or for grid injection of upgraded biogas (Table 2). In Europe it is called gas grid injection and outside Europe, it is SoCalGas (Southern California Gas Company) "Rule 30", which is stricter than European one and even Pacific Gas & Electric's "Rule 21". This is because of incremental specification for 17 "constituents of concerns" (CoCs) trace elements (it identified 17 for landfill gas, and 9 for digester gas) [14, 15]. The energy content (calorific value) of biogas is that 1 Nm^3 (volume) of biomethane contains 10 kWh primary energy, equivalent to 36 MJ, while natural gas energy content is 11.0 kWh. Considering 1 L of petrol equals to 9.06 kWh, implying that 1 Nm^3 biogas corresponds to 1.1 L of petrol while 1 Nm^3 of natural gas corresponds to about 1.2 L of petrol. This is the energy content of biogas in relation to other fuels. Other biogas utilization technologies and H_2S requirements are shown in Table 3.

Table 2 Vehicle and grid injection specification standard requirement in some countries [4, 10, 14, 33]

Compound	Unit	Germany	Sweden	France	California	Switzerland	Netherlands	Spain
Wobbe index(H)	MJ/Nm^3	46.1–56.5	44.7–46.4	48.2–56.5	47.6–51.6	47.9–56.5	43.46–44.41	48.3–57.8
Lower (L)			37.8–46.8	43.9–47.3	42.5–46.8		*Unlimited	
Methane content	Vol%	–	≥97	≥86	–	≥96	≥85	≥95
Carbon dioxide	Vol%	≤6 (dry)	≤3	≥2.5[a]	3	≤4	≤6[b]	2.5
Hydrogen	Vol%	≤5	≤0.5	≤6	–	≤4	<12	–
Oxygen	Vol%	≤3	≤1	≤0.01	<0.2	≤0.5	≤0.5	0.01
$CO_2 + O_2 + N_2$	–	–	≤5	–	–	–	–	<4
H_2S	Ppm	<5	<15.2	≤5	88	≤5	≤5	15
Total sulfur	Ppm	<30	<23	<30	265	<30	<45	50
Mercaptans	Ppm	≤15	–	≤6	106	≤5	≤10	17
Ammonia (NH3)	Ppm	≤20	≤20	≤3	≤0.001 mol%	≤20	≤3	≤3
Siloxanes (Si)	mg m^{-3}				0.1 or free		≤5 ppm 6.2 (Si)	≤10
Halogenated compounds	mg m^{-3}	≤1	≤1	≤1[c] <10[d]	≤0.1 ppm	≤1	≤50[c] ≤25[d]	≤1
Water dew point	°C	Ground Temp	≤−5[e] ≤−9 at 200 bar	≤−5 at P_{max}	–	−8 at P_{max}	≤10 at 8 bar	≤2 at 7 bar

[a]France allows flexibility in O_2 and CO_2 under certain conditions

[b]Nertharlands also allowed <10–10.3 for regional grid

[c]Chlorine compounds

[d]Flourine compounds

[e]Ambient temperature

*Switzerland allowed unlimited gas injection

Table 3 Biogas utilization technologies and H_2S requirements [3, 16, 33]

Technology	H2S tolerance (ppm)
Heating (boilers) and stirling engines	<1000
Kitchen stoves	<10
Internal combustion engines	<500 ppm (depending on the kind of engine; it can be <50 ppm)
Turbines	<10,000
Micro-turbines	<70,000
Fuel cells	
Proton exchange membrane (PEM)	<1
Phosphoric acid fuel cell (PAFC)	<20
Molten carbonate fuel cell (MCFC)	<10 in fuel (<0.1–0.5 at the anode)
Solid oxide fuel cell (SOFC)	<1
Natural gas upgrade	<4 (variations among countries)

Biogas Upgrading Technologies

Biogas purification and upgrading had been researched extensively in recent years. Hosseini and Wahid [2] reviewed biogas purification processes with the focus on contaminants removal, while Ryckebosch et al. [7] reported on various techniques for biogas transformation regarding their conditions, functioning, bottlenecks and efficiency. Bauer et al. [16] reviewed the commercial technologies on biogas upgrading. Most recently, Munoz et al. [10] provided a state of the art review on the biogas upgrading technologies with emphasis on biotechnologies for CO_2, H_2S, Siloxanes and halocarbon removal. Sun et al. [12] worked on appropriate biogas upgrading technology, focusing on product purity and impurities, methane recovery and loss, upgrading efficiency, investment and operating cost.

From the literature, the main techniques for biogas upgrading and purification are: water scrubbing, adsorption (physical and chemical), cryogenic separation, membrane technology, biological upgrading and in-situ upgrading methods.

CO_2 Removal from Gas Stream

Removal of CO_2 is necessary in order to increase the density and calorific value of the gas to meet Wobbe Index quality and specifications (Table 2). The current technologies are: pressure swing adsorption, physical absorption (water and organic solvent scrubbing), chemical absorption, cryogenic separation, membrane separation, biological methane enrichment. These are discussed in the order of old, current trends, and future technologies and ideas.

3.1.1 Physical Absorption (Water Scrubbing and Organic Solvent Scrubbing)

The separation principle of absorption is based on different solubility of various gas components in a liquid scrubbing solution. The absorbed gas components are physically bound to the scrubbing liquid. In this case water is a selective absorbent and it is widely used in water scrubbing of biogas at an industrial scale, with 41% share of the global biogas upgrading market because of its less sensitivity to biogas impurities [17]. The solubility of CH_4 is 26 times lower at 25 °C than that of CO_2 [18]. Also according to Persson et al. [3], the different biding forces of the more polar CO_2 or H_2S and the non-polar methane are used to separate these compounds.

Therefore, H_2S can be removed together with CO_2 in principle because the solubility of H_2S in water is higher than that of CO_2. It is however advisable to separate the H_2S prior to CO_2 removal because the dissolved H_2S is very corrosive and odour nuisance can cause operational problem. Biogas scrubbing is carried out in a column packed with Pall or Raschig to support an efficient gas–liquid mass transfer, in a countercurrent (compressed gas at 6–10 bar the bottom and water pressures from the top) [7, 16]. The used water is regenerated in desorption column with, either air or steam that release the CO_2 from the water at a decreased pressure (Fig. 1). It should be noted that N_2 and O_2 cannot be separated because they are non-condensable. Energy consumption is for gas compression, recirculation pumps and water regeneration. Constant purging of water is necessary to avoid H_2S poisoning and fouling.

An organic solvent such as methanol and dimethyl ethers of polyethylene glycol (DMPEG) can be employed in CO_2 removal. The solvent can simultaneously absorb CO_2, H_2S and H_2O since they have higher solubility in polyethylene glycol than CH_4. The scrubbing and regeneration process is the same as water solvent (Fig. 1). The trade names for the solvents are Selexol® and Genosorb® and they exhibit higher affinity for CO_2 and H_2S than water by five times, especially Selexol®, which is a mixture of dimethyl ethers of polyethylene glycol [19]. As a result, smaller absorbent volume is needed with compact size and little pumping with the same quantity of biogas, thereby reducing the investment and operating cost. According to Bauer et al. and Sun et al. [12, 16], a consistent biomethane content of 96–98.5% and less than 2% methane losses, can be achieved in an optimized full-scale plant, with the similar energy consumption as water scrubbing [7, 8, 17]. This process can produce high purity CO_2, and additional drying of the upgraded gas is not necessary due to the fact that water and halogenated hydrocarbon (from landfill) are absorbed by glycol [3].
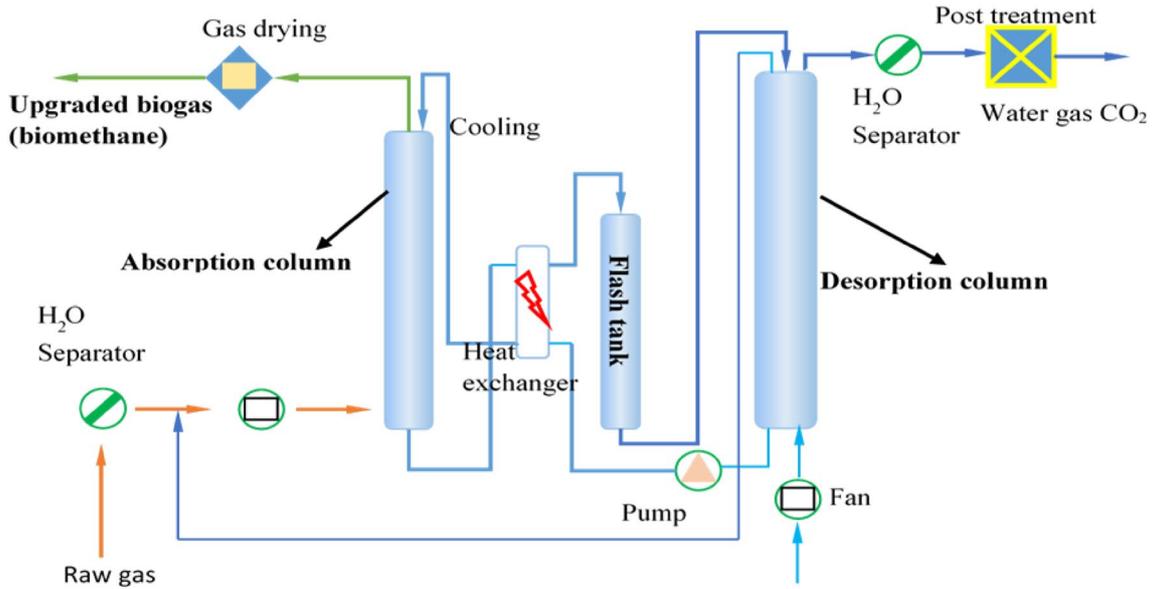
Fig. 1 Biogas upgrading by water scrubbing and organic solvent scrubbing to remove CO_2

3.1.2. Chemical Absorption

This is the same way as water/glycol scrubbing for biogas–liquid mass transfer principles, but chemical reaction takes place between the solvent and the absorbed substances. It relies on CO_2 reactive absorbents such as alkanol amines (mono ethanol amine (MEA)) or di-methyl ethanol amine (DMEA), and alkali aqueous solutions such as KOH, K_2CO_3, NaOH, $Fe(OH)_3$, $FeCl_2$ [20]. The unit consists of a packed bed (random or structural) coupled with desorption unit equipped with reboiler to simplify process configuration, with no risk of biomass growth as result of high pH of the amine solutions [4]. Amine solution is widely used to absorbed CO_2 and there is little or no methane losses (0.1–1.2%), with methane recovery greater than 99% because the chemical solvent reacted selectively with CO_2. Although some reports [7, 8, 16, 20] reported methane losses up to 4% due to CH_4 dissolution in alkanolamine. It also operated like water scrubbing countercurrent flow configuration, and H_2S should be treated prior to chemical scrubbing because of amine poisoning (Fig. 2). The regeneration is usually accomplished with steam or heat and CO_2 with purity of 93% reportedly recovered in the process [21]. Despite its high CO_2 removal efficiency, energy consumption is relatively high (high regeneration heat), there is likely possibility of salt precipitation and foaming to occur coupled with O_2 poisoning of amine and other chemicals [4, 21].

3.1.3 Pressure Swing Adsorption (PSA)

The process take place in vertical columns packed with absorbents under adsorption, depressurization, desorption and pressurization sequences, and the molecular sieves material is regenerated (Fig. 3). In the pressurized column methane-rich gas passed through while CO_2 is adsorbed. The most commonly used adsorbents are zeolite, activated carbon, activated charcoal, silica gel and synthetic resins. This can be used to separate CO_2, N_2, O_2 and H_2S from the gas streams by selectively adsorption of CO_2 over CH_4 onto the porous adsorbents with a high specific area, since CH_4 molecule is larger than the other gas molecules [4]. It is also advisable to dry (cool) the gas and also remove H_2S prior to CO_2 adsorption because H_2S will adsorbed irreversibly to the molecular sieves [6].

After saturation with CO_2, biogas is led to a new column, while CO_2 saturated column is stepwise depressurized (almost atmospheric pressure), to release CO_2/CH_4 mixture with high methane content, which is vacuum and recycle back to the PSA inlet. According to Bauer et al. [4], several columns were linked together to create a continuous operation and to reduce energy need for gas compression. The CH_4 recovery rate of 96–98%, with 2–4% methane losses had been reported [7, 16]. The off-gas must be treated (burnt in a flox burner) to avoid release methane to the atmosphere, or use for combustion.
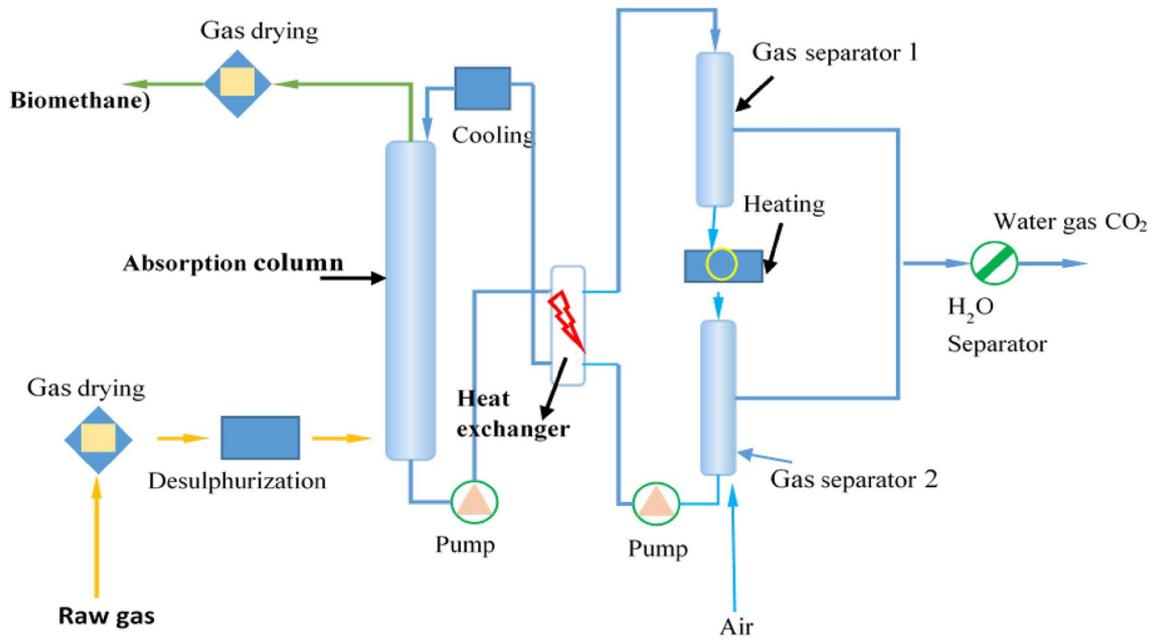
**Fig. 2** Biogas upgrading by chemical absorption (Amine scrubbing) of CO_2
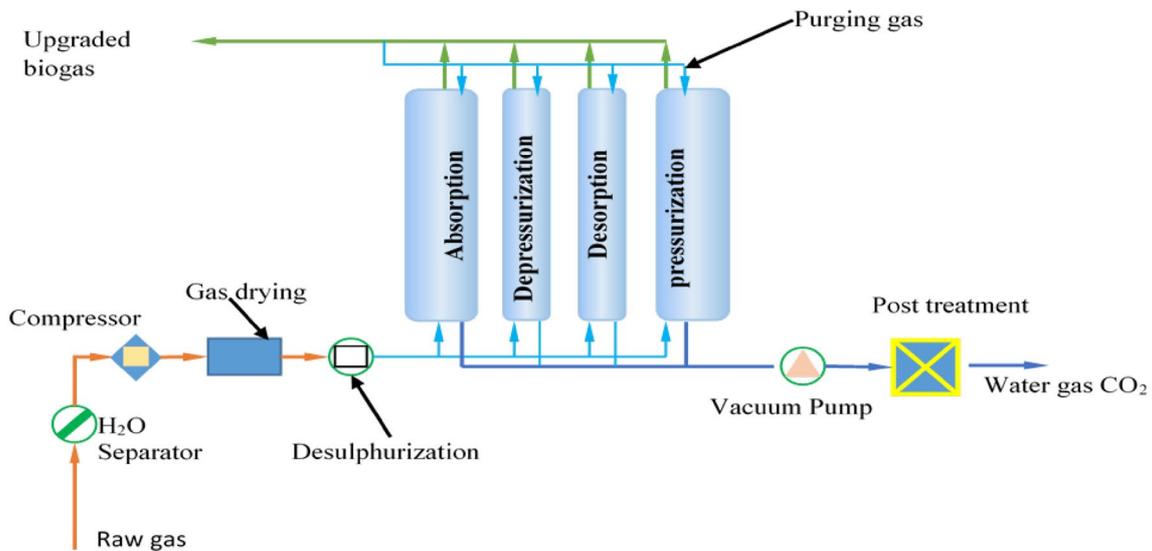
Fig. 3 Biogas upgrading by PSA of CO_2

3.1.4 Cryogenic Separation of CO_2

This new technology uses temperature difference to separate the gases. CO_2 has a boiling point of $-78\,°C$, while methane is $-160\,°C$, resulting in CO_2 separation from the biogas by cooling the gas mixtures at elevated pressure (Fig. 4). This difference in condensation temperatures can be exploited to separate other gases like N_2, O_2 and siloxanes from the biogas through condensation and distillation. According to Hosseini and Wahid [2], the process

is of specific value when the final product is liquid biomethane (LBM), which is equivalent to liquid natural gas (LNG). The process is more advantages for treating landfill gas, for pure CO_2 production (98%), high-purity methane with less than 1% losses and can be utilized directly for vehicles or injected to grid as gas. The energy consumption is however high with raw biogas compressed at 200 bar, which can amount to 5–10% of the biomethane produced [6, 12, 15].

Fig. 4 Flowsheet of cryogenic separation of biogas (removal of CO_2)
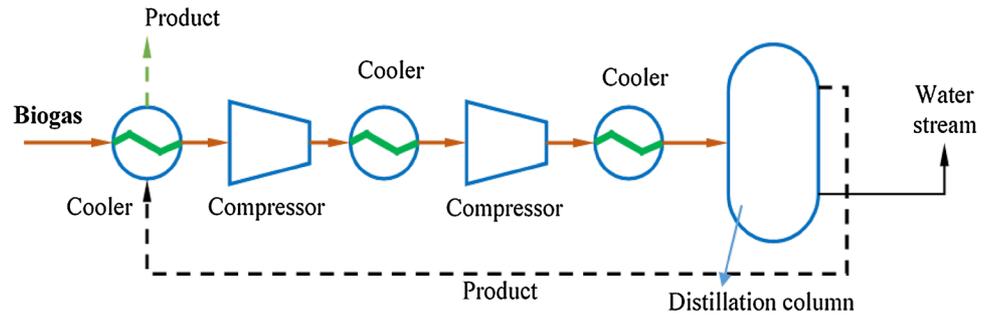
3.1.5. Membrane Separation

The separation is based on the selective permeability property of the membranes, which can be gas–gas separation (gas phase on both side of the membranes) or gas–liquid separation (liquid absorbs the H_2S and CO_2 molecules diffusing through the membranes). The liquid solution can be amine and the system is highly selectively compared to the solid membrane systems, and operated well at low pressure [3]. The material used is micro porous hydrophobic membrane, which separates the gaseous molecules stream flowing in one direction with the liquid flowing in countercurrent flow from the other side and diffused through the membrane. The amine solution can be regenerated with heating to release the CO_2, which can be collected separately (Fig. 5).

On the other hands, the gas–gas separation works at high pressure greater than 20–40 bar or at lower pressure of 8–10 bar, resulting in 92–97% methane production [16]. This technology allows CO_2, H_2S, H_2O, O_2 pass through the membrane to the permeate side while retaining CH_4 on the inlet side. Some methane losses are possible since the CH_4 may also pass through the membrane in an effort to achieve higher purity [3, 12]. Higher purity of CH_4 can be achieved with larger size or several membranes in series. Therefore, there is need to balance the desire for high purity methane and low methane loss. Recirculation of off-gases can help in reducing this loss. Membrane is based on different molecules of different sizes with different permeability through the membrane, and is also driven by pressure difference between the two sides of the membrane and the biogas temperature [7]. Deng and Hagg [21] worked on the efficiency of CO_2-selective polyvinylamine/polyvinylachohol blend membrane and reported that the optimal process can deliver 98% CH_4 purity. Scholz et al. [22] reviewed membrane based technologies used for commercial biogas upgrading. He reported that single stage permeation process are not able to produce high CH4 purity and simultaneously obtain a high CH4 recovery. He concluded that, multistage concepts are mandatory.

3.1.6 Hydrate Formation

The process was firstly proposed by Yoon and Lee [23] who investigated clathrate phase equilibrium for the water-phenol-carbon dioxide system based on the equilibrium partition of the components between gaseous phase and the hydrate phase. Kang et al. [24] used this principle to work on gas hydrate process of recovery of CO_2 from fuel gas. According to Tajima et al. [25], the basic mechanism of the separation process is a selective partition of the target component between the hydrate phase and the gaseous phase. Generally, the hydrate phase is stable under high pressure-low temperature conditions.


Fig. 5 Membrane biogas purification process combined with H_2S removal (hybrid system)
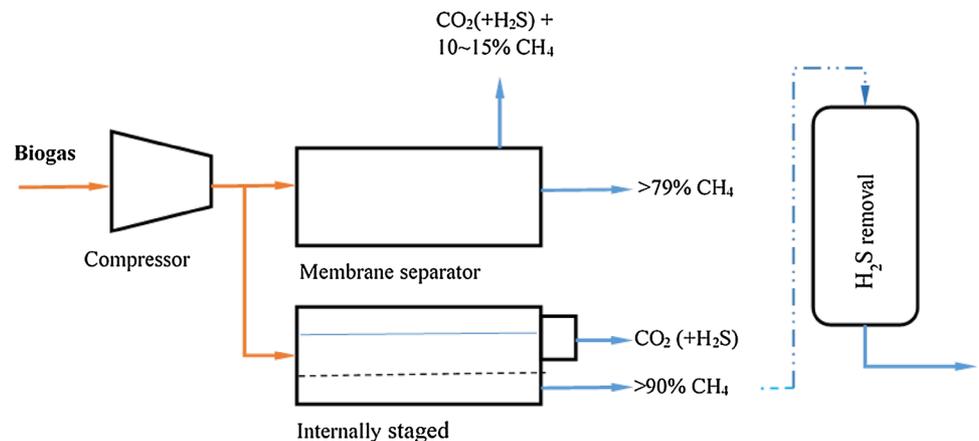
This has attracted other researchers to look at the possibility of employing this technology to reduce CO_2, H_2S, and other contaminants from biogas and syngas streams. For example, Wang et al. [26], investigated the recovery of hydrogen from refinery (hydrogen + methane) gas mixtures using hydrate technology, while Yang et al. [27] worked on progress and perspectives in converting biogas to transportation fuels. The process has also been successfully utilized to remove CO_2 from contaminated natural gas. According to [3], there was 16% reduction in the CO_2 content from CH_4/CO_2 ratio of 75/25%, but methane loss was still relatively high. It was also reported that the CO_2 capture by hydrate formation consumes a large amount of energy, as a result of high pressure required for hydrate formation [12, 25–27]. This technology can be improved upon to reduce energy consumption, methane loss and simplify the separation process for adaptable for future use.

3.1.7 Biological Methane Enrichment (Biotechnological)

Strevett et al. [28] reported the microbial conversion of CO_2 and H_2 to CH_4 based on the ability of hydrogenotropic methanogens capacity to use CO_2 as their carbon source and electron acceptor, and H_2 as electron donor in the energy yielding reaction.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (\Delta G_o = -131 KJ) \tag{1}$$

Other studies of CO_2 conversion using H_2 as electron donor were also reported in recent years. Kim et al. (2013) used CO_2 off-gases from electronic production waste to produce methane under mesophilic and thermophilic conditions. Luo et al. [30] worked on simultaneous H_2 utilisation in in-situ biogas upgrading with CH_4 content of 95% under various conditions, while Bauer et al. [4] investigated process performance and microbial activities during co-digestion of manure with whey. Several microorganisms' species from Archaeal family such as *Methanobacterium* sp., *Methanothermobacter* sp., *Methanococcus* ap., *Methanosarcina* sp., *Methanosaeta* sp., *Methanoculleus* sp. and *Methanospirillums* sp. were reported in stand-alone bioreactors and anaerobic digesters upgrading CO_2 to CH_4 by H_2 injection [10, 29, 30].

It is equally possible to upgrade syngas to methane since biomass gasification process contained CO, CO_2, H_2, based on the ability of methanogens to convert CO to CH_4 and CO_2, with the following reaction [10]:

$$4CO + 2H_2O \rightarrow CH_4 + 3CO_2 \tag{2}$$
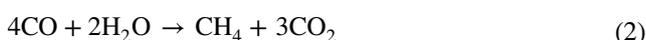
Also, Yan and Zheng [31] employed microalga photosynthesis to sequester anthropogenic CO_2 and reported that CH_4 content of the upgraded gas could reach 90–95%.

3.1.8 Perspectives on CO_2 Removal

Table 4 summaries the advantages and disadvantages of the technical alternatives and features of CO_2 removal from biogas streams. The chemical and physical absorption technologies are feasible and had been used widely in practice. Water as absorbent is cheap, efficient and environmentally friendly, but required intensive energy for pressurization and regeneration. More effective absorbents are very expensive and usually have negative environmental impacts. Yet, these technologies can be improved, especially their efficiency and reduction in their energy demand by looking at possibility of upgrading biogas at low temperature and pressure to save cost. Ideally, biogas produced exit digesters at minimum 35 °C, heat exchanger can be used to increase or decrease the heat need for various upgrading systems. For example, the saved heat can be used for water regenerations in water scrubbing, PSA, steam generation during the stripping of CO_2 for water and solvent recirculation.

Innovative approach to solvent based CO_2 absorption is required, and this must be economically viable with minimum environmental impacts. This will also depend on the selection of appropriate absorbents, the separation process, the intensity of the energy requirement, effective integration of biogas purification, and the upgrading process to save cost.

Cryogenic is a promising upgrading technology for CO_2 removal, especially with capability to produce liquid CO_2, which can be utilized in technologies that requires pure CO_2. It can also produce liquid biomethane (LBM) which is equivalent of liquid natural gas (LNG) for transportation fuel [1]. The energy consumption is very high for separating the gases into various components, but with recent interest in LBM production, the solution to the existing problem can be overcoming through research and development.

Hybrid systems involving the integration of two or more purifications and upgrading methods in order to exploit their advantages and also bridge their drawbacks is another possible option for CH_4/CO_2 separation. The integration of different technologies into one unit will lead to reduction in CH_4 losses, minimising capital cost and recurrent cost, reduce footprint of the conditioning systems. Innovative solution can overcome other impurities such as H_2S degradation or contamination of the absorbent, and thereby allow the absorbent to be easily and cheaply regenerated with minimum of gases concentration.

It is worthwhile noting that the valorization or the storage of CO_2 recovered is also an option in biogas upgrading. However, it is out of the scope of the review.

Table 4 Alternatives and technical features of CO_2 removal from gas streams [3–5, 7, 8, 10, 30]

Technology/alternatives	Advantages	Disadvantages
Absorption (water scrubbing)	High efficiency (>97% CH_4) Simultaneous removal of H_2S (when H_2S <300 cm^3/m^3) Capacity is adjustable by changing temperature or pressure Low CH_4 losses (<2%), tolerant to impurities, Regeneration possible	Expensive investment and operation Cost: 0.105 € m^{-3} (250 Nm^3/h) and 0.052 € m^{-3} (2000 Nm^3/h) Power cost: 0.4–0.5 kWh m^{-3} produce gas Clogging due to bacterial growth Possible foaming, low flexibility toward variation of input gas
Absorption (organic solvent–polyethylene glycol)	High efficiency (>97% CH_4) Simultaneous removal of organic components, H_2S, NH_3, HCN and H_2O Energetic more favorable than water Low CH_4 losses, regeneration possible with low-temperature waste heat	Expensive investment and operation Power cost: 0.21 kWh m^{-3} of gas Difficult operation Incomplete operation when stripping/vacuum (boiling required), reduced operation when dilution of glycol with water
Chemical absorption (Amines)	High efficiency (>99% CH_4) Cheap operation, regenerative, more CO2 dissolved per unit of volume compared with water, very low CH_4 losses (<0.1%) Power cost: 0.05–0.25 kWh m^{-3} of gas	Expensive investment, heat required for regeneration, corrosion, decomposition and poisoning of the amines by O_2 or other chemicals, precipitation of salts, foaming possible
PSA/VSA (Carbon Molecular sieves, Zeolites Molecular sieves Alumina silicates)	Highly efficient (95–98% CH_4), H_2S is removed, low energy used: high pressure but regenerative, compact technique, also for small capacities, tolerant to impurities	Expensive investment and operation, extensive process control needed, CH_4 losses when malfunctioning of valves
Membrane technology (Gas/gas or gas/liquid)	H_2S and H_2O are removed, simple construction, simple operation, high reliability, small gas flows treated without proportional increase of costs Gas/gas removal efficiency <92% CH_4 (1 step) or >96% CH_4, H_2O is removed Gas/liquid removal efficiency >96% CH_4, cheap investment and operation, Pure CO_2 can be produced	Low membrane selectivity: compromise between purity of CH_4 and amount of upgraded biogas, multiple steps required (modular system) to reach high purity, CH_4 losses Cost: 50 Nm^3/h (0.432 ct Nm^{-3}); 200 Nm^3/h (0.211 ct Nm^{-3}) Power cost: 0.22 kWh m^{-3} produce gas CH_4 losses <10%
Cryogenic separation	90–98% CH_4 can be reached, CO_2 and CH_4 in high purity, low extra energy cost to reach liquid biomethane (LBM)	Expensive investment and operation CO_2 can remain in the CH_4, High energy required for cooling Addition of H2, still on experimental basis (not on large-scale)
Biological removal Air/oxygen dosing digester slurry Biofilter/Biotrickling filter (BiogasCleaner®, Biopuric®, DMT filter®) Bioscrubber (Thiopaq™)	Removal of H_2S and CO_2 Enrichment of CH_4 No unwanted end products DMT filter® can handle air flow rates of between 10 m^3/h and 100,000 m^3/h without any problem	

H₂S Removal from Biogas Stream

Hydrogen sulfide along with other S bearing compounds (mercaptans etc.) are the most common contaminants in biogas and their quantity, which can vary from 100 to 10,000 ppm, depends largely on the composition of the organic matter (but, mostly protein-rich). They must be removed before any utilization because they are highly corrosive to pipes, pumps and engines and they have environmental concerns due to their conversion to sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4) [2]. Ammonia, like H_2S, is highly corrosive when combusted and can transformed into nitrogen oxides (NO_x), which are part of greenhouse gases that are causing climate change and polluting the environment. As such, H_2S and NH_3 need to be removed early in the upgrading process, preferably in the digestion chambers or in the gas stream of the upgrading process.

3.2.1 Physical and Chemical Absorption

The upgrading process takes place in conventional gas–liquid contactors (packed bed or spray towers) using either water or organic solvent in the physical absorption process or using aqueous chemical solutions to convert H_2S to elemental sulfur or metal sulfide [32]. Single pass absorption and regenerative absorption are commonly used, but high water consumption is needed without the regeneration step. Therefore, Selexol (mixture of dimethyl ethers of polyethylene glycol), which exhibits higher affinity for H_2S than water by five times can be used, resulting in smaller absorbent volume with compact size and require regeneration step [7]. This is suitable for the removal of low concentration of H_2S or in combination with CO_2 removal (Fig. 6).

To achieve an efficient H_2S mass transfer, the addition of chemical reagents, such as NaOH, $FeCl_2$, Fe^{3+}/MgO, $Fe(OH)_3$, Fe^{3+}/$CuSO_4$ and Fe^{3+}/EDTA

(ethylenediaminetetraacetate), will reduce liquid to gas ratio because of the quick chemical reactions with these solvent [7, 12]. Petersson and Wellinger [33] reported the reaction of H_2S with NaOH and produced soluble salt of sodium sulfide (Na_2S) and sodium hydrogen sulfide (NaHS), where the precipitate is not regenerated with consequence of disposal problem. The dilution of iron salt ($FeCl_2$) solvent with H_2S is based on the formation of insoluble FeS that also needs to removed and disposed, while $Fe(OH)_3$ addition can remove H_2S, resulting in formation of Fe_2S_3 and regeneration is possible with oxygen or air [32].

Regarding the chemical absorption of H_2S, an iron-chelated Fe^{3+}/EDTA solution (0.2 mol) is the most popular catalyst to be used, resulting in production of elemental sulfur (S) during the reduction of Fe^{3+} to Fe^{2+} according to the following reaction:

$$S^{2-} + 2F^{3+} \rightarrow S + 2Fe^{2+} \tag{3}$$

The regeneration of iron-chelated Fe^{3+}/EDTA solution occurs by its oxygenation according to Eq. 4, followed by conversion of pseudo-catalyst into its active form Fe^{3+} in Eq. 5:

$$0.5O_2(g) + H_2O(l) \rightarrow 0.5O_2(aq) \tag{4}$$

$$0.5O_2(aq) + 2Fe^{2+} \leftrightarrow 2Fe^{3+} + 2OH^- \tag{5}$$
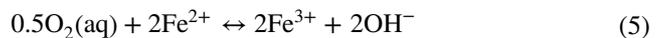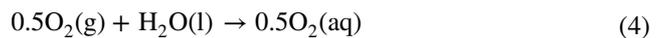
Large consumption of chemical is avoided due to the regeneration Fe^{3+}/EDTA solution and it is H_2S specific, with H_2S removal rate of 90–100% at a gas flow rate of 1 dm^3/min with catalytic solution flowing rate of 83.6 cm^3/min [7]. The iron-chelated based technologies were also reported to remove 50–90% of the mercaptans presented in the biomethane, without any significant reduction in the concentration of CO_2 with operation cost of 0.2–0.3 €kgS^{-1} [2]. The available materials for

Fig. 6 Biogas upgrading by water scrubbing of H_2S
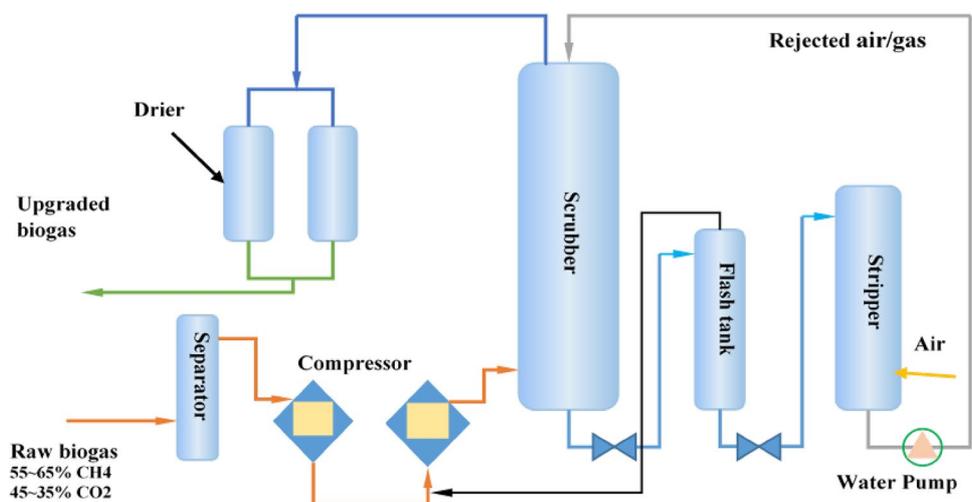
chelated and non-chelated are Lo-Cat®, SulFerox®, and Sulfothane® Bailon et al. [6].

3.2.2. Dosing with Air/Oxygen into Biogas System (In-situ)

Microorganisms can be employed for desulphurization of biogas. This technique is based on the conversion of H_2S to elemental sulfur by a group of specialized microorganisms through microbiological oxidation process. The microorganisms employed are Thiobacillus family and they use the CO_2 from the digester as their carbon source. Depending on the H_2S concentration, small amount of oxygen (2–6% of air in biogas) is needed for the biological reaction to take place (Eq. 6), by injecting air directly into the digester.

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \qquad (6)$$
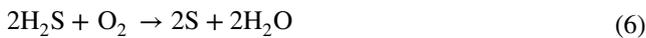
H_2S concentration can be reduced by 95% to less than 50 ppm, depending on the temperature, the reaction time, and the amount of air added. However, safety measures must be taken to avoid overdosing of air, as biogas air in the range of 6–12% is highly explosive [3, 33]. However, it is worthwhile noting that this approach is not suitable for upgrading biogas to natural gas quality since excessive oxygen and inert gas use have to be remove from the treated gas [5].

3.2.3. Iron Chloride (FeCl₂) Dosing into the Digester (In-situ H₂S Precipitation)

H_2S can be reduced by adding Fe^{2+} or Fe^{3+} in the form of $FeCl_2$, $FeCl_3$ and $FeSO_4^2$ into the digester or the influent mixing tank. According to Persson et al. [3], $FeCl_2$ is the most regularly used as the Fe^{2+} reacts with S^{2-}, leading to insoluble iron sulfide (FeS) formation (Eq. 7).

$$Fe^{2+} + S^{2-} \rightarrow FeS \qquad (7)$$

The resultant FeS can be removed from the system with discharged solids. When it is spread as fertilizer, it is oxidized by atmospheric oxygen, forming soluble salt which acts as nutrients to the plants. Although this method is effective in reducing H_2S, but less effective to reduce it up to the level of vehicle and injection into the gas grid specifications. H_2S reduction to 100–200 ppm has been reported, depending on the amount of iron chloride added [5].

3.2.4. Adsorption Using Iron Oxides/Hydroxides Fe₂O₃/(Fe(OH)₃)

This is a process based on two parallel adsorbent columns packed with either activated carbon, iron oxide (Fe_2O_3), iron hydroxide ($Fe(OH)_3$) or zinc oxide (ZnO), configured in adsorption and regeneration mode. The principle is that H_2S reacts easily with Fe_2O_3, $Fe(OH)_3$ or zinc oxide

to form insoluble FeS or ZnS, respectively. The materials used to immobilize the chemical reagents are steel wool (cover with rust), wood chips covered with iron oxide, or pellets made of red mud (aluminum manufacture waste) [2]. However, wood chips impregnated with iron oxide are mostly used, because it has a larger surface to volume ratio than plain steel and inexpensive [16].

It was reported that at H_2S concentration of 1,000–4,000 (ppm), 100 g of pellets can bind 50 g of sulfide. The conventional available materials (iron sponge) grades are; 100, 140, 190, 240 and 320 kg Fe_2O_3, with density of 800 kg/m^3. However, recently, a numbers of proprietary iron oxide materials have been offered as improved alternatives to the conventional ones, such as Sulphur-Rite®, SulfaTreat®, SOXSIA®, Meda-G2®, and Sulfa-Bind® [5, 33].

3.2.5. Adsorption on Activated Carbon

H_2S can be removed using adsorption into non-impregnated (virgin), catalytic-impregnated, and impregnated activated carbons. The catalytic-impregnated and impregnated activated carbons will catalyze H_2S oxidation to elemental sulfur and water at higher rate than the virgin activated carbon (AC) [2]. As in biological desulphurization, oxygen (4–6%) can be added (catalytically) to convert H_2S to elemental sulfur and water (Eq. 8) [7]:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \qquad (8)$$

The required pressure for this reaction to occur is between 7 and 8 bar and temperature 50–70 °C. The formed elemental sulfur is adsorbed by the AC (Fig. 7). In other to improve the rate of reaction, chemical adsorption is done by impregnating the AC with alkaline or oxide such as sodium carbonate (Na_2CO_3), potassium iodine (KI), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium bicarbonate ($NaHCO_3$), and potassium permanganate ($KMnO_4$). This can enhance the removal capacity from a normal 10–20 kg H_2S/m^3 (virgin carbon) to 120–140 kg H_2S/m^3 (impregnated carbon) [6]. According to Petersson and Welinger [33] only KI or $KMnO_4$ impregnation supports the partial oxidation of H_2S without any added oxygen. As a result, they are more preferred option for any desulphurization that will lead to biomethane injection to national grid or for vehicle fuel utilization. Two connected columns were used for continuous operation for adsorption and desorption, with heat (steam injection) and depressurization usually employed for regeneration. The drawback of this technology is the replacement of the activated carbon instead of regeneration when the solid is saturated with sulfur, and there is a growing environmental concerns over appropriate disposal methods. In addition, dust and water must be removed prior to AC treatment [10, 34].

Fig. 7 Pressure swing adsorption for H₂S removal
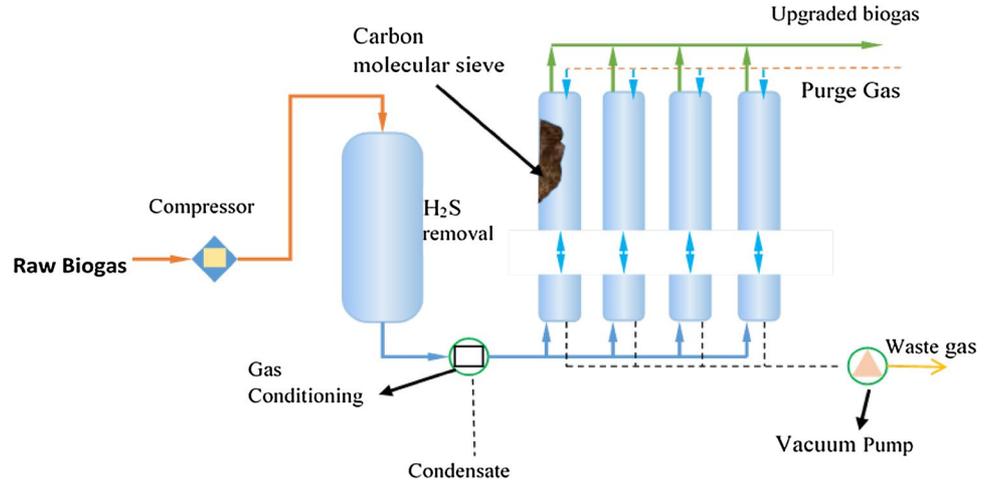
3.2.6. Biological Desulphurization and Biofiltration of H₂S

This technology employed specialized microorganisms to reduce the level of H_2S in biogas by converting it to elemental sulfur and some sulphates, similar to the technique of addition of air or oxygen into the digestion tank. The technique is on the basis of lithautotrophic bacteria to use H_2S as electron donor and CO_2 as carbon source, and also for the development of end-of-pipe solutions for biogas upgrading (Montebello [36]; Mora et al. [37]). About 4–6% of air/oxygen was used as electron acceptor and provided the energy needed for lithotrophic growth in order to oxidize H_2S (Eqs. 9 & 10) [36].

$$H_2S + 0.5O_2 \rightarrow S + H_2O \qquad (9)$$

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad (10)$$

Bailon and Hinge [5] had proved that it is possible to use NO_3^- (NO_2^-) as electron acceptor instead of using O_2 in the biofiltration unit for the oxidation of H_2S (Eqs. 11, 12) due to the fact that at the low O_2/S and NO_3^-/S ratio, elemental sulfur is produced.

$$3H_2S + NO_3^- \leftarrow 3S + 0.5N_2 + 3H_2O \qquad (11)$$

$$3H_2S + 4NO_3^- \rightarrow 3SO_4^{2-} + 2N_2 + 6H^+ \qquad (12)$$
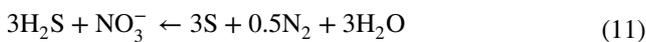
The sulfur oxidizing microorganisms used are mainly from the family of Thiobacillus, Thiomonas, Paracoccus, Acidithiobacillus, Sulfurimonas or Halothiobacillus [35]. The optimum temperature is in the range of 28–35 °C, with pH of 6–8. However, Montebello [35] discovered that some extremophile species such as Acidithiobacillus ferrooxidants or Acidithiobacillus thioxidants, present an optimum biocatalytic activity in the low pH range of 2–4. This technology has been implemented mainly in biotrickling filter (BTF), due to its efficient gas–liquid mass transfer, cost effectiveness, and easy control of other variables like nutrients supply, pH and temperature [10, 35, 36]. H_2S can be reduced from 3000–5000 ppm to 50–100 ppm, and ammonia (NH_3) is also jointly removed [3]. The packed bed columns materials for supporting biofilm growth in BTF desulphurization are pall rings, HD-QPAC or polyurethane foam etc.

3.2.7. Membrane Separation

This is similar with CO_2 removal process by membrane separation. The separation is based on the selective permeability property of the membranes, which can be gas–gas separation or gas–liquid separation. This allows the permeability of H_2S while retaining the CH_4 on the other side of the membranes. In the gas–liquid separation, alkaline liquid is used on the microporous hydrophobic membrane, which can support H_2S removal by 98% during desulphurization, leaving only 2% in the upgraded gas [7, 21, 22]. The gas stream molecules flow in one direction diffusing through the membrane, while H_2S is absorbed by the liquid on the other side. Iovane et al. (2014) recently worked on experimental test with polymeric membrane (150×1210 mm) for the biogas purification from CO_2 and H_2S and reported the H_2S removal efficiency of 54–94% at pressures of 25–41 (N/cm²).

3.2.8 Perspectives on H₂S Removal

Table 5 shows the summary of the alternatives and technical features of H_2S and other contaminants removal from gas streams. It should be note that H_2S is poisonous and corrosive in nature, which make regeneration almost impossible, and very expensive to manage, where possible. The possible solution is to focus on research and development that can produce a system for sulfur recovery at less cost, while minimizing its impact on equipment and the environment. One possible approach is to develop a hybrid system

Table 5 Alternatives and technical features of H_2S and other contaminants removal from gas streams [3, 5, 7, 8, 10, 32]

Technology/alternatives	Reactions and advantages	Disadvantages
Absorption in water	H_2S <15 cm^3 m^{-3}, Cheap when water is available, CO_2 is also removed [2]	Not regenerative, expensive operation: High pressure, low temperature, difficult technique
Addition of iron chloride in digester (FeCl$_3$/ FeCl$_2$/FeSO$_4$)	$2Fe^{3+} + 3S^{2-} = 2FeS$ $Fe^{2+} + S^{2-} = FeS$ Elemental S is formed, cheap investment: storage tank and dosing pump, low electricity and heat requirement, simple operation and maintenance, compact technique, H2S not in biogas wire, no air in biogas. Operation cost: 0.024 € m^{-3} of biogas	Low efficiency (100–150 cm^3 m^{-3}), expensive operation (iron salt), changes in pH and temperature not beneficial for digestion process, correct dossing is difficult, required specialized supervision, high pressure problems
Iron oxide/iron hydroxide (Fe(OH)3/Fe$_2$O$_3$) -bed Rust steel wool, impregnated wood chips or pellets	$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$ $2Fe(OH)_3 + 3H_2S = Fe_2S_3 + H_2O$ $2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6$ S High removal efficiency: >99%, Mercaptanes are also removed, Cheap investment, Simple Can handle 0.3–500 kg/d oh H2S	Sensitive for water, expensive operational costs, regeneration is exothermic: Risk of ignition of chips, reaction surface reduced each cycle, released dust can be toxic, reagent disposal
Chemical absorption Fe(OH)$_3$ Fe-EDTA Cooab™	$S^{2-} + 2Fe^{3+} =$ S $+ 2Fe^{2+}$ $0.5O_2 + 2Fe^{2+} = 2Fe^{3+} + 2OH^-$ High removal efficiency: 95–100%, cheap operation, small volume required, regenerative, low CH$_4$ losses, can remove 50–90% mercaptans, cost of 0.24–0.3 € kgS^{-1} Can handle 0.5–15 ton/day of H$_2$S Capita cost: 3–120 € (m^3/h)$^{-1}$	Difficult technique, regenration through oxygenation, $CO_2=H_2CO_3$ (using EDTA) leads to precipitation Build-up of thiosulfates from chelates + H$_2$S (using EDTA), Required specialized supervision, High pressure problems [8]
Chemical absorption NaOH FeCl$_3$	Low electricity requirements, Smaller volume, less pumping (compare with water absorption), Low CH4 losses Operating cost: 0.03 € m^{-3} of biogas	Expensive investment and operation, More difficult technique, Not regenerative
Biological/Biotechnological Air/oxygen dosing digester slurry Biofilter/biotrickling filter (BiogasCleaner®, Biopuric®, DMT filter®) Bioscrubber (Thiopaq™)	$2H_2S + O_2 = 2$ S $+ 2H_2O$ $H_2S + 2O_2 = SO_4{}^{2-} + 2H^+$ High removal possible: >97% Elemental S is formed, used bacteria or microorganisms at room temperature, Cheap investment and operation: low electricity and heat requirements, no extra chemicals or equipment required, Simple operation and maintenance BiogasCleaner® is automated bio-trickling filters for H2S removal Biotrickling filter has >99% H$_2$S removal efficiency. Commercially available in full-scale plants Can handle 50–20,000 kg/d of H$_2$S. Operating cost: 0.013–0.016 € m^{-3}	Concentration of H$_2$S still high (100–300 cm^3 m^{-3}) Excess O$_2$/N$_2$ in biogas (means difficult upgrading or required addition cleaning), Overdosing air will result in explosive mixture Require strict control of bacterial conditions Optimization is still an issue
Adsorption with activated carbon (Impregnated with KI 1–5%)	$2H_2S + O_2 = 2$ S $+ 2H_2O$ High efficiency (H$_2$S <3 cm^{-3} m^3) High purification rate Low operating temperature Compact technique High loading capacity	Expensive investment and operation, CH$_4$ losses (it absorbs CH$_4$), H$_2$O and O$_2$ prior treatment before removing H$_2$S, H$_2$O can occupy the binding places needed by H$_2$S, Regeneration at 450 °C, Residue present till 850 °C
Membranes	Removal of H$_2$S >98% is possible, CO$_2$ is also removed	Expensive operation and maintenance, highly complex solution

Fig. 8 Hybrid solution for the removal of CO_2, H_2S and other contaminants
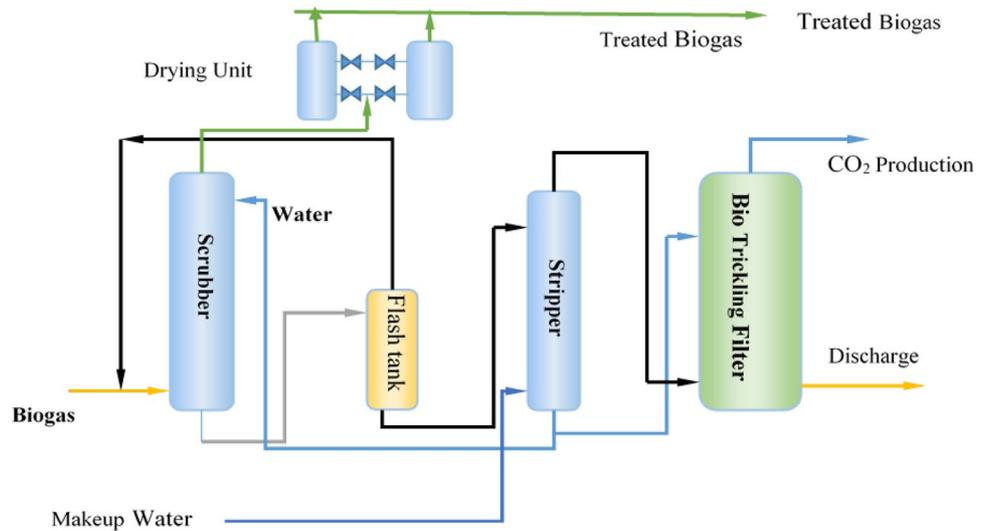
that can combine two or more technologies for H_2S, CO_2 removal along with other contaminants from biogas stream. In this system, water scrubbing can be used to remove both H_2S and CO_2, and the scrubbing wastewater can be circulated and regenerated in an air stripping unit (Fig. 8). This waste and air from the scrubber can then be treated in biological disulphurisation unit (Bio-Trickling Filter). Cooling and drying of the biogas in the same process will enable the removal of water, remaining H_2S and other remaining contaminants, such as silicon organic compounds. This process can be controlled, optimized and monitored with Programmable Logic Controller (PLC) control system, thereby ensuring that H_2S, CH_4, H_2O, CO_2 and Wobbe Index are measured in real time situation.

Removal of Water

The biogas that leaves digesters is always saturated with water and the absolute water content depends on the temperature (at 35 °C, the water content of the biogas is usually 5%). Generally, the lower the temperature, the lower the water content in the raw biogas. This water must be dried if the biogas is to be used for grid injection or vehicle fuel, and even gas turbines and combined heat and power (CHP) (Tables 1, 2). Water can be removed by physical separation (condensation) and chemical drying (adsorption).

The physical drying methods by condensation are demisters (liquid particles are separated by wired mesh, with microspores 0.5–2 nm that can attain dew point of 2–20 °C), cyclone separators (utilizing centrifugal force to separate water droplets), moisture traps (by expansion, causing low temperature to condense water), water traps (design with biogas pipe to collect and remove water) [3, 4, 7]. However, they are less efficient in separating water since it can only decrease the biomethane dew-point to 0.5 °C,

and this will lead to operational problem such as freezing the heat exchanger's surface [7, 10].

The chemical drying is basically absorption of water in glycol (drying agent), which has a binding component that can reduce the dew point from −5 to −15 °C, and can be regenerated at temperature of 200 °C [3]. Water can also be dried using silica gel, magnesium oxide, activated carbon, alumina and other chemical agents that have binding components, and decrease the dew point to −40 °C under 6–10 bar [3]. For continuous operation, two columns of packed bed (with drying agents) are required for operation and regeneration mode in parallel. Raw biogas is passed through them at high pressures to dry it and, regenerated by evaporation through decompression and heating. Hygroscopic salts that dissolved to absorb water from the biogas can be used, but they need to be replaced when saturated [6, 12].

General Discussion and Suggestions for Future Development

The main purpose of biogas upgrading is aimed at: (i) purification process which is targeted specifically to remove the trace components that can affect the end-users, grid transmission, machineries, storage facilities, (ii) CO_2 removal in order to adjust (increase) the heating value and the relative density of the biogas that conforms with Wobbe Index requirements and, (iii) to a lesser extent, upgrading using dry reforming for the production of syngas ($CO + H_2$). These are used for the production of chemical via Fisher-Tropsch Process. While the biogas purification is compulsory, the biogas upgrading is optional. However, it will be beneficial if these two processes (purification and upgrading) can be integrated. This is because the contaminants

removal can be carried out together with CO_2 removal simultaneously. No doubt, this can offer significant cost reduction of biogas conditioning. The purification and upgrading methods discussed extensively in this paper have the ability and capacity to simultaneously remove both the contaminants and the CO_2. For examples, membrane separation, adsorption, cryogenic, biofiltration and biological methods can all use multi-step operation, advanced multi-functional materials, biogas recycling, contaminants conversions and other techniques to increase the efficiency of the integrated biogas conditioning system.

It may be necessary for synergy, cost saving and practical to consider siting anaerobic digestion (AD) biogas plants together with biorefineries to be able to produce biomethane for transportation fuel, biobased chemicals and other biobased materials. It will also be possible to link biogas produced from the landfills to the biorefineries complex, thereby reducing, or avoiding, the separate cost of biogas conditioning, were it is stand-alone operation. This will at the same time enable the AD biogas plants to play its roles in waste management and sustainable energy supply by utilizing on-site wastes, CO_2 waste and surplus heat and electricity for its operation.

There is also the need for further research on the use of locally available waste materials as sorbents for the removal of H_2S, CO_2 and other biogas impurities. Materials such as anaerobic digested sludge, water treatment sludge, and waste from industrial processes are promising and cheap alternatives for biogas conditioning as the current treatment technologies are energy intensive and relatively expensive. The authors are currently working on the valorization of calcium carbonate-based solid wastes, for removing the contaminants such as H_2S from the biogas stream. Solid wastes containing mainly calcium carbonate and various inorganic elements including Mg, AL, Fe, Si, Na were found reactive for the selective removal of H_2S from the biogas matrix. Furthermore, the coupling of a solid waste and a commercial activated carbon (AC) allowed improving the sorption performance compared to pure commercial calcium carbonate ($CaCO_3$) and AC. The results obtained open a new promising way for the valorization of calcium carbonate-based wastes for the removal of H_2S from the gas phase, in particular for the purification of biogas.

Another possible pathway for biogas utilization without wasting the heating value of the biogas due to flaring as a means of disposal is catalytic reforming of the biogas (Fig. 9). This has the potential to fully utilise the energy in the biogas. This option is very attractive because the availability of CO_2 and CH_4 is relatively inexpensive. Most large plants emit large amount of CO_2 and methane is being flared at many gas plants, while landfill gas contained 50% CO_2 and 50% CH_4. Therefore, the conversion of biogas into higher-value compounds is very attractive. It is possible

to explore these three catalytic reforming methods; dry reforming, steam reforming and auto-thermal for the utilization of biogas.

Dry reforming of biogas is an endothermic reaction that can directly convert CO_2 and CH_4 into H_2 and CO, known as syngas, which is a valuable gas mixture and can be used as a combustion enhancer due to its high reactivity to improve the combustion efficiency, thereby reducing the engine emission during combustion [6]. Alternatively, the resultant syngas (low CO_2/H_2 ratios) can be further upgraded to produce H_2-rich feed for use in fuel cells, or in the alternative converting to liquid fuels (gasoline, kerosene, aldehydes, and alcohols) [7]. The only technical challenge of dry reforming relates with the deactivation of catalyst due to the carbon deposit and high temperature and metal and support sintering. This has limited its application in biogas reforming, but getting the right catalyst will eliminate the carbon deposit and make it more acceptable, especially because of its applicability in the areas where there is water shortage. More research work in this area is ongoing, especially with the work of Rego de Vasconcelos [38], who is focusing on using phosphates-based catalyst for synthetic gas (syngas) production using CO_2 and CH_4 to reduce carbon deposition on the catalyst. Up-to-date, there has not been industrial application of DRM yet.

On the other hand, steam reforming is the most widely used process to convert natural gas to syngas and it is responsible for over 50% hydrogen production in the world [39]. Therefore, biogas can be an alternative raw material to conventional steam reforming technology. This is because biogas is similar to natural, and also has additional benefits, such as, it is a renewable resource; it reduces methane emission to the atmosphere; it is commercially produced in large quantities and helps in diverting waste from the landfill and produces nutrient-rich fertilizer as by-product. Steam reforming consists of two reactors (reform reactor and shift reactor). Catalytic reforming reaction of methane, hydrocarbons, naptha or ethanol with water (pre-vaporised by steam generator) takes place in the reform reactor. Three H_2 moles per CH_4 and H_2O mole fed (main objective of the reform) and one CO mole are the products of this reactions. The CO produced in the reform reactor reacts with water steam in the shift reactor (water-gas-shift reaction), to produce H_2 and CO_2. The end products of these two reactors are a mixture of H_2 and CO_2 [40, 41].

The presence of water has reduced the possibility of carbon generation and deposition on the catalyst surface, hence it is more acceptable and widely used in natural gas reforming for the production of hydrogen. This is a better path way for biogas utilization.

Lastly, auto-thermal reforming (ATR) is another promising catalytic method that can be used to convert biogas into syngas, using air as a co-reactant. The added air

Fig. 9 Catalytic reforming
option for biogas utilization
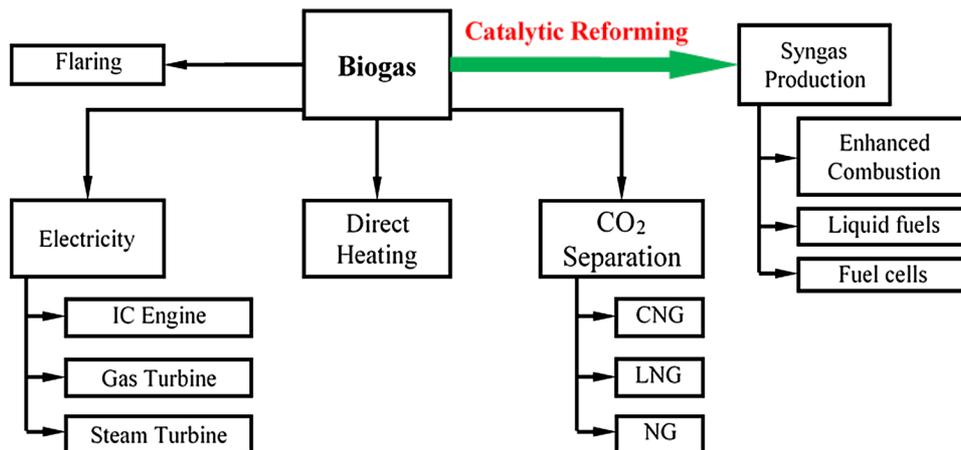
combusts with a portion of CH_4 within the catalytic reactor, thereby producing CO_2, H_2O and heat, that can drive the endothermic dry reforming reactions [42]. The ATR also maintains the catalyst activity by providing additional oxidant that reduces the potential for carbon formation in the reactor, especially for biogas mixtures with high CH_4 content, thereby preventing carbon deposition on the catalyst surface.

Cryogenic separation can produce pure CO_2, CH_4, N_2, and O_2 and are very useful especially, CO_2. The utilisation of the recovered CO_2, can further lower the cost of biogas upgrading as it can be use or sold for enhanced oil recovery (EOR), algae production and mineralization, carbon sequestrations, methane and syngas productions. Finally, there is need for biogas conversion standardization globally and clearer information provided for specific application of biogas upgrade quality. This has become necessary due to confusions, because different countries, equipment manufacturers, and utility company give different specifications for the same thing.

Conclusions

The production of biogas from waste and renewable resources is a promising answer to the environmental and energy challenges facing world. The upgraded biogas (biomethane) can be used as a replacement of fossil fuels such as production of heat and stream, electricity production and co-generation, vehicle fuel, and feedstock for the production of bio-based chemicals and substrate in fuel cells, starting reactants in chemical processes, substitute for natural gas for domestic and industrial use, gas grid injections. This paper reviewed the state-of-the-art of biogas purification and upgrading technologies. Gas quality requirements supersede costs as criterion for selection

of appropriate technology. This is because the selection of appropriate technology depends on the specific biogas requirements, site specific, local circumstances and are case sensitive. The physical and chemical technologies based on adsorption, absorption, chemical reaction, cryogenic and membrane separations are mature and capable of providing biomethane that meet Wobbe index for grid injection and vehicle utilization. However, they are still very expensive and this high costs are discouraging more upgrading plants implementations.

Some novel technologies such hydrate separation, biotechnologies (Biofilter / Biotrickling filter and in-situ upgrading), cryogenic separation, and chemolito-troph-based bioreactors (which can convert CO_2 from the biogas into methane). This is particularly possible by the conversion of excess electricity grid power during the night into H_2 to serves as electron donor for the chemolitotroph-based bioreactors. This will support the new concept of power to gas initiatives. It had so far been evaluated only at laboratory and pilot scale, therefore industrial scale testing and optimization are still needed to show their full potential for biogas upgrading. Biotrickling filter has shown H_2S removal efficiency more than 99% and its operation costs are lower than that of chemical precipitation, chemical scrubbing or adsorption. Efforts should be directed for more research into these new areas to stimulate its developments. Lastly, dry reforming (DRM) is a potential option that needs to be considered, for biogas purification and upgrading as many efforts are concentrated in research and development (R&D) nowadays.

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