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Advances, challenges, and perspectives of biogas cleaning, upgrading, and utilisation

Ayub Golmakani, Seyed Ali Nabavi*, Wadi Basil, Vasilije Manovic*

Energy and Power, Cranfield University, Bedford, Bedfordshire MK43 0AL, UK

Corresponding author: Seyed Ali Nabavi (s.nabavi@cranfield.ac.uk); Vasilije Manovic (v.manovic@cranfield.ac.uk).

Abstract

Biogas as a renewable energy resource can be broadly recognised as a carbon-neutral fuel, which reduces anthropogenic greenhouse gas emissions, mitigates global warming, and diversifies energy supply. However, the biogas share in the global renewable energy supply chain, and technology deployment and maturity are not commensurate with the potential. The first half of this study critically reviews state of the art developments in biogas cleaning and upgrading technologies by considering their present status, current challenges, and barriers associated with their future development. The second part of this paper aims to address critical gaps in converting biogas to biomethane, proposing required pre-treatment steps for different technologies. The third part focuses on current policies concerning the strict regulations implemented for flaring consent applications. In this section, biogas upgrading technologies were compared by estimating the global warming potential (GWP) resulting from waste gases (WG). It was observed that due to high methane losses, WGs from membrane technologies have the highest GWP, but with flaring they have the lowest GWP. In the last part of this review, the recent applications of biogas in cogeneration (CHP), tri-generation (CCHP), quad-generation systems, heat, and vehicles are discussed. The use of biogas by different technologies, and their resulting efficiencies were analysed in CHP applications, including microturbines, micro humid air turbine (mHAT), solid oxide fuel cells (SOFC) and hybrid systems of SOFC-microturbines

Keywords: Biogas cleaning, Biogas upgrading, biogas utilisation, biomethane, global warming potential, methane emissions

Contents

1. Introduction

The rise in the global population has led to growing environmental concerns due to anthropogenic greenhouse gas (GHG) emissions and the amplification of detrimental industrial, agricultural, and municipal wastes. Biogas can address these concerns by producing energy from wastes and, consequently, mitigating global warming[1]. In addition to environmental benefits, there are numerous economic benefits of biogas, such as the production of a high quality digestate from anaerobic digesters for its use as a fertilizer, or biogas can potentially offer a cheap and readily available local source of heat and power in remote and small communities. The significant environmental and economic benefits of biogas has led to a phenomenal growth in the number of biogas upgrading plants in Europe, increasing from 483 to 729 from 2018 to 2020[2]. Currently, it is estimated that 20% of global gas demand can be supplied by the full utilization of available organic wastes towards the production of biomethane. However, significant technological barriers exist in current biogas cleaning and upgrading technologies, and only 5% of the biogas produced worldwide is being used in the production of biomethane[3].Additionally, biogas can potentially play a key role in the world's energy supply security and diversification[4].

Biogas can be potentially considered as a carbon-neutral source of energy, as its carbon originates from organic wastes (sludge, food wastes, livestock manure, agricultural, and organic household waste) which in turn can stem from exiting CO_2 in the atmosphere[5,6]. Therefore, biogas can be categorised as a renewable source of energy, and is produced from biomass digestion in nature, landfills or by anaerobic digestion of sewage sludge[7–9]. It can be directly burnt or upgraded and used as transportation fuel, injected in the gas grid[8,10], or, used in micro-turbines[11], micro humid air turbines (mHATs)[12], solid oxide fuel cells (SOFCs)[13], and hybrid systems of integrated SOFCs and micro-turbines[14]. The main constituents of biogas are CH_4 and CO_2, with small quantities of harmful contaminants, such as H_2S, H_2O, and siloxanes. H_2S causes corrosion, and its high concentrations (800 ppm) in biogas can lead to respiratory paralysis, unconsciousness or even death[15]. During combustion, siloxanes in biogas are converted to silica which leads to abrasion of automobile spark plugs, valves or cylinder heads[16]. Water in biogas causes severe corrosion due to reaction with H_2S, NH_3 and CO_2 resulting in acid formation. The CO_2 concentration in biogas is higher than all other gases and its removal substantially enhances the calorific value of biogas[7,17–21]. The type and quantities of contaminants present in biogas depend primarily on the biogas sources[22–25]. The typical range of biogas compositions is provided in Table 1[18].

Table 1: Typical range of biogas compositions[18,26–29]

Compounds	**Landfills**	**Anaerobic digestion**
CH_4 (vol %)	35-65	53–70
CO_2 (vol %)	15-50	30–47
H_2O (vol %)	0-5	5–10
H_2S (ppm_v)	0-100	0–10.0
Siloxanes ($mg.m^{-3}$)	0-50	0–41
VOC ($mg.m^{-3}$)	0-4500	0.5-1543
NH_3 (ppm_v)	0-5	0–100
O_2 (vol %)	0-5	0–1
CO (vol %)	0-3	
N_2 (vol %)	5-40	0–3
Hydrocarbons ($mg.m^{-3}$)		0–200
Halogenated hydrocarbons (ppm_v)	20–200	

There are two main reasons for biogas treatment and upgrading: (1) removal of impurities that are undesired in the natural gas grid, appliances or end-users (biogas cleaning); and (2) removal of CO_2 to increase the calorific value and decrease the density of treated biogas to meet the specified Wobble index (biogas upgrading)[5,30–33]. Furthermore, removal and storage or utilisation of CO_2 can potentially make biogas a carbon neutral or carbon negative source of energy, depending on the technologies utilised, making it a contributing factor in managing global anthropogenic CO_2 emissions. Upon upgrading biogas, the final product is referred to as biomethane, and its quality is defined based on the end use. Biomethane typically contains 95-99% CH_4, 1-6% CO_2 and 0.02-0.05% H_2S[18–21,34].

Table 2 summarises recent reviews on biogas cleaning, upgrading and utilisation. This review sets out to improve on previous reviews, by comprehensively examining the current state-of-the-art developments in biogas cleaning and upgrading technologies. The review discusses the present status and challenges of each technology, as well as current drawbacks towards commercialisation and industrial-scale construction. Moreover, it investigates liquid and solid sorbents, membranes, and biofiltration methods, and suggests the steps required to address key challenges in their widespread use for biogas cleaning and upgrading processes (Sections 2 and 3). At the end of section 3, a detailed analysis was conducted to address the critical debate over flaring policies and regulations worldwide, through evaluating the global warming potential (GWP) of various biogas technologies. The possibility of flaring waste gases is investigated and GWP before and after flaring is compared. In Section 4, the review addresses the need of a proper removal sequence for biogas impurities. The panoply of biogas sources (whether landfill or anaerobic digestion) leads to a diverse range of impurities in biogas; *and each technology comes with its own unique limitations and sensitivity to contaminants;* consequently, there is no ‘one size fits all’ solution for biogas upgrading, since the process is also dependent on other factors, such as; end-use specifications, geographic location, and related atmospheric conditions. For example, the use of membrane technology requires all pre-treatment steps, including H_2O, H_2S, and siloxanes, due to the elevated sensitivity of membrane materials. On the other hand, when utilizing water scrubbing, upgrading biogas from agricultural waste has no mandatory pre-treatment steps, while for biogas from anaerobic digestion (AD) sludge, a pre-scrubbing siloxane removal step is mandatory. This section also specifies mature technologies for removal of each impurity, as well as suggests different routes for biogas cleaning and upgrading. In Section 5, the state-of-the-art developments in biogas utilisation toward decarbonising the industrial sector are highlighted, these include biogas applications in combined heat and power (CHP), combined cooling heat and power (CCHP), solid oxide fuel cells (SOFCs), and hybrid systems of SOFC-CCHP or SOFC-microturbines are discussed. This section highlights the state-of-the-art developments in biogas utilisation toward decarbonising the industrial sector and identifies the major technological hurdles and research gaps to enable the further development of current processes and overcome milestones towards the large-scale roll out and sustainable growth of biogas. It also introduces the current opportunities and potential pitfalls of biogas utilization, and its role in the transformation of global energy systems towards renewable and/or negative emission energy sources.

Table 2. Summary of review studies for biogas cleaning and upgrading technologies.

Source	**Date**	**Scope of review**
Lombardi et al.[35]	2020	• Techno-economic assessment of 5 main upgrading technologies including high pressure water scrubbing, amine scrubbing, potassium carbonate scrubbing, adsorption, and membranes
Moreno et al.[36]	2020	• Evaluating the effect of gas permeation, membrane materials, membrane modules, and process configurations on biogas upgrading using membrane technology
Nyamukamba et al.[37]	2020	• review of siloxane removal technologies for biogas upgrading
Mehrpooya et al.[38]	2020	• review of cryogenic methods for biogas upgrading using solar energy
Prussi et al.[4]	2019	• Brief review of available biogas upgrading technologies • Special focus on future market of biomethane produced from biogas in transportation
Moreno et al.[39]	2019	• Review of biogas upgrading technologies • Cost comparison of various upgrading technologies
MosayebNezhad et al.[40]	2019	• Review of biogas usage in micro Humid Air Turbines (mHAT)
Habeeb et al.[41]	2018	• Review of various technologies for H_2S removal
Ruiling et al.[42]	2017	• Review of siloxane removal technologies
Olumide et al.[43]	2017	• Review of biogas upgrading technologies • Cleaning of H_2S and water
Arespacochaga et al.[44]	2015	• Investigating the sources of siloxanes in biogas and their life cycle • Siloxane removal technologies • The upper limits of siloxanes for each energy conversion system
Andriani et al.[45]	2014	• Optimisation of biogas upgrading technologies
Bauer et al.[46]	2013	• Review of commercially available technologies for biogas upgrading
Ryckebosch et al.[7]	2011	• Review of various techniques for biogas cleaning and upgrading
Stelt et al.[47]	2011	• Review for upgrading of biomass by thermal convection at low temperatures
Weiland[48]	2010	• Review of key parameters for producing biogas and reliability of this system
Basu et al.[49]	2010	• Review of membranes materials for biogas upgrading
Abatzoglou et al.[50]	2009	• Review of technologies for removing ammonia, H_2S and siloxanes in biogas

Raf et al.[51]	2006	• Associated fouling problems in industrial equipment due to siloxanes • Siloxane abatement technologies

2. Biogas cleaning

Biogas cleaning refers to the removal of all impurities from biogas except CO_2. Several technologies have been introduced for removal of impurities, some of which are commercially available, while others are still under development and assessment. The main contaminant removal technologies are physical and chemical absorption, adsorption, membrane separation, refrigeration and, recently, biological techniques.

2.1 Removal of H_2S

H_2S is one of the main obstacles that have hindered the utilisation of biogas in various industries[52]. The presence of H_2S in biogas can cause severe corrosion in the system. H_2S concentration is required to be kept well below 1000 ppm$_v$ for direct combustion, 100 ppm$_v$ for internal combustion engine and 16 ppm$_v$ for compressed natural gas production (CNG)[53,54]. The limits on H_2S concentration in biogas for different applications are provided in Table 3. H_2S can be removed using (a) adsorption, (b) absorption, (c) membrane, and (d) biofiltration approaches, which are discussed in the following sections.

Table 3. H_2S limits for different applications[55].

	Gas heating (boiler)	Kitchen stove	Stationary engine (CHP)	Vehicle fuel	Natural gas grid
H_2S concentration	250 ppm	10 ppm	<1000 ppm	5 mg/m^3	15 mg/m^3

Removal of H_2S is very important for the use of biogas in fuel cells and catalytic methanation processes, as it can damage the catalyst by adsorbing on the active surface, thus preventing the desired reaction. The sensitivity of the methanation process to H_2S is much higher than for fuel cells which, in turn, is much higher than in internal combustion engines[56].

2.1.1 Adsorption of H_2S

This approach involves selective adsorption of H_2S by solid sorbents at pressures between 4-7 bar and 25 ºC. The process typically consists of fixed-bed upward/downward gas-solid contactors. For non-regenerative adsorbents, the process comprises a semi-batch vessel, with biogas flowing through the bed until the adsorbent is saturated (single-bed arrangement). This method is associated with minimised capital cost. However, since the life span of the adsorbents utilised is relatively short, this process is more suitable for small-scale biogas upgrading[7,57,58]. Alternatively, to avoid any interruption in the system during replacement of the adsorbents, a dual lead/lag vessel can be used, presented in Figure 1. In this process scheme, two vessels are arranged in series and the gas first flows through the lead vessel followed by the lag vessel. Once the adsorbent inside the lead vessel is saturated, the vessel is taken offline to be reloaded with fresh adsorbent. During this short time period, the lag vessel is used to remove all the inlet H_2S. Once the adsorbent loading is completed in the lead vessel, the position of the vessels is switched, and the original vessel in the lead position changes to the lag vessel and vice versa[57,59].

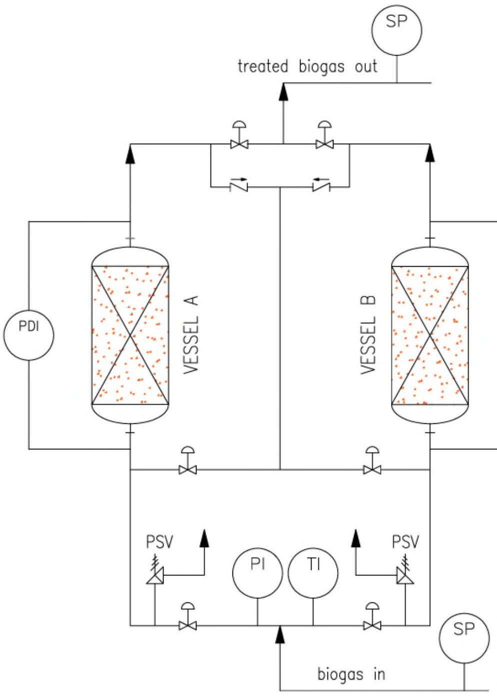


Figure 1. Dual lead/lag vessels for H_2S adsorption[59]. PSV: pressure safety valve, PDI: pressure differential indicator, PI: pressure indicator, SP: sample point, TI: temperature indicator.

For regenerative adsorbents, if a continuous process is required, two types of systems can be used: (1) a dual-vessel system, consisting of two parallel vessels, one of which is online for H_2S adsorption, while the other is undergoing regeneration; and (2) simultaneous adsorption-regeneration within a single bed, in which, while the H_2S is being adsorbed, a small flow of air is supplied to the system for the revivification of the saturated adsorbents[50].

Table 4: Summary of adsorbents for H_2S removal at 25 °C and 1 bar.

Type	**Sample**	**BET ($m^2.g^{-1}$)**	**Pore volume ($cm^3.g^{-1}$)**	**H_2S capacity ($mg.g^{-1}$)**	**Ref.**
Iron oxide-based (Regenerative, commercial)					
	Fe_2O_3 iron sponges	58.4	0.157	138	Wang et al.[60]
	Fe-M (Fe exchanged montmorillonite)	63	0.124	12.7	Abatzoglou, Nguyen et al.[50,61]
	Fe_2O_3 iron sponges			100-200	Truong, Abatzoglou et al.[62,63]
	Fe_2O_3 iron sponges			150	McKinsey et al.[64]
Activated carbons (ACs) (non-Regenerative, commercial)					
	S4A7	426	0.27	6.2	Kazmierczak et al.[65]
	S4A6	387	0.24	3.5	Kazmierczak et al.[65]
	Sewage-sludge mixture	82		87.1	Ortiz et al.[66]
	N-modified carbide	1297		90.5	Seredych et al.[67]
	CKC	663	0.22	1.16	Coppola et al.[68]

AC.FW/CFS	220	0.1	66.6	Hervy et al.[69]
AC.UWP	625	0.27	12.9	Hervy et al.[69]
N-enriched palm shell AC			98.7 – 211.3	Nor et al.[70]
Virgin AC	1101	0.44	1.7	Barelli et al.[71]
Functionalised adsorbents (non-Regenerative, lab-based)				
ZrG-1	201	0.119	52.8	Seredych et al.[72]
AC-ZnW	1470	0.32	30.9	Nguyen et al.[73]
AC-FeW	1430	0.30	39.6	Nguyen et al.[73]
AC-CuW	1470	0.32	496.6	Nguyen et al.[73]
AC Cu-Cr	1599	0.66	27.15	Barelli et al.[71]
AC KOH	817	0.36	20.43	Barelli et al.[71]
AC KOH-KI	1042	0.42	6.6	Barelli et al.[71]
Cd/GO	50		80.4	Florent et al.[74]
$Zn(OH)_2$/GO	47		155	Mabayoje et al.[75]
Wet EFB-HBC			3.25	Meri et al.[76]
Virgin GAC	1678	0.748	53	Siriwardane et al.[77]
MgO-GAC	1358	0.595	275	Siriwardane et al.[77]
$Cu_{45}Fe_8$/SBA-15	206.3		31.86	Song et al.[78]
Cd/GO	50		80.4	Florent et al.[74]
GAC-PEI	925	0.51	106	Roddaeng et al.[79]
CAC-$ZnAc_2$			1.7	Zulkefli et al.[32]
M-Z20/M41	686	0.7	54.9	Yang et al.[80]
M-Z20/S15	213	0.4	41	Yang et al.[80]
M-Z30/M48	323	0.3	53.2	Yang et al.[80]
TRI-PE-MCM-41			112	Belmabkhout et al.[81]
ZnO/SBA15			18.5	Hussain et al.[82]
ZnO/MCM41			5.9	Hussain et al.[82]
Z30/M48	419	0.36	14.8	Li et al.[83]
Zeolites (non-Regenerative, commercial)				
5A			0.5	Alonso et al.[84]
13X			1	Alonso et al.[84]
Clinoptilolite			1.4	Alonso et al.[84]
4A	49.5		7.45	Liu et al.[85]
13X			53	De et al.[86]
Cu-13X			39.9	Micoli et al.[87]
Cu-ETS-2			47	Rezaei et al.[88]
Zn-13X			7.5	Micoli et al.[87]
Cu-ETS-2			47	Rezaei et al.[88]
13X Ex-Cu	239	0.05	11.5	Santos et al.[89]
Metal organic frameworks (MOFs) (non-Regenerative, lab-based)				
MOF-74(Ni)			169	Chavan et al.[90]
MOF-Ni CPO	1193		408	Allan et al.[91]
MOF-MIL-53(Al)-TDC			618	Zarate et al.[92]
MOF Mg-CUK-1			47.6	Zarate et al.[92]
MOF-74(Zn)			54.4	Zarate et al.[92]
MOF MIL-101(Cr)			13.6	Zarate et al.[92]
MOF Y-FTZB-fcu	1310	0.56	30.6	Bhatt et al.[93]
MOF Y-fum-fcu	691	0.28	37.4	Bhatt et al.[93]
MOF Y-1,4-NDC-fcu	546	0.21	51	Bhatt et al.[93]
MOF HKUST-1-E	301	0.397	92	Petit et al.[94]
MOF MG-1-E	141	0.116	199	Petit et al.[94]
MOF MG-2-E	406	0.264	121	Petit et al.[94]
MOF: HKUST-1	434	0.29	73.3	Pokhrel et al.[95]
MOF: HKUST-1/GO	369	0.4	73.3	Pokhrel et al.[95]

The available adsorbents for H_2S removal can be classified in five categories: (1) iron oxide- or hydroxide-based adsorbents; (2) activated carbons (ACs); (3) functionalised adsorbents; (4) zeolites;

and (5) metal organic frameworks (MOFs), Table 4. This Table also provides information on which of these materials is commercial, and which are experimental materials from laboratory studies.

2.1.1.1 Iron oxide-based adsorbents

Iron hydroxide or iron oxide reacts with H_2S to form iron sulphide. This process is called "iron sponge" since steel wool is generally used as the reaction bed[7,96]. The iron sponge process for H_2S removal is feasible when the total produced sulphur amount is less than 10 t/d[97]. Although steel wool has a low surface area, wood chips can be used to increase its surface area. Recently, red mud with surface bonded iron oxides has been employed as a reaction bed to remove H_2S, due to its availability, low price, as well as capability of forming insoluble mineral sulphide[7,98]. Further studies show that Fe-based adsorption of H_2S is highly efficient, potentially reducing the concentration of H_2S down to 1 ppm$_v$[18,34], based on Equations (1) and (2)[60].

$$\mathrm{Fe_2O_3} + 3\mathrm{H_2S} \rightarrow \mathrm{Fe_2S_3} + 3\mathrm{H_2O} \qquad (1)$$

$$\mathrm{Fe_2(OH)_3} + 3\mathrm{H_2S} \rightarrow \mathrm{Fe_2S_3} + 6\mathrm{H_2O} \qquad (2)$$

These reactions are endothermic, and water should be removed prior to desulphurisation to avoid the agglomeration of adsorbents and the reduction of active surface area[7,50,99]. Thereafter, the produced Fe_2S_3 can be regenerated to form elemental sulphur and iron oxide according to Eq. (3)[60].

$$2\mathrm{Fe_2S_3} + 3\mathrm{O_2} \rightarrow 2\mathrm{Fe_2O_3} + 6S \qquad (3)$$

The regeneration reaction is exothermic and requires controlled monitoring of temperature and airflow to avoid ignition of wood chips and material losses[62]. Iron oxide-based adsorbents have been effectively demonstrated by Truong et al., developing adsorbents with an adsorption capacity of 100-200 mg H_2S/g adsorbent at H_2S inlet concentrations of 300-1000 ppm$_v$ in biogas. Furthermore, they provided key guidelines for the scale-up of the process to account for the sensitive regeneration step when employing iron oxide-based adsorbents[62].

2.1.1.2 Activated carbons

Activated carbons are another class of adsorbents with a wide range of H_2S adsorption capacity, mainly from 1 to 90 mg H_2S/g adsorbent, at a low cost[100]. Activated carbons can be produced from various cheap sources, such as sawdust, wood chips, used wood pallets, food wastes, sludge, etc. This gives activated carbon a big advantage over other adsorbents. Hervy et al.[69] recently developed a series of activated carbons using recycled wastes, containing used wood pallets (UWP), and a 50/50 (wt%) mixture of food waste and coagulation-flocculation sludge (FW/CFS). The adsorbents were functionalised by steam activation and achieved an adsorption capacity of up to 66.6 mg H_2S/g adsorbent (AC.FW/CFS). In another work, Justyna et al.[65] used microwave radiation to produce activated carbons from sawdust. They found that the adsorption capacity of developed sorbents mainly depends on the temperature of activation. Although the developed activated carbons showed relatively high NO_2 capacity, the H_2S capacity was low and limited to 4.1 and 6.2 mg H_2S/g adsorbent under dry and wet conditions, respectively. Yong et al.[70] used nitrogen-enriched palm shell to develop a series of activated carbons (N-PSAC) using microwave heating, in which the highest reported H_2S capacity of 98.7 – 211.3 mg H_2S/g adsorbent, for a mixture of 5% H_2S, was achieved.

2.1.1.3 Zeolites

Zeolites are considered as one of the most attractive sorbents for H_2S removal since their properties can be widely tuned by incorporating different metals and metal oxides. Zeolite 13X is one of the most studied and commercially available zeolites, due to its large surface area, which can achieve an H_2S adsorption capacity of up to ~53 mg H_2S/g adsorbent and selectivity of 11.9 for H_2S/CO_2 at 77 psig and 24 ºC[101,102].

Alonso et al.[84] compared two synthetic zeolites (5A and 13X) with a natural zeolite (Clinoptilolite) and concluded that the H_2S adsorption capacity of natural zeolite (1.4 mg H_2S/g adsorbent) was higher than the synthetics studied. Zeolites appear to be suitable materials for H_2S removal due to their high surface area and porosity, which are key factors for adsorbents; however, regenerability stability problems exist, and should be addressed for future use[39,85].

2.1.1.4 Functionalised sorbents

The surface chemistry of support materials can be modified with functionalised substances, such as metal oxides and amines, using impregnation, tethering and, recently, melt infiltration approaches to enhance their H_2S removal performance. Melt infiltration approaches can provide a higher loading and more uniform distribution of functionalising agents within the pores. Consequently, a higher selectivity and H_2S adsorption capacity can be achieved[80]. On the other hand, in traditional loading methods, including impregnation, even distribution of agents is challenging. Yang et al.[80] compared the performance of three molecular sieve adsorbents (SBA-15, MCM-41, and MCM-48) supports loaded with zinc oxide (ZnO), developed using impregnation and melt infiltration methods. They found that sorbents prepared with melt infiltration had more evenly dispersed ZnO in the pores compared with the impregnated samples, and achieved significantly larger adsorption capacity of about 2.6, 1.59 and 1.37 times for MCM-41, MCM-48 and SBA-15, respectively[80,82,83].

Nguyen et al.[73] impregnated activated carbons with a bentonite binder containing transition metals such as copper, iron, and zinc salts. Although there was a reduction in the active surface area and micropore volume of the absorbents, the oxidation properties of bentonite resulted in an increase in the H_2S removal efficiency only in bentonite containing copper. Copper played the role of a catalyst in the oxidation of H_2S to elemental sulfur, which is followed by the oxidation of sulfur into SO_2, which weakly adsorbs and is a pollutant, and is carried away into the product as further H_2S is adsorbed and reacts with the ‘catalyst’. Seredych et al.[72] developed graphite oxide/zirconium hydroxide composites with graphite oxide content varying from 5% to 50%. They reported that the synthesised sorbents can simultaneously adsorb water and H_2S, and show improved performance compared to conventional activated carbons.

2.1.1.5 Metal organic framworks

MOFs comprise of metal ions (clusters) connected by organic linkers that form three dimensional frameworks with astounding porosity and surface area[103]. State of the art MOFs showcase promising H_2S adsorption capacities, however, most of them suffer from poor cyclic and structural stability[104]. Weird et al.[105] studied the regenerability of MIL-47(V), MIL-101(Cr) ,MIL-53(Al, Cr, Fe), and MIL-100(Cr) MOFs after H_2S adsorption, and observed that MIL-100 and MIL-101 did not regenerate completely with a significant drop in their H_2S adsorption capacity, thus, showing poor cyclic stability. Comparatively, MIL-53 (Fe) MOF suffered from poor structural stability, leading to the collapse of its structure after H_2S adsorption as a result of iron sulfide formation. The incorporation of clusters like Al and Cr resulted in MOFs like MIL-47(V) and MIL-53(Al, Cr) showing superior regenerability behavior compared to Fe based MOFs like MIL-53 (Fe). This study highlights the flexibility of tailoring MOFs through the careful selection of clusters and structure type, thus aiding in the development of MOFs with high cyclic and structural stability[105]. In addition, the development of MOFs with high mechanical, thermal and chemical stability in order to work in high severity conditions (high temperature and pressure, moisture, acidic or basic environments, etc.) will contribute to their commercial application in industrial plants[104]. This can be addressed by the smart selection of metal-organic linker combinations, synthetic procedures, and in the development of novel composite materials[104].

2.1.2 Absorption of H_2S

H_2S removal by absorption is suitable for upgrading biogases with low concentrations of H_2S, or for combined CO_2/H_2S removal[5]. H_2S can be removed with CO_2 simultaneously, but it is highly recommended to remove H_2S before CO_2. Since CO_2 concentration (15-50%) is significantly larger than H_2S (<100 ppm_v), a larger column is required for decarbonisation compared with desulphurisation. However, it should be noted that the required material for H_2S is more corrosion-resistant. Therefore, when a column is used for simultaneous removal of H_2S and CO_2, the column should be made of high–grade corrosion-resistant material, which can result in increased capital costs[5,106,107].

The absorption of H_2S from biogas can be accomplished by either physical or chemical processes, using typical gas-liquid contactors, such as spray and packed bed towers. The physical process involves the dissolution of H_2S in physical solvents, such as water, dimethyl ether of polyethylene glycol (DMPEG), methanol, propylene carbonate, and ethers of polyethylene glycol. The main criteria for selection of physical solvents are high capture capacity, high selectivity, low viscosity, and minimal corrosivity[7,108]. There are two types of physical scrubbing processes: (1) single-pass absorption, which is associated with high solvent consumption (includes caustic scrubbing processes); and (2) regenerative absorption (absorption-desorption approach) which can potentially impose high energy requirements for each regeneration. Since this strategy is often used for simultaneous H_2S and CO_2 removal, higher H_2S removal efficiency can be obtained when the H_2S concentration is lower[18]. In all cases, the cost of water scrubbing as a physical absorption process for H_2S removal is yet to be explored.

Chemical absorption is associated with the chemical reaction of dissolved H_2S with the solvent to form metal sulphides or elemental sulphur[7]. Chemical stripping of H_2S can be accomplished by addition of reagents such as NaOH, $FeCl_2$, and $Fe_2(OH)_3$, and Fe(III)-EDTA catalyst into water. The NaOH solution reacts with H_2S and forms precipitated Na_2S or NaHS[50,109], Figure 2. These products are not regenerable and need to be disposed of. Since alkaline solutions tend to absorb CO_2 alongside H_2S, low pH solutions such as zinc-oxide liquid ($ZnO + H_2S \rightarrow ZnS + H_2O$) may be more favourable to avoid any CO_2 absorption. However, if the reagents are not regenerable, it can significantly increase the process cost[108,110]. Utilisation of $FeCl_2$ and $Fe_2(OH)_3$ solutions can address the limitations of NaOH, as they lead to the formation of insoluble FeS, and Fe_2S_3, and Fe_2S_3 can be regenerated by dosing oxygen or air in a closed system[109]. In addition, H_2S can be catalytically removed by a chelated iron to form sulphur ($\mathrm{S}^{2-} + \ 2\mathrm{Fe}^{3+} \ \leftrightarrow \mathrm{S} + 2\mathrm{Fe}^{2+}$) and separated by sedimentation. afterwards, the Fe-EDTA solution can be regenerated by oxidation, following the conversion of Fe^{2+} into its active form Fe^{3+} ($\frac{1}{2}O_{2(aq)} + 2Fe^{2+} \leftrightarrow 2OH^- + 2Fe^{3+}$)[111].

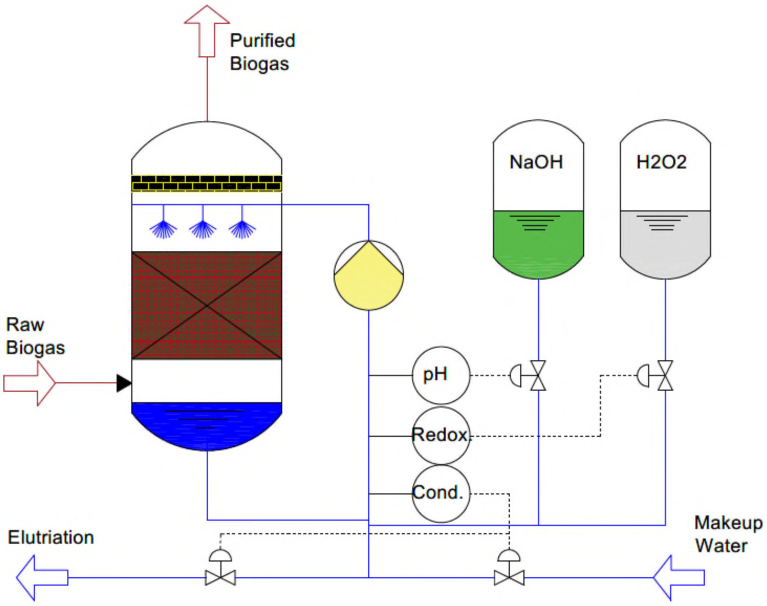


Figure 2. Example of chemical scrubbing plant[112].

Amine solutions are also used for H_2S removal. Diethanolamine (DEA), for example, has been long used in refineries for desulphurisation. However, when gas streams contain both CO_2 and H_2S, DEA has a higher affinity towards CO_2 molecules and, thus, is not recommended if selective removal of H_2S is required. Tertiary amines, compared to DEA, showed better H_2S/CO_2 selectivity when CO_2 concentration was low, due to faster H_2S uptake kinetics. However, their selectivity in the presence of high CO_2 concentrations are not sufficient[113,114]. Alternatively, hindered amines have been developed and achieve significantly higher H_2S selectivity compared to tertiary amines[115].

Caustic scrubbing is the traditional method of removing H_2S, which is much more sensitive compared to amines to the existence of CO_2 in the biogas stream. This technology was the first option for H_2S removal in gases with a negligible amount of CO_2. Currently, some special designs have been developed for caustic scrubbing of streams with high CO_2, by considering the higher kinetic rate for H_2S absorption in comparison with CO_2, which allows the majority of CO_2 present in the gas to slip away from the contactor[116]. In general, the physical and chemical absorption of H_2S is associated with high water and/or chemical reagent consumption.

2.1.3 Membrane separation of H_2S

This approach is associated with the selective permeability of some membranes to H_2S molecules, and retention of CH_4 downstream of the membrane[18]. Therefore, the micro-pores of the membrane should allow diffusion of H_2S molecules, while blocking CH_4 molecules. There are two types of membranes: (1) pressure-driven dense membranes, in which the gas phase is present on both sides of the membrane tubes (inside and outside); and (2) gas-liquid membrane, in which the gas flows through the membrane, and a liquid phase absorbs the diffused gas molecules on the outside of the porous tubes[7]. In this method, the gas might instead flow on the outer surface of the membrane while liquid flows on the inside of the membrane configuration. The liquid should have a high absorption capacity for H_2S, e.g., sodium hydroxide (NaOH) or amine-based liquid solutions. The main differences between gas-liquid membranes and pressure-driven dense membranes are; lower pressure requirements in gas-liquid membranes, and their necessity for liquid regeneration.

The membrane configuration can be single-stage or double-stage, Figure 3. In both configurations, biogas enters the membrane elements from the middle of the pressure vessel, H_2S diffuses through the membranes, and pure CH_4 exits downstream of the unit. Compared to single stage (Figure 3a), the serial arrangement of units in the double-stage configuration (Figure 3b) enables higher removal efficiency and larger CH_4 recovery. The simultaneous removal of biogas impurities is another alternative in enhancing CH_4 recovery. Dolejs et al.[117] used a hydrophilic water-swollen membrane for simultaneous removal of CO_2 and H_2S from a biogas stream. They achieved CO_2 and H_2S removal efficiencies of 82 and 77 (vol%), respectively, at a low feed pressure of 2.2 bar. The hydrophilic properties of the membrane create a water swollen barrier that hinders CH_4 diffusion, while CO_2 and H_2S with higher water solubilities are absorbed.

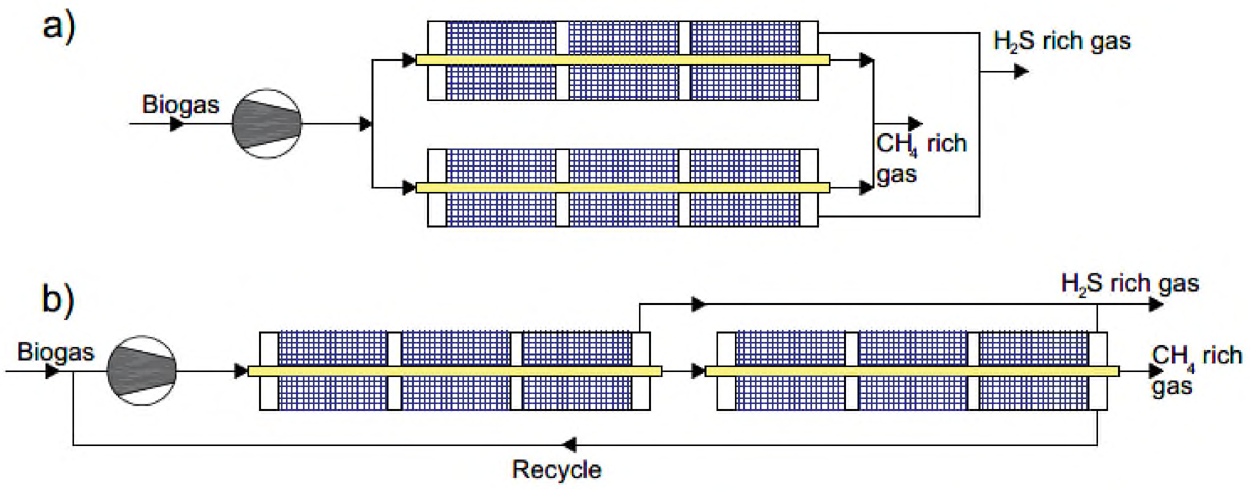


Figure 3. a) Single-stage configuration b) Double-stage configuration.

Table 5 summarises different types of membranes used for H_2S removal, including their characteristics and performance. Tilahun et al.[118] performed a comprehensive study on parameters affecting H_2S removal in a gas-liquid polydimethylsiloxane (PDMS) membrane. The results showed that H_2S removal efficiency (RE) improves with an increase of biogas retention time (GRT) and absorbent pH, particularly for GRT > 10 min, in which an increase in GRT from 3.4 to 19 min resulted in an increase of 2.5 times in H_2S removal efficiency. Although promoting H_2S removal, it was found that an increase in GRT led to a considerable reduction in H_2S/CH_4 and H_2S/CO_2 selectivity. In addition, an increase in the membrane thickness decreased H_2S removal efficiency, since the H_2S diffusion rate through the membrane was reduced. Michal et al.[119] investigated different configurations of membranes to optimise selectivity, and reported that H_2S/CH_4 selectivity increased from 2.7 to 6.7 if a double-stage membrane configuration is used. They also observed that reducing the feed temperature in the double-stage configuration further increased the selectivity.

The multi-layer membrane concept is associated with the development of very thin membranes, which result in higher removal efficiency and reduced cost. On the other hand, they suffer from poor mechanical stability and difficulties in handling[120]. In turn, composites can be used to enhance the mechanical stability of multilayer membranes, where a thin selective layer is placed on a low-cost microporous support. In order to prevent the penetration of the selective layer into the micropores of the support, an additional gutter layer is placed between these two layers[121]. Hoda et al.[122] designed a novel multilayer composite membrane with polyacrylonitrile (PAN) microporous support, poly[1-(trimethylsilyl)prop-1-yne] (PTMSP) as an interlayer and soluble polyimide (Matrimid® 5128) as a selective layer. They found that an increase in pressure from 5 to 25 bar compresses the membrane and the permeation of H_2S through the membrane is reduced, and consequently, the H_2S/CH_4 selectivity decreased from 52 to 24.

Table 5: Membranes for H_2S removal.

Type	Contact	Inlet H_2S concentration	GRT	P_{feed}	T_{feed}	Thickness	Liquid	Liquid pH	RE (%)		Selectivity		Ref.
		(ppm_V)	(min)	(barg)	(°C)	(mm)			H_2S	CO_2	H_2S /CH_4	H_2S/ CO_2	
	Gas-Liquid												
PDMS													
			19			1	NaOH	10	100	79.3	21.4	1.26	Tilahun et al.[118]
			3.4			1	NaOH	10	40	15.3	59	2.6	Tilahun et al.[118]
			19			2	NaOH	10	99.7	60.5	27.8	1.65	Tilahun et al.[118]
			3.4			2	NaOH	10	36.2	8.92	62.4	4.06	Tilahun et al.[118]
			19			1	NaOH	7	97.9	69.9			Tilahun et al.[118]
			3.4			1	NaOH	7	20	12			Tilahun et al.[118]
								>7	98		62		Tilahun et al.[118]
Hollow fibre PP													
		5000		0.5	25		MDEA		97		10		Mirfendereski et al.[123]
		20000		0.5	25		MDEA		>99		40		Mirfendereski et al.[123]
	Gas-Gas												
Hollow fibre					35		-	-			2.7		Zak et al.[119]
Hollow fibre*					35		-	-			6.7		Zak et al.[119]
Hollow fibre*					17						13.7		Zak et al.[119]
Polyurethane											27.4		Sadeghi et al.[124]
Composites													
PUU				5	25						52		Gholizadeh et al.[122]
PUU				15	25						39		Gholizadeh et al.[122]
PUU				25	25						24		Gholizadeh et al.[122]
PUU				5	35						44		Gholizadeh et al.[122]
Butadiene-sulfone				5	35						3.8		Saeidi et al.[125]
PPO				4.5	23						3.1		Chenar et al.[126]
CA				35	35						34	1.6	Achoundong et al.[127]
PDMS+PESf				30	35						3.2	0.66	Saeidi et al.[128]

6FDA-mPDA-durene	34.5	22	15	0.41	Yahaya et al.[129]
PIM-6FDA-OH	4.5	35	7		Yi et al.[130]
Zeolite (ceramic)	1	25	3.24		Maghsoudi et al.[131]

6FDA: 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane, **CA:** cellulose acetate, **MDEA**: methyldiethanolamine, **PDMS**: polydimethylsiloxane, **PESf**: poly(ether sulfone), **PP**: polypropylene, **PPO**: poly(2,6-dimethyl-1,4-phenylene oxide), **mPDA**: m-phenylenediamine , **PIM**: polymer of intrinsic microporosity, **PPO**: poly(2,6-dimethyl-1,4-phenylene oxide), **PUU**: poly(urethane-urea), **GRT**: gas retention time, **RE**: removal efficiency *all the membranes have single-stage configuration except this one which is double stag

2.1.4 Biofiltration of H_2S

Biological biogas desulphurisation by means of biotrickling filters (BTF) is one of the most promising strategies, and can remove over 98% of the H_2S from biogas, at H_2S concentrations of up to 15,000 ppm[8,132]. In this process, H_2S is trapped in a bed material containing immobilised active sulphide-oxidising bacteria (SOBs), whose function is to biochemically react with H_2S and form elemental sulphur or sulphuric acid, depending on the occurrence of partial or complete oxidation[132]. Various SOBs exist for H_2S removal, classified as phototrophic and chemotrophic bacteria. Phototrophic bacteria are mostly used for anoxic BTF units due to their unique ability to grow under anaerobic conditions, using light and inorganic substrates. They can operate for long periods of time in fixed-film reactors, under varying load conditions, without the need of separating biomass continuously. Chemotrophic bacteria need a constant dose of oxygen to operate in fixed film reactors, and unlike sulfate production by phototrophic bacteria, they produce elemental sulphur[133].

BTF units consist of packed bed columns that operate with a recirculating aqueous phase that contains the nutrient required for SOB growth, Figure 4. SOBs are aerobic species that are immobilised and grow as a biofilm along the packed beds in the presence of oxygen. The immobilised SOBs mainly use oxygen, Eqs. (4) and (5) and nitrite, Eqs. (6) and (7) as terminal electron acceptors for H_2S removal[18,134,135]. Therefore, lower O_2/S and NO_3^-/S ratios promote the formation of elemental sulphur.

$$\mathrm{H_2S} + 0.5\mathrm{O_2} \rightarrow \mathrm{S} + \mathrm{H_2O} \tag{4}$$

$$\mathrm{H_2}S + 2\mathrm{O_2} \rightarrow \mathrm{SO_4^{2-}} + 2\mathrm{H^+} \tag{5}$$

$$3\mathrm{H_2S} + \mathrm{NO_3^-} \rightarrow 3\mathrm{S} + 0.5\mathrm{N_2} + 3\mathrm{H_2O^+} \tag{6}$$

$$3\mathrm{H_2}S + 4\mathrm{NO_3^-} \rightarrow 3\mathrm{SO_4^{2-}} + 2\mathrm{N_2} + 6\mathrm{H^+} \tag{7}$$

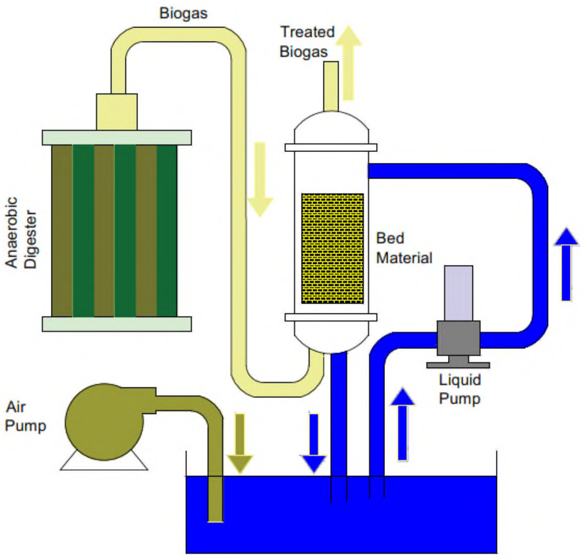


Figure 4. Schematic diagram of biotrickling filtration for H_2S removal[8].

Aerobic and anoxic processes are the two main strategies for H_2S removal in biofiltration methods. In the aerobic process, air is injected to promote the formation of elemental sulphur according to Eq. (4) and (5). However, it can increase the potential risk of an explosion since oxygen concentrations can dilute the methane to below its upper flammability limit (5-15%), and so, the oxygen dosage needs to be precisely monitored[136,137].

In the anoxic process, denitrifying bacteria are used to drive the oxidation process based on Eq. (6) and (7). With this approach, there is no risk of an explosive environment forming due to any excess oxygen. In addition, when compared with aerobic bioreactors, this process benefits from a lower production of biomass[138,139].

The most important factors that can affect the performance of BTFs are: (1) oxygen availability and mass transfer; (2) empty bed retention time (EBRT); (3) diffuser type for biological removal; (4) clogging detection and wash-out strategies; (5) influence of liquid velocity and flow pattern; (6) effect of pH on BTF performance; (7) effects of temperature; and (8) inlet H_2S concentration[8]. The optimum operating temperature associated with suitable growth conditions of microorganisms is around 28–35 °C. In addition, most SOBs show optimum activity in a neutral environment with a pH of 6-7.5, or acidic environment with a pH of 2-3 (mainly extremophile species such as

Acidithiobacillus ferrooxidans or Acidithiobacillus thioxidans). The BTF packing material also plays an important role, as the SOBs are stabilised inside the beds. The criteria of an ideal packing material are large surface area, high porosity, high chemical and structural stability, lightweight, suitabilesurface conditions for bacterial attachment and growth, and low cost[17]. A list summarising the design, operation, and efficiency of different lab-scale and industrial-scale BTF units is provided in Table 6.

Although biological desulphurisation has been recently of great interest due to its economic advantages, simplicity, potential scalability, and being environmentally benign[8], some issues do exist, such as clogging of the packed bed due to the accumulation of produced elemental sulphur, which needs to be addressed to further reduce the operational costs[140,141]. Recently, it has been shown that oxidation of the packed bed in the absence of biogas supply can reduce the removal of accumulated sulfur by 80%. However, the potential utilisation for large-scale application and associated cost remains to be evaluated[8,142]. Another disadvantage of this method is the high amount of nitrogen in the treated gas (biomethane) when air is used as the oxidant. This drawback can be resolved by utilisation of pure oxygen[112], but the cost of the air separation unit (ASU) for oxygen production needs to be considered within the operational costs and any techno-economic analysis.

Table 6. Comparison of various H_2S biofiltration units.

Type	Media	EBRT (s)	Loading (g $m^{-3}h^{-1}$)	pH	Inlet H_2S	Flow rate (m^3 h^{-1})	EC (g.$m^{-3}h^{-1}$)	H_2S RE (%)	Ref.
Anoxic									
	Compost	119	7.3		0.24 g m^{-3}	0.14	7.3	100	Das et al.[143]
	Compost	119	17.7		0.58 g m^{-3}	0.14	17.7	100	Das et al.[143]
	Compost	119	33		1.08 g m^{-3}	0.14	6.8	20	Das et al.[143]
	Compost/biochar	119	33		1.07 g m^{-3}	0.14	33	100	Das et al.[143]
	Compost/biochar	80	39		0.87 g m^{-3}	0.2	27.1	70	Das et al.[143]
	Polypropylene/sludge				500 ppm_v	0.05		>85	Sorea et al.[144]
	Tube/C. limicola	404	1451		91-164			100	Syed et al.[145]

	Expanded schist	300	18.5		1100 ppm$_v$		30.3	100	Ben at al.[146]
	Cellular concrete	240	18.9		900 ppm$_v$		25.2	100	Ben at al.[146]
	Polyurethane foam	144-204		7.5			99.8-130	99	Fernandez et al. [147]
	Metallic pall rings	180		6-6.5	2000 ppm$_v$		52	99	Mont. et al.[141]
	Polyurethane foam	210	3-20	7	100-500 ppm$_v$	0.06	19.2	>99	Khan. et al.[54]
	Pall ring	120-1020	9-201	7	1400-14600 ppm$_v$	<0.06	170 max.		Fernandez et al. [148]
	Polyester fibres	300-960		6.5	500-1500 ppm$_v$		177-182	93-96	Soreanu et al.[149]
Aerobic									
	PVC	96	67.4					95.7	Tayar et al.[150]
	Alkaline BTF	40	3.6		0.04 g m^{-3}			70	Garcia et al.[151]
	Alkaline BTF	40	2.7		0.03 g m^{-3}			95	Garcia et al.[151]
	Monolith BTF	41	127		1000 ppm$_v$		122	95	Qiu et al.[152]
	Wood chips	289	174	1.6-3.6	10000 ppm$_v$		169	97	Aita et al.[153]
	Polyurethane foam	144	130	7.3-7.5			130	>99	Ferna. et al.[147]
	Plastic pall rings	228-354		1.7	2107 ppm$_v$		54	99	Rodri. et al.[140]
	Metal wire, plastic tubing and paper strips	3600-6000			2800-3700 ppm$_v$		40-100	96	Ramos et al.[154]
	Metallic pall rings	126		2.5	2000-10,000 ppm$_v$		52-223	80-100	Fortuny et al.[155]
	HD-QPAC	180			2000 ppm$_v$		55	99	Maest. et al.[156]
	Porous lava		428	8-9	900 ppm$_v$		428	99	Cho et al.[157]
	Wood chips	20-60	75	6.5-7.5	450 ppm$_v$		75	100	Kim et al.[158]
	Alginate bead	45		5.8	450 ppm$_v$			92	Chung et al.[159]
	Porous ceramic	18	670		2200 ppm$_v$		670	>99	Lee et al.[160]
	Pig manure/sawdust	27	45	6.8-8.4				>90	Elias et al.[161]
	Peat			6	300 ppm$_v$		55	100	Oyaruz et al.[162]
	Polyurethane foam	167	370	3.5-7	12300 ppm$_v$		280	>70	Fortuny et al.[163]
	Coconut fibre	40	139	1-4	2235 ppm$_v$		114	82	Chaip. et al.[164]
	Plastic ring/coconut	180	153	0.5-4	6395 ppm$_v$		150	>97	Charn. et al.[165]
	Wood chips	30	8.14	6.8-8.5	50 ppm$_v$			<97	Jones et al.[166]
	Wood chips	289	173.7		13.96 g m^{-3}	0.02	130	75%	Aita et al.[153]

EBRT: empty bed retention time, RE: removal efficiency, EC: elimination capacity

To resolve the associated clogging problem in biofilters, Qiu at al.[152] proposed the use of a honeycomb-monolith as a filter bed, to enable cleaning of the bed at regular intervals by pigging.

They achieved an elimination capacity (EC) of 122 g H_2S m^{-3} h^{-1} for a H_2S inlet concentration of 1000 ppm_v and at an EBRT of 41 s.

Jaber et al.[146] used expanded schist and cellular concrete waste as packing materials for H_2S removal from a gas stream that mimics biogas (using nitrogen instead of CH_4 for safety reasons). They investigated the effect of various operating conditions, such as EBRT, H_2S concentration and molar ratio of N/S, on the biofilter performance. They obtained 100% removal efficiency (RE) by utilising expanded schist for a biogas stream with a 1100 ppm_v H_2S inlet concentration at an EBRT of 300 s. The same H_2S removal efficiency (RE=100%) was achievable by cellular concrete at an EBRT of 240 s with inlet H_2S concentrations up to 900 ppm_v. Dus et al.[143] developed a series of H_2S sorbents using waste and wood-derived biochars for H_2S removal under anaerobic conditions. They compared the H_2S removal efficiency of compost and a mixture of compost and biochars at various operating conditions including EBRT, inlet loading, and inlet H_2S concentration, and achieved up to 100% removal efficiency at an EBRT of 119 s[143].

2.1.5 Technology comparison and required investigations

Table 7 gives a summary of the advantages and disadvantages of the aforementioned H_2S removal technologies.

Table 7. Comparison of various technologies for H_2S removal.

Method	Advantage	Disadvantage	RE (%)
Adsorption	Simple unit, minimum capital cost	High operating cost due to adsorbent replacement after saturation, usage for small-scale biogas upgrading units, sensitive to humidity especially in case of activated carbon	>99
Absorption	Most commercial technology, simultaneous H_2S/CO_2 removal at low CO_2 concentrations in biogas, High RE	Usage for biogas streams with low concentration of H_2S, high capital cost for building a cooling unit prior to absorption column, high energy consumption for absorbent regeneration, high corrosion	90-100

Membrane	Limited space requirement, ease of scalability	Low chemical and mechanical stability for H_2S mixtures, low purity of produced biomethane, replacement is required after a while due to pores blockage and fouling	20-100
Biological	Environmentally benign, ease of scalability, simplicity	Explosion risk for aerobic process, clogging due to elemental sulphur production and wash out need, low performance at high H_2S concentrations, high amount of N_2 in treated biogas for aerobic process	20-100

RE: removal efficiency

Considering the above-mentioned technologies, the following improvements need to be considered to enhance H_2S removal from biogas streams; (i) development of new membrane materials with higher CH_4/CO_2 selectivity to address the low CH_4 purity and to improve their recovery, wettability and chemical stability in the presence of sulphur compounds; (ii) utilisation of new methods like melt-infiltration instead of traditional impregnation or ion exchange methods to upgrade the surface chemistry of all adsorbents; (iii) addressing the issues of functionalised adsorbents for H_2S removal such as high cost and SO_2 emissions to the environment; (iv) development of novel packing materials capable of mitigating plugging, stemming from biomass growth or solid deposits of elemental sulphur for biofiltration; (v) deployment of biofiltration for biogas treating with high H_2S inlet concentration; (vi) development of advanced monolithic designs to mitigate plugging during biofiltration; (vii) optimising pigging frequency and pig geometry in demonstrations or large-scale applications of monolithic designs in biofiltration technology; and (viii) addressing the poor chemical and structural stability of MOF adsorbents by the smart selection of metal-organic linker combinations, synthetic/post synthetic procedures, and development of composite materials.

2.2. Removal of siloxanes

It is estimated that annual worldwide production of siloxanes is over 1 Mt[51,167–169]. Table 8 summarises the use of siloxanes in various applications[170].

Table 8. The use of siloxanes in various applications[170].

Source	Type
Industry	Silicon oils, flexible fillers for the building trade, resins, sealants, elastomers, softeners, paints, sludge waste of wastewater treatment plants, anaerobic digestion plants, fire retardants
Home effluents	Shampoos, detergents shaving creams, cosmetics, deodorants, paint brush washing water, roof or floor tiles degradation, nappies
Textile applications	Softeners, defoamers or antifoaming agents, water repellents
Medical	Coating pacemakers, tubing gels, use as implants in cosmetic surgeries, hypodermic needles, elastomer usage, silicone components
Cosmetics	Hair conditioning polymers, moisturisers, emollients
Cars	Car waxes, fuel additives, lubricants, hydraulic fluids, greases
Paper coating	Thermal curing, UV curing and electron beam curing for foil backing

The effluent wastewater of such industries contains siloxane, which is emerged in the sludge of wastewater treatment plants; therefore, produced biogas from anaerobic digestion of such sludge also contains siloxane. Although the siloxane amount in sludge is low (in ppm values), the extremely low tolerance of equipment in the industry to siloxane compounds makes their removal of utmost importance. For example, high-temperature fuel cells cannot tolerate silica values above 69 ppb, to prevent deposits on the anode. The siloxanes in biogas convert to silica (SiO_2) which deposits on turbine blades, heat exchangers, cylinder heads, etc., leading to abrasion of moving parts, or deposits on the inner surface of exchangers, reducing heat transfer efficiency[167,168,171–173].

Table 9 presents the various types of siloxanes commonly found in a sample of biogas. About 60% of siloxanes in biogas are in the form of hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), hexamethyldisiloxane (L2), and octamethyltrisiloxane (L3). Also, about 50% of silicon in biogas is in the form of silanols, such as dimethylsilanediol (DMSD) and trimethylsilanol (TMS)[174].

Table 9: Siloxanes present in a sample biogas[29].

Synonym	Full Name	Formula
L2	Hexamethyldisiloxane	$C_6H_{18}OSi_2$
L3	Octamethyltrisiloxane	$C_8H_{24}O_2Si_3$
L4	Decamethyltetrasiloxane	$C_{10}H_{30}O_3Si_4$
L5	Dodecamethylpentasiloxane	$C_{12}H_{36}O_4Si_5$
D3	Hexamethylcyclotrisiloxane	$C_6H_{18}O_3Si_3$
D4	Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$
D5	Decamethylcyclopentasiloxane	$C_{10}H_{30}O_5Si_5$
D6	Dodecamethylcyclohexasiloxane	$C_{12}H_{36}O_6Si_6$
TMS	Trimethylsilanol	C_3H_9SiOH
DMSD	Dimethylsilanediol	$C_2H_8O_2Si$

The requirement for siloxane removal is highly dependent on the source and end-use application of the biogas. The siloxane concentration in agricultural biogas is almost negligible, thus, there is no need for siloxane removal. On the other hand, the siloxane concentration in landfill and sewage-sludge biogas is usually larger than 50 mg m^{-3}, which is above the limited siloxane concentration by engine manufacturers, and needs to be removed[42]. Since biogas comprises a wide range of compounds in varying concentrations, a highly efficient approach for the selective removal of silicon compounds is essential. Several strategies have been proposed for removal of siloxane from biogases, including: (1) absorption; (2) adsorption; (3) cryogenic; (4) membrane; and (5) biological methods.

2.2.1 Absorption of siloxane

Siloxane can be removed by absorption using organic solvents, such as tetradecane, in spray or packed bed towers, reaching a removal efficiency of 97-99%. However, the solvent regeneration step is energy-intensive, this approach is therefore associated with high operational costs[175]. Table 10 lists several absorbents and their efficiencies for siloxane removal from various sources.

When employing chemical absorption, a removal efficiency of 95% at 60 °C for D5 and L2 siloxanes can be achieved, using concentrated HNO_3 (65%), and H_2SO_4 (48%) aqueous solutions[175]. In this approach, any reduction in acid concertation or operating temperature can result in a reduction in RE. Though, the utilisation of acids can lead to severe corrosion and their practical application has to be considered carefully due to their associated health and environmental risks[7,175,176]. Although the removal efficiency of acid absorbents to target L2, D4, and D5 siloxanes has been satisfactory, the RE for other siloxanes (especially light ones L3, D3) has not been investigated. Strict safety concerns when dealing with acid environments increases the operating costs, and the high level of corrosion resulting from acid solutions mandates the use of high-grade materials, which causes the capital costs to increase as well. In exploring less corrosive solutions as possible alternatives, Huppmann et al.[177] used low-cost alkaline solutions for siloxane removal, but the removal efficiency was very low (RE<16%). Additionally, at high temperatures (60 °C), sodium carbonate precipitated in the absorption column, which is a serious concern. From Table 10., it seems that Selexol, which utilises the dimethyl ether of polyethylene glycol is currently the best absorbent due to its high removal efficiency for all siloxanes[178].

Table 10: Absorbents for siloxane removal.

Absorbent	Biogas source	Siloxane		Gas flow ($m^3.h^{-1}$)	Gas temp. (°C)	Removal efficiency (%)	Ref.
		Type	Concentration ($mg.m^{-3}$)				
NaOH							
(300 g/L)	WWTP			0.03	20	D4: 3	Huppmann et al.[177]
(300 g/L)	WWTP			0.03	60	D4: 16 - $NaCO_3$ is produced.	Huppmann et al.[177]
(pH 10-12)	Landfill	L2-L4, D3-D5	500-200			L2, L3, L4, D3 and D4 100% D5: 30%	Schneider et al.[179]
H_2SO_4							
(970 g/L)	WWTP			0.03	20	D4: 26%	Huppmann et al.[177]
(1840 g/L)	WWTP			0.03	60	D4: 99%	Huppmann et al.[177]
(97%)		L2, D5		0.012	60	D5, L2>95	Schweigk. et al.[175]
(97%)		L2, D5		0.012	20	D5<70, L2<61	Schweigk. et al.[175]
(48%)		L2, D5		0.012	60	D5, L2>95	Schweigk. et al.[175]
(24%)		L2, D5		0.012	60	D5<73, L2<70	Schweigk. et al.[175]
Others							
Oil	Landfill					<50	Rossol et al.[180]
Water	Landfill	L2-L4, D3-D5	500-200			About 0%	Schneider et al.[179]
Selexol	Landfill	all		2550	35	99%	Wheless et al.[178]
Water (pH 7)	Landfill	all	20	6	10	About 0%	Rasi et al.[181]
HNO_3 (65%)		L2, D5		0.012	60	D5, L2>95	Schweigk. et al.[175]

WWTP: wastewater treatment plant

Biogas produced is at a temperature of approximately 50 °C, and since absorption efficiency is higher at low temperatures, there is always a cooling unit installed prior to the absorption columns. Finding an absorbent with a high efficiency at high temperatures eliminates the need for cooling units, decreasing the plant's capital cost[42]. Although absorption is a good technology for siloxane removal, high energy consumption for regeneration is always a major drawback that limits the extensive use of this technology. In vacuum conditions, the boiling point of absorbents and consequently their energy consumption decrease; therefore, the use of stripping columns under vacuum can contribute to the reduction of energy consumption[182,183].

2.2.2 Adsorption of siloxane

Several adsorbents have been used for siloxane removal, including polymer beds (Tenax TA 60/80 mesh and Amberlite XAD II 20/60 mesh), molecular sieve 13X, silicagel particle size (1-3 mm), alumina, and activated carbons[42,184–187].

The adsorption of heavy siloxanes is easier than light siloxanes. Among siloxanes, L2 is the smallest and lightest, and its adsorption is much more difficult than other siloxanes. It is the first siloxane which elutes from the bed during adsorption; therefore, if an adsorbent is going to be investigated for its effectiveness of adsorption, it is better to test it for light siloxanes[182,184,188]. On the other hand, the regeneration of adsorbents is an important factor which should be taken into consideration. Adsorbents which adsorb heavy molecules need higher energy for regeneration; consequently, it is better to consider the heavier siloxanes present in the mixture for regeneration studies[189,190]. The moisture content also has major effects on siloxane removal efficiency of some adsorbents, and biogas should be pre-dried for them; for this reason, the effect of moisture content should be studied for every adsorbent[18,50]. Other components in biogas such as CO_2, H_2S, and volatile organic carbons compete with siloxanes and, therefore, they might affect siloxane loading[189,191].

Table 11 summarises various adsorbents for siloxane removal, their classification, and compares their removal efficiency (RE), regeneration efficiency (RGE) and regeneration times (RGT).

Table 11: Comparison of various adsorbents for siloxane removal.

Type	Name	BET m^{2}g^{-1}	Pore volume cm^{3}g^{-1}	Inlet silox. mg.m^{-3}	Loading mg.g^{-1}	RE %	RGE %	RGT	Ref.
Activated carbons (non-Regenerative, commercial)									
	MWV-2	2142	1.5	1000 ppm$_v$	1732		0	0	Cabrera et al.[192]
	JCB-1	1487	1.09	1000 ppm$_v$	1108		0	0	Cabrera et al.[192]
	MWV-1	1757	1.19	1000 ppm$_v$	989		0	0	Cabrera et al.[192]
	MC6AD	977	0.56			>90	0	0	Vagen. et al.[193]
	Sil40 Extra	818	0.39			>90	0	0	Vagen. et al.[193]
	CA-1	1104	0.45		242				Nam et al.[184]
	CA-1	1104	0.45		123 for L2				Nam et al.[184]
	CA-2	879	0.47		307				Nam et al.[184]
	CA-2	879	0.47		47 for L2				Nam et al.[184]
	CA-3	302	0.18		155				Nam et al.[184]
	CA-3	302	0.18		72 for L2				Nam et al.[184]
				192		98			Kajoli. et al.[194]
	AC-9	1600		4500	192	>99	0	0	Matsui et al.[195]
	AC-20	900		4500	56	>99	0	0	Matsui et al.[195]
	AC-9	432	0.379		21.9 for D4				Yu et al.[185]
	AC-8	1573	0.922		224 for D4				Yu et al.[185]
	Coconut	930		400	52 for D4				Sigot et al.[187]
Molecular sieve (Regenerative, commercial)									
	PpTek			50	14	98	98	40-50	Soreanu et al.[196]
				192		95			Kajoli. et al.[194]
	13X			4500	77				Matsui et al.[195]
	13X	700		400	113 for D4				Sigot et al.[187]
Silicagel (regenerative, lab-based)									
	NCA-1	656	0.36		202				Nam et al.[184]
	NCA-1	656	0.36		17 for L2				Nam et al.[184]
				192		90			Kajoli. et al.[194]
				4500	104				
	Grace				230				Finocc. et al.[186]
					100		95	10	Schwei. et al.[175]
	Chameleon	690		400	216-250 for D4				Sigot et al.[187]
Activated alumina (regenerative, lab-based)									
	NCA-2	250	0.38		146				Nam et al.[184]
	NCA-2	250	0.38		8 for L2				Nam et al.[184]

RE: removal efficiency, RGE: regeneration efficiency, RGT: regeneration times

2.2.2.1 Activated Carbon

Activated carbons are capable of 95% siloxane removal as long as the biogas is pre-dried. Otherwise, the presence of water vapour can drastically reduce their removal efficiency, and the regeneration of saturated activated carbon is not economical[50]. It should be highlighted that the adsorption of siloxane by activated carbons is the only commercial strategy at the moment because of their low cost and the availability of a wide range of raw materials for their production[7]. The adsorption capacity of activated carbons has a direct relation to surface area and pore volume, by increasing the pore volume or surface area, their adsorption capacity for siloxanes increases[193].

The major drawback of using adsorbents in siloxane removal, and more-so for activated carbon, is the possible polymerisation of siloxane to larger siloxane molecules during the adsorption step, which makes regeneration impossible. In other words, once the activated carbon is fully saturated with siloxanes, it will need to be replaced with fresh adsorbent. As a result, it is necessary to select an AC material with a high siloxane adsorption capacity[183,197,198].

Moreover, ACs have considerable CH_4 adsorption capacity which will result in an increased methane loss. Matsui et al.[195] examined more than 22 AC samples for siloxane removal and reported an adsorption capacity of 56 to 192 mg siloxane./g adsorbent, with removal efficiencies greater than 99%. They eventually commercialised two of their adsorbents with the best loading values[195]. From the available literature, it has been proven that activated carbons with pore diameters of 1.7–3.0 nm are the best adsorbents for siloxane removal, specifically for D4[185]. Overall, the adsorption capacity of activated carbons for siloxane removal depends on several factors, with the major ones discussed in this section. In all cases, it is important that moisture is eliminated from the biogas stream prior to adsorption, as activated carbon adsorbents have considerably higher adsorption capacities in dry environments. In one study by Arespacochaga et al., they showed that at a relative humidity of 50-70%, the siloxane removal efficiency of activated carbon can decrease by up to 90%[44].

2.2.2.2 Silicagel

Silicagel is one of the most effective adsorbent for siloxane removal, with an efficiency of up to 99%. In addition, it can be readily regenerated through a thermal process at 250 °C, with 95% of the captured siloxane desorbed. However, similar to activated carbons, humidity adversely affects their removal efficiency and needs to be eliminated before siloxane removal[18,50]. Although lab-scale assessments show superior performance of silicagels to activated carbons, large-scale studies are yet to be explored to evaluate their performance in practical applications[185]. Activated carbons are good for mixtures with high concentrations of L2, but for mixtures of heavier siloxanes, silicagel performs better. Sigot et al.[187] compared the removal of D4 by silicagel with a coconut-based activated carbon and zeolite 13X. They reported a 250 mg siloxane$_{.}$/g of adsorbent adsorption capacity for silica gel, which was superior to both activated carbon and zeolite 13X.

In a more comprehensive study, Nam et al.[184] compared a variety of adsorbents to better understand each material's effectiveness for siloxane removal. In their work, they investigated the adsorption capacity of three types of activated carbons, including coconut activated carbon (CA1), coal activated carbon (CA2), and impregnated activated carbon (CA3), and compared them with silicagel (NCA1), and activated alumina (NCA2). The L2 removal efficiencies of the activated carbon adsorbents were higher than activated alumina and silicagels. The reason was attributed to the larger pore size of noncarbon adsorbents, which resulted in a lower L2 adsorption[184].

2.2.2.3 Molecular sieves

Molecular sieves have a very good selectivity for siloxane removal from biogas since the separation is based on the average size of adsorbent pores. They have a very high adsorption capacity for siloxanes which makes them suitable for streams with low concentrations of siloxane (less than 1 mg siloxane$_{.}$/g adsorbent). One example has been commercialised by PpTek Ltd. (UK)[196], who have developed a molecular sieve for siloxane removal with an adsorption capacity of about 14 mg siloxane$_{.}$/g adsorbent. The main advantage of their filter is that it can be regenerated about 40-50 times[196].

2.2.2.4 Activated aluminium oxide

Activated aluminium oxides have a great adsorption capacity for siloxanes, and can reach levels comparable with the adsorption capacities of activated carbons, but what gives them an edge over activated carbons is their ability to also remove water[199]. Alexandru et al.[199] studied the removal of D4 by activated alumina at high temperatures, and the results revealed that D4 concentration could be reduced to 1.12 ppm_v for biogas streams with inlet D4 concentrations within the range of 32.3-72.7 ppm_v.

2.2.3 Cryogenic condensation of siloxane

A few research studies have been undertaken for siloxane removal by condensation, presented in Table 12. At temperatures below 5 °C and atmospheric pressure, the maximum siloxane removal efficiency by condensation is below 20%. This value for trimethylsilanol (TMS) increases up to 27% because of its high water solubility, and for D5, its value decreases to 12-18% removal efficiency[175].

Light siloxanes, such as L2, L3, and D3, require temperatures as low as -30 °C (at 1 bar) to be condensed, while heavier siloxanes, like D4 and D5, can be condensed at ~ 5 °C (at 1 bar).As a result, to achieve an acceptable removal of light siloxanes, elevated operating pressure are needed[42].

Cryogenic condensation can achieve up to a 99.3 % siloxane removal if the biogas temperature can be reduced to -70 °C. However, employing condensation for the removal of siloxanes is not recommended, especially for light siloxanes, since they require deep chilling (<-70 °C) at high pressures. Although this method requires no hazardous chemicals or dehydration prior to siloxane removal, it is associated with a high cost that limits its scale-up feasibility. It has been therefore recommended as a method for drying purposes only, and not for siloxane removal[63,196].

Table 12: Comparison of various cryogenic systems for siloxane removal.

Temperature (°C)	Pressure (bar)	Inlet siloxane (mg.m^{-3})	Siloxane RE %	Ref
4	26		50	Wheless et al.[200]
-29			95	Wheless et al.[178]
5		0.6 for D5	12	Schwei. et al.[175]
5		9.7 for D5	18	Schwei. et al.[175]
5	1.1	13.8	10.7	Arespacochaga et al.[201]
-30		7-15	80-90	Rossol et al.[180]
-25	1		25	Hagmann et al.[202]
-70			99.3	Hagmann et al.[202]
-40	1	50	50	Ajhar et al.[176]
-50	1	50	70	Ajhar et al.[176]

RE: removal efficiency

2.2.4 Membrane separation of siloxanes

The most important advantage of membranes for siloxane removal is their low energy consumption in comparison with other technologies such as absorption or adsorption. It has been reported that inorganic membranes are more suitable for siloxane removal since they are more resistant to corrosive environments and have more mechanical stability. However, high-density polymer membranes can also be used for siloxane removal due to their acceptable mechanical stability and corrosion resistance[42,182]. Ajhar et al.[203] developed a series of polydimethylsiloxane (PDMS) based membranes. Although an 80% removal efficiency was obtained, there was a considerable methane loss of 7%. In a subsequent study, the feasibility of siloxane removal using a commercially available PDMS membrane was assessed, and more than 90% removal efficiency was achieved. However, due to considerable CH_4 losses by PDMS membranes, it was suggested that alternative membrane materials should be considered[204].

Membranes do not seem to be the ideal solution for siloxane removal, hence, few studies have been done in this area. Additionally, this method is costly in comparison with other methods because biogas contains several harmful impurities that can irreversibly damage the membrane. For example, biogas from wastewater treatment plants might have small particles of oil that occupy the free volume within the bulk of the polymer. This leads to an increase in the transport resistance across the membrane as more free volume is occupied by species other than the diffusing gases. As a result, the removal efficiency and permeability of the membrane decreases, and the membranes will need to be replaced at regular intervals, which increases operating costs greatly[205].

2.2.5 Biofiltration of siloxanes

There are only a few studies that assess the feasibility of biotricklings filter packed column for siloxane-based substances. These studies show that the removal efficiency of this method is limited to a maximum of 74%. The low removal efficiency is attributed to the strong mass transfer limitations due to the extremely low aqueous solubility of siloxane[206–208]. Although it appears that the efficiency of biological approaches for siloxane removal is currently low, it is proposed that a higher removal efficiency can be potentially achieved by using high mass transfer bioprocesses such as two-phase partitioning or Taylor flow bioreactors, similar to monolith reactors operating based on segmented flow in their capillaries [18,209].

The cost of siloxane removal using this technology depends on the processing capacity, processing technology, composition and concentration of siloxanes, and the required purity of biomethane in different applications. However, the mass transfer rate of the gas into microorganisms' cells (aqueous phase) is low, resulting in an unacceptable siloxane removal efficiency, and long EBRTs are needed to achieve a reasonable removal efficiency. Table 13 summarises various BTFs for siloxane removal. When comparing the elimination capacity of siloxanes with H_2S, the rate is at least 1000 times less than that of H_2S, and consequently, has low removal efficiencies. Although the microorganisms are highly capable of degrading siloxanes, poor availability of siloxanes due to their low solubility causes this great potential to be suppressed. The way forward must concentrate on solving the transport problem from gas to aqueous solution, to eventually increase mass transfer and siloxane removal efficiency. Popat et al.[206] compared the siloxane removal efficiency of a biotrickling filter under aerobic and anaerobic conditions. They reported a siloxane (D4) removal efficiency of 43% for a gas operating at aerobic conditions with an EBRT of 19.5 min, and inlet siloxane concentration of 45 mg m^{-3}. The RE decreased to 15% for a gas operating at anaerobic conditions with EBRT of 4 minutes[206]. The reported siloxane RE values are not high enough and the inlet biogas siloxane concentrations are low, chosen as such since the microorganisms are not compatible with high concentrations of siloxanes. To further asses this technology's effectiveness for siloxane removal, the development of microorganisms capable of working at environments with high siloxane concentration is necessary[207].

Table 13. Comparison of various BTFs for siloxane removal

Type	Media	EBRT min	Load. g.m^{-3}h^{-1}	pH	Inlet silox. mg.m^{-3}	Flow L.min^{-1}	EC mg.m^{-3}h^{-1}	Siloxane RE. %	Ref.
Aerobic									
	Cattle bone	19.5			45 for D4	0.5	30-100	43	Popat et al.[206]
	Pall rings/ Pseudomonas	3.6	1.28		46-77 for D3	0.5		10-20	Accetolla et al.[207]
	Porous lava/ P. aeruginosa	13.2		2	50		168	74	Li et al.[210]
	Cattle bone	19.5			45 for D4		30-100	43	Popat et al.[206]
	Microbial consortium	2.1			45 for D3		200	>10	Accetolla et al.[207]
Anaerobic									
	Lava Rocks	4			45 for D4	0.5	30-100	15	Popat et al.[206]
	Activated sludge	4			45 for D4		101	15	Ruiling et al. [42]

2.2.6 Technology comparison and required investigations

A summary of the advantages and disadvantages of the siloxane removal technologies is provided in Table 14.

Table 14. Comparison of various technologies for siloxane removal [161–176].

Method	Advantage	Disadvantage	RE (%)
Adsorption	Most commercial technology, highest removal efficiency, simple unit, low capital cost	Adsorbent replacement after several regenerations (for activated carbon after one time needs replacement), sensitiveness to humidity especially in case of activated carbon, minimum two units are required, high operating cost	90-99
Absorption	High removal efficiency	High energy consumption for regeneration, flammable solvents, environmental pollution, drying unit after absorption unit is required	95-99
Cryogenic	No need for biogas drying facilities beforehand, no waste material	High energy consumption	10-25 (at 4-25 °C and pressure<4 bar) 99 (at -70 °C)
Membrane	Low energy requirement	Need to be replaced after a while for mechanical destruction and fouling, the RE decreases because of fouling and pore blocking over time	>80
Biological	Environmentally friendly	Low removal efficiencies, high EBRT needed for some siloxanes, low mass transfer rate, fouling risk	Less than 74

Although siloxane removal technologies have achieved promising performances, the following strategies can further improve their efficiency: (i) developing absorbents that remove siloxanes from biogas at temperatures as high as 50 °C; (ii) new process solutions such as utilising vacuum conditions to reduce the energy consumption during regeneration of absorbents; (iii) further investigating the effects of other components in biogas such as CO_2, H_2S, volatile organic compounds, and moisture on siloxane adsorption capacity of different adsorbents; (iv) measuring the L2 adsorption capacity of each adsorbent instead of all siloxanes, while, when studying the regeneration capability of different adsorbents, heavier siloxanes should be considered within the mixture; (v) addressing the transport problem from gas to the membrane body in BTF units, to fully exploit their great potential in degrading microorganisms; (vi) developing microorganisms/bacteria compatible with biodegrading high concentrations of siloxanes and with sufficient growth on packing; and (vii) increasing the RE of siloxanes by the BTF method, since they currently are unacceptable from a commercial point of view

2.3 Removal of H_2O

The three main methods for removal of water vapour from biogases are (1) condensation (refrigeration); (2) adsorption drying; and (3) absorption drying.

2.3.1 Condensation method

In this method, biogas is cooled down at atmospheric pressure to condense the excessive water vapour. The condensed water droplets are then separated using: (1) demisters, in which the water droplets are separated using a wired mesh; (2) cyclone separators, in which the water droplets are separated using centrifugal force, equal to hundreds of times the force of gravity; (3) moisture traps, in which the condensation occurs by the expansion of biogas, and subsequently a drop in temperature that condenses the water vapour; and/or (4) water taps in the gas pipe, used for the collection of condensed water[7,109].

The condensation method is the simplest water vapour removal strategy, it prevents the direct contact of water vapour with downstream equipment, such as compressors, pipes, and packed beds, and minimises the possibility of corrosion in the upgrading system. However, since the dew point temperature cannot decrease below 0.5 °C at atmospheric pressure, this approach is considered to be the least efficient one. Any further reduction in dew point can potentially cause the water to freeze on the surface of the heat exchangers and lead to operational failure. Lower dew points down to – 18 °C can be achieved, if the biogas is compressed before the cooling process[7]. Biogas cooling is accomplished using electrical cooling, or underground pipelines equipped with water traps[18].

2.3.2 Adsorption drying

Removal of water vapour using solid adsorbents such as silica and alumina is one of the most common strategies. In this approach, the water vapour molecules bind with the surface of solid adsorbents. Since only a small amount of water can be adsorbed at atmospheric pressure, this approach is usually performed at elevated pressure (6-10 bar) within packed columns and can get to dew points as low as -40 °C. The adsorption drying units usually consist of two parallel columns working simultaneously, in which one column adsorbs water, while the other one is being regenerated through blow down, purge and heating processes (to evaporate adsorbed water)[7,18,211].

Although this approach is associated with lower operational costs and high efficiency, the investment cost is very high, and the process requires the removal of dust and oil particles prior to the water adsorption step[18,184]. The schematic diagram of a dryer package unit is presented in Figure 5. A set of double pre-filters is used for the removal of oil and dust before the introduction of the gas to the dryer package unit. A set of after-filters is used after the dryer package unit to prevent any potential adsorbent loss from the dryer in case of a malfunction. For each set of filters, a pressure differential transmitter (PDT) is utilised to monitor clogging. The dryer package unit consists of two beds that operate in adsorption and regeneration modes, respectively. A list of adsorbents that can be utilised in this system is tabulated in Table 15 and discussed in the following sections.

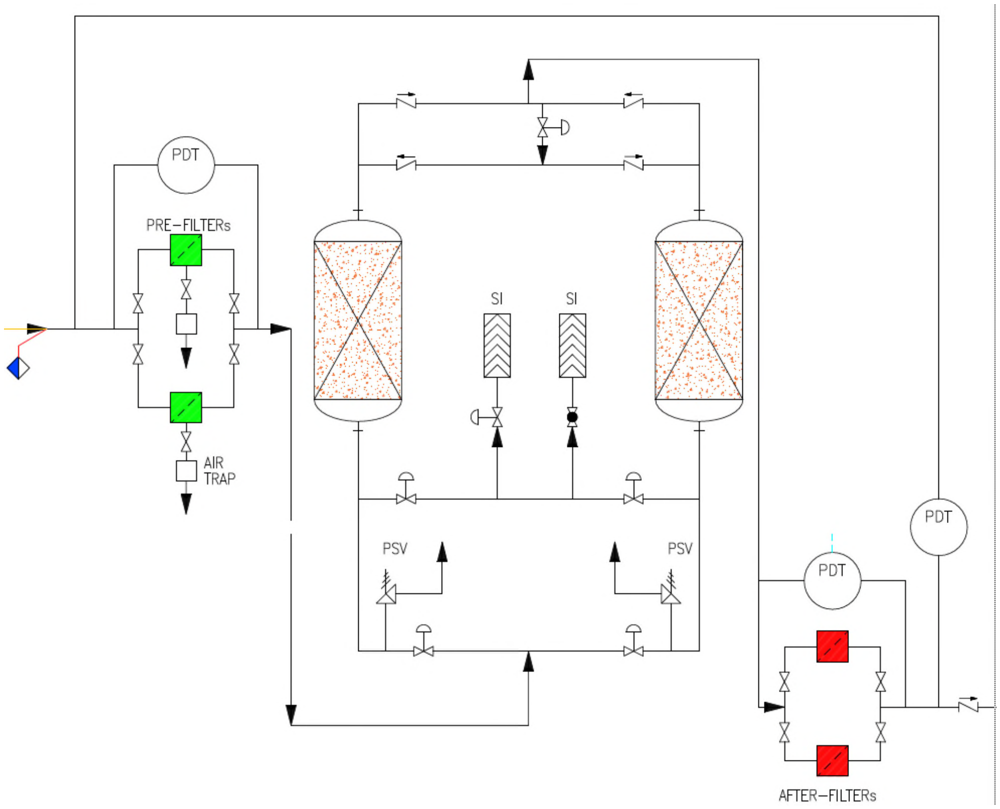


Figure 5. Proposed schematic diagram of a dryer package. PDT: pressure differential transmitter, PSV: pressure safety valve, SI: silencer[190].

Table 15. Various adsorbents for water removal.

Adsorbent	BET m^2/g	V_{pore} cm^3/g	Temp. °C	P_{H2O} kPa	Loading (mol/kg)	Ref.
Silica based(Regenerative, commercial)						
	863	0.472	30	3	23.3	Cevallos et al[212]
			25	0.0271	0.98	Wang et al.[213]
			25	1.6	15.5	Wang et al.[213]
			30	2.5	18.1	Seo et al.[214]
	840		28	2	13.9	Rezk et al.[215]
	575	0.806	30	3.3	8.33	Zhu et al.[216]
	595		20	2.3	44	Knez et al.[217]
Silicagel-$CaCl_2$	256	0.529	30	3.3	40.5	Zhu et al.[216]
Si-SBA	760	1.02	25	3.1	48	Ribeiro at al.[218]

SBA-TSB3- Al	573	1.15	25	3.1	58.7	Ribeiro at al.[218]
Silicagel-Na_2SO_4			20	1.7	55.5	Sukhyy et al.[219]
Silica-NH_2-MAS	997	0.63	25	2.2	38.9	Pei et al.[220]
Silica-NH_2-PSS	1006	0.637	25	2.2	37.8	Pei et al.[220]
Silica-NH_2-PAAS	949	0.626	25	2.2	33.3	Pei et al.[220]
Silicagel-alumina	293	1.21	20	2.3	56	Knez et al.[217]
SiO_2–$CaCl_2$	640	1.9	25	2.5	61.1	Mrowei et al.[221]
SBA15-$CaCl_2$	52	0.17	50	3.0	25	Ponomarenko et al.[222]
Activated alumina (Regenerative, commercial)						
			30	3	7.5	Solomon et al.[223]
			25	0.25	4.5	Li et al.[224]
			25	1.5	9	Li et al.[224]
			35	10	2.3	Ferreira et al.[225]
	332		20	2.3	36	Knez et al.[217]
	190	0.06	30	3	15	Solomon et al.[223]
Zeolites (Regenerative, commercial)						
Clinoptilolite	179.44				4.3	Wahono et al.[226]
Clinoptilolite+plasma activation	153.15				9.16	Wahono et al.[226]
Zeolite 13X			25	0.015	8.4	Wang et al.[213]
Zeolite 5A			25	0.0147	7.44	Wang et al.[213]
Zeolite 13X			25	1.83	14.2	Wang et al.[213]
Zeolite 5A			25	1.58	13.8	Wang et al.[213]
SAPO-34			30	>2.5	18.3	Seo et al.[214]
NaX			30	>2.5	18.6	Seo et al.[214]
Functionalised activated carbons (Regenerative, lab-based)						
CSAC*-KOH	2349	1.036	25	2.2	41	Sun et al.[227]
AC-Silcate-$CaCl_2$	83	0.0589	27	0.9	12.7	Tso et al.[228]
Polymers (Regenerative, lab-based)						

		30	2.8	71	Lee at al.[229]
		30	2.5	43.6	White at al.[230]
MOFs (Regenerative, lab-based)					
HKUST-1	1500-2100	28	2	25	Rezk et al.[215]
MIL100	1600	28	2	17.8	Rezk et al.[215]
MIL101(Cr)	4150	30	>2.5	89.4	Seo et al.[214]
MIL100(Fe)	2300	30	>2.5	48.5	Seo et al.[214]

*CSAC – Coffee shell activated carbon

2.3.2.1 Silica based materials

Silicagels are natural and non-toxic minerals and mostly exist in beaded form. Silica gel is primarily represented by the molecular formula of $(SiO_2).nH_2O$. They are widely used as desiccants due to their extreme hygroscopicity. Silicagels can be classified as macro-porous, displaying low water adsorption capacity and fast saturation when exposed to air; while also as micro-porous, due to its large adsorption capacity. The required temperature for the regeneration of silicagels is around 90-150 °C[231,232]. Wang et al.[213] compared silicagel with zeolite 13X and 5A, and reported that for partial pressures < 1 kPa, the water adsorption capacity follows zeolite 13X>zeolite 5A>silicagel, while for pressures > 1 kPa this order is reversed and silicagel has the largest adsorption capacity. The concentration of water in biogas sources is 2-10%, and the operatin pressure for adsorption is above 5 bar. Therefore, the partial pressure of water in biogas is above 10 kPa, implying that silicagel has superior performance compared to zeolite 13X and zeolite 5A for biogas drying. Additionally, the water adsorption capacity can be further improved with the impregnation of hygroscopic salts into the silicagel structure. Sukhyy et al. [219] enhanced silicagel performance by sodium sulphate impregnation, obtaining a water adsorption capacity of 55.5 mol H_2O/kg adsorbent at 20 °C[219,233,234].

The hydrothermal synthesis of silicagel with long-chain surfactants resulted in the discovery of new mesoporous silicates like MCM-48, MCM-50, SBA15. These adsorbents feature high surface area and high microporous volume, which lead to high water adsorption characteristics[234–237]. Zhang et al.[220] developed three amine-functionalised mesoporous silicates (Silicate-NH_3) with three different impregnating salts that include sodium polystyrene sulphonate (PSS), sodium polyacrylate (PAAS) and sodium malate (MAS). They concluded that water uptake of MAS-impregnated silicate was higher than for the other salts. The water adsorption capacity of amine-functionalised mesoporous silicates (>33.3 mol H_2O/kg adsorbent) was more than two times higher than mesoporous silicate (15.5 mol H_2O/kg adsorbent)[220]. Ribeiro et al.[218] used SBA-15 for water adsorption and, by insertion of alumina precursors into the SBA-15 structure, they found larger water adsorption capacities in comparison with other conventional adsorbents used for water removal[218]. The aluminium insertion increased the hydrophilicity of SBA-15, and naturally, its water adsorption capacity. This research proposed a new series of adsorbents with an enhanced degree of water adsorption that could be used for many industrial applications. They were able to achieve adsorption capacities as high as 58.7 mol H_2O/kg adsorbent. (1057 g H_2O/kg adsorbent) at 25 °C and a 3.1 kPa partial pressure for water[218].

2.3.2.2 Zeolites

Natural zeolites are alumina-silicate minerals of metals like sodium, calcium or potassium and are found in the form of Clinoptilolite, Heulandite, Analcime, Natrolite or Phillipsit. Their wide-open crystalline lattice enables them to hold water vapour in their structure, however, they require higher regeneration temperature than silicagels. The regeneration in silica gels more readily occurs at lower temperatures since throughout the heating process, the aperture size of the skeleton in silicagels changes from 3 to 8 Å[238,239]. Wahono et al.[226] used natural clinoptilolite zeolite for biogas drying. They used plasma activation treatments after dealumination by HCl, and could enhance the water adsorption capacity from 0.078 to 0.165 g H_2O/g. Despite the low price of natural zeolites, only a few studies have been performed to assess their applicability for biogas drying. On the other hand, synthetic zeolites also referred to as molecular sieves or hydrous aluminosilicate substances have shown more promise for biogas drying. They have three-dimensional crystalline and porous structure, with the chemical formula of ($M_{2/n}O\cdot Al_2O_3\cdot xSiO_2\cdot yH_2O$)[240]. Different structural and surface characteristics arise in synthetic zeolites due to the synthesis conditions used, such as the control of temperature or the substitution of aluminium or silicon with other materials[241]. Seo et al.[214] used zeolite NaX and SAPO 34 and achieved a water loading of 18.6 and 18.3 mol H_2O/kg, respectively, at 25 °C and 2.5 kPa partial pressure. Wang et al.[213] used zeolite 13X and 5A and obtained water loadings of 8.4 and 7.44 mol H_2O/kg, respectively, at 25 °C and 0.015 kPa water partial pressure.

2.3.2.3 Activated alumina

The hydrides and oxides of aluminium are referred to as alumina, are produced from thermal dehydroxylation of aluminium hydroxide, and characterised by a highly porous surface. They feature a large number of capillary channels, large surface area (150-500 m^2/g), heat of adsorption of ~3 MJ/kg, and a high affinity towards water. The pore structure of the formed alumina can be controlled by the temperature of the thermal process and its duration. The high affinity towards water removal is attributed to the surface acidity resulting in abundant Lewis acid sites on alumina[242,243]. Knez et al.[217] reported that alumina can achieve up to 69.4 mol H_2O/kg adsorption at 20 °C and 2.3 kPa water partial pressure.[242,243].

2.3.2.4 Functionalised activated carbons

Activated carbon can be a considered a good adsorbent due to its high surface area and pore volume, with further improvement of its water adsorption capacity possible through its impregnation with hygroscopic salts. Sun et al.[227] impregnated coffee-shell AC with potassium hydroxide (KOH) to target the adsorption of water vapour. The effect of various parameters including activation time and temperature as well as KOH ratio was investigated. At optimal conditions, a loading capacity of 41 mol H_2O/kg adsorbent at 25 °C and 70% relative humidity was obtained. Tso et al.[228] developed a composite using activated carbon as an adsorbent base, and impregnated first by soaking it in a 10 wt.% sodium silicate solution, and then in a 30 wt.% $CaCl_2$ solution. The difference in the adsorption capacity of water at atmospheric pressure between 25 °C and 115 °C was 805 g H_2O/kg adsorbent. The adsorption capacity reported confirms that temperature swing adsorption (TSA) processes could be successfully employed using their synthesised composite carbon, with potential to be extended towards other novel carbon based formulations[228].

2.3.2.5 Polymers

The widespread application of desiccant materials in food industry, electronics, and pharmaceutical has favored the development of new desiccant polymers similar to conventional desiccants such as; ACs, silicagels, activated alumina, and hygroscopic salts like LiCl, NaCl and $CaCl_2$[229,244]. The impregnation or ion modification of polymer structures using hygroscopic salts will have the advantage of the high sorption capacity of hygroscopic salts, while addressing the deliquescence problem of hygroscopic salts, by holding the dissolved salt through capillary forces within the void volume of the polymer structure[229]. Jia et al. [245] incorporated the surface functional groups of carbon–oxygen complexes such as; $NaHCO_3$, Na_2CO_3, NaOH, and C_2H_5ONa into the structure of hypercrosslinked polymer adsorbents (HPA). This resulted in water adsorption capacities of up to 80% of their weight, making thema promising adsorbent for biogas drying. The unique characteristics of polymers are the combined high adsorption capacity, low-temperature regeneration, and long life cycle they demonstrate. Czanderna et al.[246] investigated the sorption capacities of 23 commercial polymers and reported some polymers showed about 60% higher sorption capacities than silicagels.. However, the main feature of polymeric adsorbents that differentiates them from other materials is related to their ease of regeneration. This was demonstrated by Young Lee's group[226,] [230], in which they developed a novel polymeric adsorbent by the ion modification of the sodium salt of polyacrylic acid into the structure of a normal polymer. Their material achieved a capacity of up to 71 mol H_2O/kg adsorbent, while being able to be regenerated at only 50 °C.

2.3.2.6 Metal organic frameworks

MOFs are characterised by an open framework with a large number of voids, and a high pore volume and surface area, making them potentially efficient for water adsorption[247–249]. Seo et al.[214] developed hierachical MOFs with mesoporous cages, MIL-101 MOF, and obtained an adsorption capacity of 1610 g H_2O/kg adsorbent (89.4 mol H_2O/kg adsorbent) at 30 °C. They compared the adsorption capacity of MIL-101 MOF with a series of conventional adsorbents, and found that its adsorption capacity is approximately 5 times larger than values for zeolite NaX (18.6 mol H_2O/kg adsorbent), SAPO34 (18.3 mol H_2O/kg adsorbent) and silicagel (18.1 mol H_2O/kg adsorbent)[214].

2.3.3 Absorption drying

In this system, drying occurs utilising water-binding components, mainly triethylene glycol (glycol-based absorption). The process conditions require elevated pressures, using two parallel packed columns, like the adsorption method, and to maintain dew points in the range of -5 to -15 °C, while the regeneration step is performed at 200 °C. Dust and oil particles can be simultaneously removed during the water absorption. Sue to its energy-intensive regeneration process and operation at elevated pressure, this approach is associated with high investment and operational costs. However, this approach is economically feasible as long as the biogas flow rate is larger than 500 $m^3 h^{-1}$ [7,18]. Alternatively, water absorption can be achieved by hygroscopic salts. This technique involves the dissolution of the salt as it absorbs the water from the biogas. Following this, the saturated salt solution is withdrawn from the bottom of the vessels. Since the salt is non-regenerable, the process is performed batch-wise, and the salt must be continuously replaced after saturation[211].

2.3.4 Technology comparison and required investigations

A summary of the advantages and disadvantages of the water removal technologies is provided in Table 16.

Table 16. Advantages and disadvantages of techniques for removal of water.

Method	Advantages	Disadvantages
Condensation method	Simultaneous removal of heavy HCs, dust and oil with water Simple technology Suitable for pre-treatment before use of other technologies	Min. dew point of 0.5 °C at atmospheric pressure Lower dew points need higher pressure but the risk of freezing increases

Adsorption dryer	Higher water removal amounts: dew point down to -40 °C Lower operational costs Regeneration possible	High capital costs The necessity for increasing gas pressure to 6 -10 bar The necessity of dust and oil removal in advance
Absorption with glycol	Higher water removal amounts: dew point -5 to -15 °C Higher removal of HCs and dust Not toxic or dangerous	High capital costs High pressure and temperature (200 °C) for regeneration Feasible at high gas flow rates (>500 m^3/h)
Absorption with hygroscopic salts	High removal efficiency Not toxic or dangerous	Regeneration is not possible

Considering the reviewed technologies, removal of water by the adsorption method has more advantages compared to other technologies; however, it is recommended that: (i) the development of new adsorbents with high loading capacities at atmospheric pressure be carried out, since current adsorption units need high pressures (5-10 bar) for efficient water removal; and (ii) the development of new adsorbents capable of working at temperatures as high as 50 °C is necessary, since that would represent the biogas temperature at the battery limit of a typical plants.

3. Biogas upgrading (CO_2 removal)

This section discusses the decarbonisation of biogas, also termed as biogas upgrading. The main technologies for decarbonisation of biogas are: (1) water scrubbing; (2) organic solvent scrubbing; (3) chemical scrubbing; (4) adsorption; (5) membrane separation; and (6) cryogenic separation. Currently, the decarbonisation of biogas at industrial scale is primarily performed using physical and chemical CO_2 absorption, but membrane and adsorption methods are often used as well. The separated CO_2 from these techniques is usually released into the atmosphere.

3.1. Physical and chemical CO_2 absorption

3.1.1 Water scrubbing

Water scrubbing is the most common biogas decarbonisation technique, making up 31% of global market share[4], and is capable of providing biomethane purity > 97% CH_4 and < 2% CO_2 (for commercial full-scale facilities 10-10000 Nm^3h^{-1}), with ideally 1-2% CH_4 losses. However, 8-10% losses in regular operation has been reported, due to non-optimal operation of the flash tank.[18,46,250]. The removal mechanism is based on the higher aqueous solubility of CO_2 compared with CH_4 (almost 26 times higher at 25 °C). A schematic of the conventional water scrubbing process is provided in Figure 6 a. The biogas is initially compressed to 6-20 bar and cooled to 20 °C and introduced into the bottom of the absorption column. The water is fed to the top of the column to provide a counter-current gas-liquid flow. Random packing is typically used within the column to maximise the gas-liquid interfacial area. The treated biogas leaves the column from the top. Since the CH_4 is partially soluble in water, the saturated water at the bottom of the column is collected and first transferred to a flash column, operating at 2-4 bar, to separate the dissolved CH_4 and transfer it back to the absorption column. Further, the saturated CO_2-rich water is transferred to the desorption column, in which regeneration occurs by bringing the water in contact with air, steam or an inert gas to desorb the dissolved CO_2, and release it into the atmosphere[7,22]. As the absorption efficiency increases substantially as the temperature is reduced, in cold countries like Sweden it is the most common technology[251].

One of the main operational problems is the accumulation of elemental sulphur. Therefore, although it is claimed that water scrubbing is capable of tolerating H_2S concentrations up to 300-2500 ppm_v, it is highly recommended that H_2S be removed prior to the introduction of the biogas to the water scrubbing unit[18]. Another drawback of this technology is foam formation in the packed bed, which can drastically reduce gas-liquid mass transfer. This issue can be resolved by the addition of antifoaming agents, however, their use leads to an increase in operational costs[46].

Another challenge is associated with the necessity of compressing the gas to high pressures, which increases both operation and capital costs[252,253]. Although water scrubbing is the most utilised approach and is associated with low cost of absorbent and performance reliability, its efficiency is relatively low[254]. Roslan et al.[253] proposed that the challenges associated with the required elevated inlet pressure can be addressed if the retention time of water in the packed bed columns is increased, carried out by the development of alternative packing material. Additionally, the effective and complete desorption of CO_2 in the regeneration column is necessary. The environmental impacts are another barrier which can potentially limit the deployment of water scrubbers for future application. Issues such as acidification, and human toxicity resulting from the use of water scrubbers make this technology controversial. The source of these environmental issues is exhaust gas from the desorption column, and the indirect emissions generated during energy consumption[252].

From an economic aspect, significant cost savings can be achieved if cheap water is available, and the regeneration step is eliminated. This configuration is represented by the single-pass scrubber, Figure 7, that uses clean water from sewage treatment plants, and can achieve up to 95% separation efficiency, with a typical water consumption of 0.18-0.23 m^3 H_2O/ Nm^3 of biogas[46,255]. David et al.[254] used inline static mixers for the desorption of CO_2 from water and could obtain 94% CH_4 recovery with an energy consumption of 0.26 kWh/Nm^3. This novel design eliminates the need for desorption columns; therefore, no fuel is consumed to regenerate the absorbent and environmental issues such as acidic water drainage to the environment is prevented. In standard water scrubbing technologies, the investment cost decreases from 5000 to 2000 € (Nm^3 h^{-1})$^{-1}$ for a treatment capacity of 250 to 500 Nm^3 h^{-1}, and remains almost constant at 1000 € (Nm^3 h^{-1})$^{-1}$ for a treatment capacity above 700 Nm^3 h^{-1}[256]. The major contributors to energy consumption processes are gas compression (0.10–0.15 kWh Nm^{-3}), water compression (0.05–0.1 kWh Nm^{-3}) and water cooling (0.01–0.05 kWh m^{-3})[18,46,250].

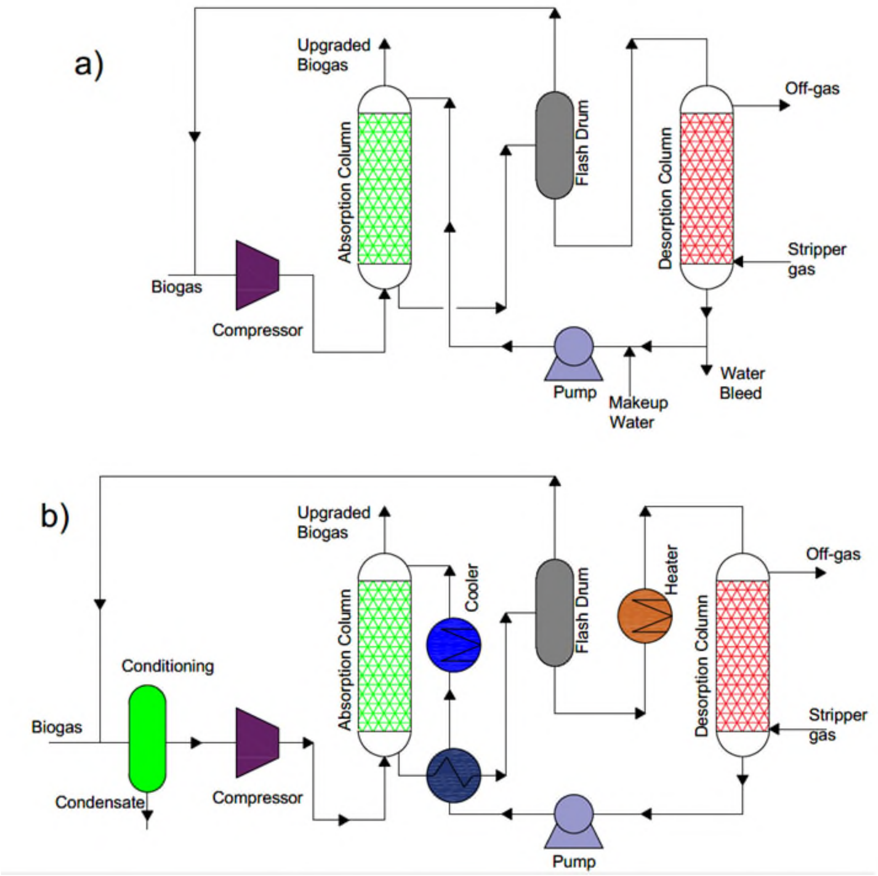


Figure 6. Decarbonisation of biogas by physical absorption processes: (a) water scrubbing, (b) organic solvent scrubbing[18].

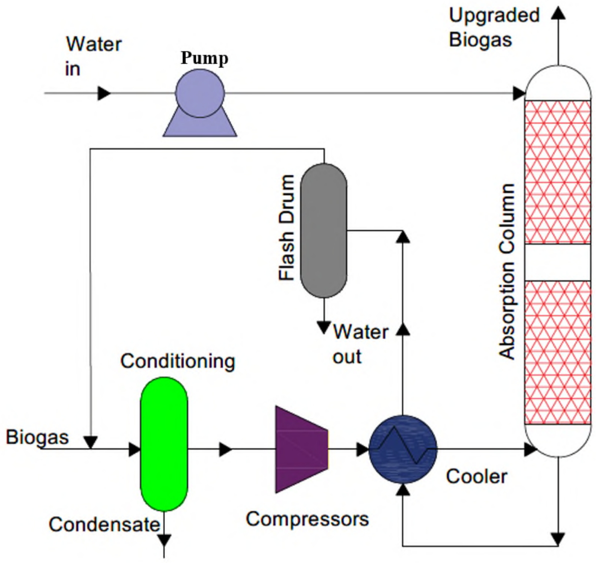


Figure 7. Single-pass water scrubbing for decarbonisation of biogas[7].

3.1.2 Organic solvent scrubbing

Organic solvent scrubbing is another physical absorption approach that almost follows the same principle as conventional water stripping processes, Figure 6 b[18]. In this process, organic solvents such as polyethylene glycol-based solvents, with higher affinity towards CO_2, are used instead of water. In this manner, plant size can be potentially reduced, which results in a decrease in both investment and operational costs. Besides CO_2, H_2S and water can also be absorbed simultaneously, due to their higher solubilities compared toCH_4. A biomethane product stream with a 96-98% CH_4 purity can be achieved, while the desorption of the adsorbed species is performed through a thermal process at 40 °C. Similar to water scrubbing, this approach leads to an almost 2% CH_4 losses[250]. In the presence of high H_2S concentration, only steam or inert gas (not air) should be used for regeneration, although it is recommended that H_2S should be removed prior to the organic solvent scrubbing process[7].

The associated investment cost of organic solvent scrubbing is reduced significantly as the capacity increases, dropping from approximately5000 € $(Nm^3\ h^{-1})^{-1}$ for 250 $Nm^3\ h^{-1}$ to 2000 € $(Nm^3\ h^{-1})^{-1}$ for 500 $Nm^3\ h^{-1}$ capacity, while at a capacity above 700 $Nm^3\ h^{-1}$, it reaches a constant cost of ~1000 € $(Nm^3\ h^{-1})^{-1}$[256]. On the other hand, the operating costs are primarily due to biogas compression (0.2-0.25 kWh Nm^{-3}) and maintenance costs (2-3% of the investment cost)[46].

3.1.3 Chemical scrubbing

Chemical scrubbing follows the same principle as water and organic solvent scrubbing, but with a simpler configuration and process, and an enhanced liquid/gas mass transfer and performance. This technology currently accounts for almost 30% of the biogas upgrading global market[4]. In this process, Figure 8, CO_2 is absorbed in a liquid and reacts with reactive chemical substances, such as alkanolamines (MEA: monoethanolamine, DEA: diethanolamine, DETA: diethylenetriamine, TEPA: tetraethylenepentamine, PEI: polyethyleneimine) and alkali aqueous solutions (NaOH, KOH, CaOH, K_2CO_3, Na_2CO_3) at an operating pressure of 1-2 bar in the absorption column, in a counter-current flow configuration[45]. The CO_2-saturated solvent is transferred to the stripper (desorption) column where the CO_2 is separated through a thermal process at 120-150 °C, and then is released into the atmosphere. The treated biomethane has a CH_4 purity of over 99% with typically a 0.1-1.2% losses in CH_4 (although for alkanolamines, up to 4% CH_4 losses have been reported)[5,7,18].

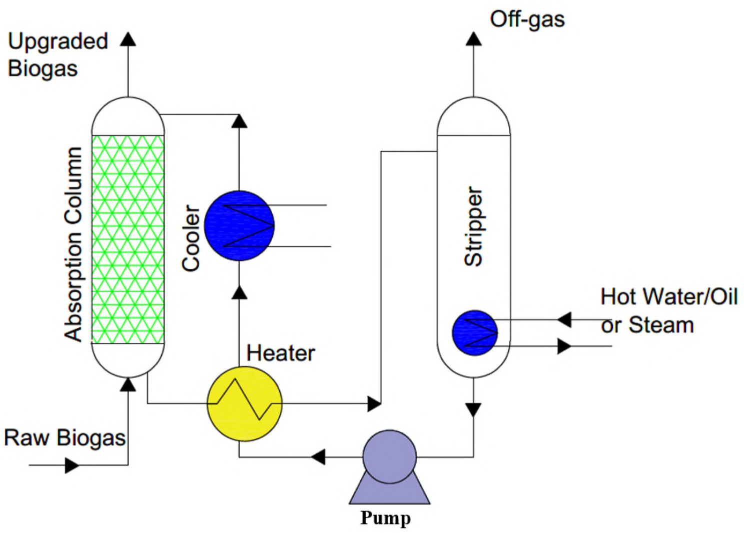


Figure 8. Chemical scrubbing for decarbonisation of biogas[18].

In amine scrubbing, the presence of H_2S in biogas can potentially result in amine poisoning; therefore, removal of H_2S before the decarbonisation step is highly recommended. Operational problems associated with amine scrubbing are foaming (can be resolved by using antifoaming agents), degradation and loss of amine, and corrosion. However, the main drawback of this technology is the high energy requirement for solvent regeneration, which considerably increases the energy penalty of the upgrading plant[5,7].

The associated investment costs of chemical scrubbing decreases from 3000 € $(Nm^3\ h^{-1})^{-1}$ for 500 $Nm^3\ h^{-1}$ to 1607 € $(Nm^3\ h^{-1})^{-1}$ for capacities above 1400 $Nm^3\ h^{-1}$ capacity[256]. The energy requirement for gas compression is around 0.12-0.15 kWh Nm^{-3}. However, the main operational cost stems from the required energy for regeneration, around 0.55 kWh Nm^{-3}, which makes this technology energy-intensive[18,46].

3.2. Adsorption

This technique is based on selective capture of CO_2 over CH_4 onto porous surfaces of adsorbents, such as activated carbon, silicagel, MOF, molecular sieves and polymeric sorbents, at an elevated pressure[7]. Adsorption processes currently make up 21% market share in biogas upgrading technologies[4]. An adsorbent's surface area, CO_2 capture capacity, and CO_2/CH_4 selectivity are the initial key parameters for assessing their performance in the decarbonisation of biogas. CO_2 molecules present in a biogas mixture can be adsorbed by one or both of the following mechanisms[106,242,257]:

1. Molecular sieving effect (steric separation): based on the size (cross-sectional size or kinetic diameter) and shape of molecules, only certain molecules of biogas can enter the pores of adsorbents whilst the remainder of molecules (mainly CH_4) are prevented from entering. This mechanism is common for zeolite, carbon-based molecular sieves, and MOFs. The kinematic diameter of CO_2 and CH_4 molecules are 3.4 and 3.8 Å, respectively. Therefore, suitable adsorbents for decarbonisation of biogas should have an average pore size smaller than 3.8 Å.
2. Kinetic effect (partial molecular sieve action): based on the difference in diffusion rate, due to several factors, including characteristics of an adsorbent's surface interface, some gas compounds enter the pores and are adsorbed faster than other compounds.

The mechanism of adsorption technology for biogas upgrading is described in Figure 9. In this process, the adsorbents are packed in four parallel interconnected vessels that operate under four different phases, namely adsorption, depressurisation, desorption, and pressurisation. In adsorption mode, the compressed biogas (4-10 bar) is introduced to the bottom of the pressurised adsorption vessel, CO_2 is selectively adsorbed, and the treated biogas (biomethane) leaves from the top of the column. Once the adsorbent is saturated, the process is switched to the next bed. Afterwards, the saturated adsorbent is depressurised which results in the release of a CH_4/CO_2 stream that is recycled back to the inlet of the pressure swing adsorption (PSA) unit (depressurisation mode). In the next step, the saturated adsorbent is regenerated by further depressurisation, or by placing it under vacuum, leading to the release of a CO_2-rich gas stream with a small quantity of CH_4 (desorption mode); finally, the bed is pressurised and prepared for the next adsorption cycle (pressurisation)[7,22,258]. The pressure profile of each cycle is provided in Figure 10. The arrows and green shaded areas on the image of each vessel represent the direction of flow, and any pressure change in response to the movement in flow. In step (1), the outlet is closed, and the feed enters the bed from the bottom (pressurisation step), the aim is to increase the bed pressure up to the adsorption pressure. In step (2), the outlet valve is opened, and the bed enters the adsorption step; the bed pressure remains constant throughout the whole adsorption step. In step (3), the outlet valve is opened, and the bed pressure decreases to atmospheric pressure (de-pressurisation step). The last step of each cycle, Step (4), depicts the desorption step (purge step), in which the bed is purged at the atmospheric conditions established in Step (3), to undergo regeneration.

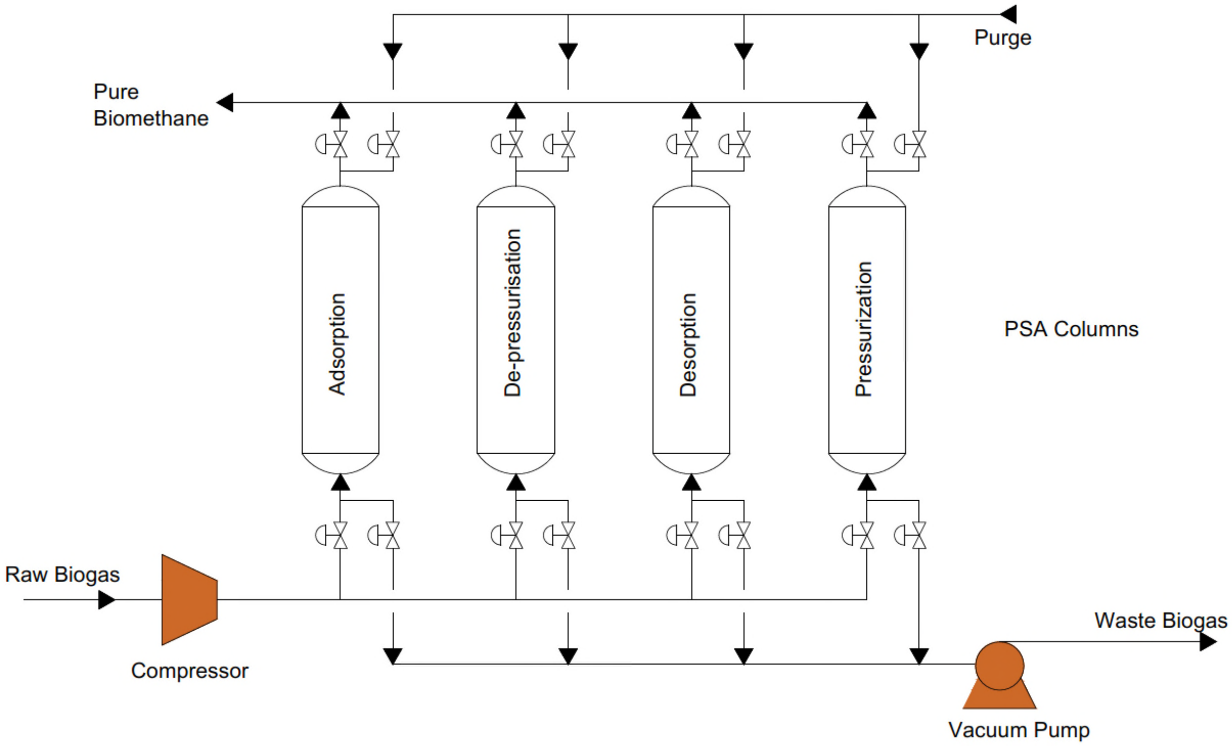


Figure 9. Biogas decarbonisation by pressure swing adsorption[190]. PSA: pressure swing adsorption.

Treated biogas from PSA processes has 96-98 % CH_4 purity, with CH_4 losses above 3%[7,46]. Besides CO_2, N_2 and O_2 can also be removed during the process. However, H_2S can adversely affect the adsorption performance by poisoning molecular sieves, and when they are employed, should be treated upstream. Similarly, water can negatively impact some adsorbent's capacity, and the gas should be dried prior to its introduction to the PSA unit[7,259]. As the throughput of a plant increases, the investment cost of PSA decreases from 3000 € $(Nm^3\ h^{-1})^{-1}$ for 500 $Nm^3\ h^{-1}$ to 2200 and 1750 € $(Nm^3\ h^{-1})^{-1}$ for 700 and 1000 $Nm^3\ h^{-1}$ and investment cost is 1500 € $(Nm^3\ h^{-1})^{-1}$ for capacities above 1400 $Nm^3\ h^{-1}$[256]. While for operational costs, the electricity consumption for biogas upgrading is around 0.2 kWh Nm^{-3}, plus a 0.17 kWh Nm^{-3} if gas drying is included[18,46].

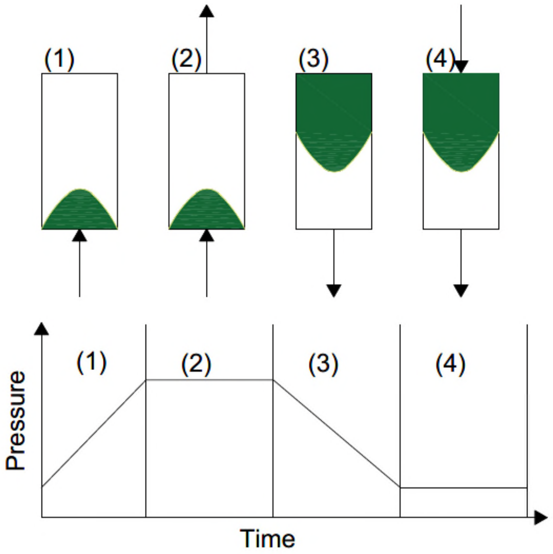


Figure 10. Schematics of the four phases in PSA along with the pressure profile of the cycle: (1) pressurisation, (2) adsorption, (3) depressurisation, and (4) desorption. A PSA column cycle is typically 2-10 min long[232,241,242,260]. The arrows and green areas represent flow direction.

Table 17 provides a parametric comparison among different types of CO_2 adsorbents, based on their surface characteristics, adsorption capacity, and CO_2/CH_4 selectivity.

Table 17. Comparison of various adsorbents for biogas upgrading

Adsorbent	S_{BET} (m^2/g)	Adsorp. capacity (mg/$g_{ads.}$) at 1 bar 25 ºC			$V_{tot.}$ (cm^3/g)	CO_2/CH_4 selectivity			Ref.
		H_2S	CO_2	CH_4		1 bar	4 bar	7 bar	
Molecular sieves (Regenerative, commercial)									
Zeolite 13X		1	298.5						Alonso et al.[84]
Zeolite 5A		0.5	273.7						Alonso et al.[84]
Clinoptilolite	38.6	1.4	173.9		0.004				Alonso et al.[84]
Zeolite 13X						9 at 30 °C	3.8 at 30 °C		Cavena. et al.[261,262]
Na-ZSM-25			70 @ 30 °C	0.46					Min et al.[263]
SAPO34	571				0.36	4.6	3		Golma. et al.[190]
ZSM-5	387				0.22	4.6	1.9		Tamna. et al.[264]
Li-ZSM-25			88 @ 30 °C	0.46		66.9 CO_2/CH_4 (50/50%) @ 2 bar			Zhao et al.[265]
MOFs (Regenerative, lab-based)									
Cu-MOF	>2000					5.5 at 30 °C	4.5 at 30 °C		Cavena. et al.[261]
MOF-5						1.5 at 30 °C	2.3 at 30 °C		Cavena. et al.[261]
MIL-53			60 @ 30 °C	30		2 at 30 °C			Hamon et al. [266]
MIL-101	96.4				0.37	931			Yan et al. [267]
Cu-BTC MOF						8			Hamon et al. [268]
Activated carbons (Regenerative, commercial)									
	1005		177		0.525				Meng et al. [269]
	650				0.42	2.5	1.9		Tamna. et al.[264]
	3100		380 @ 0 °C		1.4				Wahby et al.[270]
			113						Muru. et al. [271]
	1323				0.64				Mancila et al.[272]
						2 at 30 °C	2 at 30 °C		Cavena. et al.[261]
Polymers (Regenerative, lab-based)									
SNMC-1-600	1021		175	22.5	0.65	6.9 CO_2/CH_4 (40/60%)			Zhang et al.[273]
NKA-9-PEI(30%)	86.3		102 at 0.45 bar, 35 °C	<5	0.69	>20			Meng et al.[274]
NKA-9-PEI(40%)	68.6		117 at 0.45 bar, 35 °C	<5	0.61	>23			Meng et al.[274]
NKA-9-PEI(50%)	25.2		151 at 0.45 bar, 35 °C	<5	0.31	>30			Meng et al.[274]

NKA-9-PEI(60%)	4.5	93.8 at 0.45 bar, 35 °C	<5	0.07	>18			Meng et al.[274]
Amine functionalised materials (Regenerative, lab-based)								
SBA-15	717			0.918	5	7	9	Mafra et al.[275]
SBA-15,APTES*	344	44		0.556	45	40	30	Mafra et al.[275]
SBA-15,TMMAP**	260	48		0.385	600	1000	1000	Mafra et al.[275]
SBA-15,DEAPTES***	318	8.8		0.442	6	6	6	Mafra et al.[275]
SBA-15,N3****		57.2			10000	11000	10000	Mafra et al.[275]
Silicalite-1	390			0.31	3	2.2		Tamna. et al.[264]

*Primary amine: [3-aminopropyl-triethoxysilane (APTES)]
**secondary amine: trimethoxy[3-(methylamino) propyl]silane (TMMAP)]
***tertiary amine: (diethylamino)propyl]tri methoxysilane (3-DEAPTES)] amines
****diamine containing primary and secondary amine groups [N-[3-(trimethoxysilyl) propyl]ethylenediamine (N-3)]

3.2.1 Activated carbons

Activated carbons are an existing commercial class of adsorbents which should be studied for all separation purposes, due to their availability, low cost, high surface area, thermal stabilities, and regenerability capabilities. The effect of textural properties was studied by Wahby et al.[270,276] and they found that narrower micropore volumes (<0.5 nm) enhance CO_2 adsorption capacity, while increasing the mesoporous contribution of adsorbents enhances the kinetic rate of CO_2[276]. Moreover, due to the acidic properties of CO_2, the removal of surface acidic groups or the presence of oxygen in surface groups such as -OH[277] causes the surface to become basic, and CO_2 loading can be improved considerably.

In biogas upgrading, CO_2/CH_4 selectivity is of a bigger concern than CO_2 loading. Mancilla et al.[272] conducted a comprehensive study to improve the CO_2/CH_4 selectivity of activated carbons by analysing their surface's textural and chemical properties. They found that high CO_2/CH_4 selectivity values are favoured by intermediate BET surface areas (1323 $m^2.g^{-1}$), narrow pore size distribution centred at 0.8 nm, and the presence of sulphur surface groups[272]. Furthermore, The presence of polar surface groups enhances the CO_2/CH_4 selectivity due to the polarizability of CO_2 in comparison to the less polarizable characteristics of CH_4. One example of their effect is demonstrated by Meng et al.[269], in which the preparation of highly N-doped nanoporous activated carbons using polypyroll (PPY) activated by NaOH as a basic group was carried out, and obtained a CO_2 loading of 177 $mg.g^{-1}$ at 1 bar and 25 °C with negligible CH_4 adsorption.

3.2.2 Polymers

The cross-linked products of polymers with amine functionalised (DEA, TEPA, DETA, PEI) groups prepared by impregnation or grafting methods are novel materials recently used for biogas upgrading. Meng et al.[274] impregnated a porous polymeric resin (NKA-9) with PEI and could obtain a CO_2 loading capacity of 151 mg/g adsorbent with negligible CH_4 adsorption. This adsorbent could be regenerated by N_2 and CO_2 hot purge streams at 85 °C and 155 °C, respectively, without a considerable decrease in their loading capacity.

Zhang et al.[273] developed a melting-assisted and solvent-free method to prepare nitrogen-containing polymers, resulting in a material that showed a good selectivity of 6.9 at 1 bar for a CO_2/CH_4 mixture of 40/60%. Their adsorbent's CO_2 loading at 1 and 20 bar was 175 mg/g adsorbent and 968 mg/g adsorbent, respectively, at 25 °C. Such a large difference in loading indicates that pressure swing adsorption (PSA) can be used for biogas upgrading using these polymers. At the vacuum pressure of 0.15 bar, the CO_2 uptake capacity of adsorbent was 62 mg/g adsorbent, which shows that vacuum swing adsorption is also a good choice for this adsorbent[273].

3.2.3 Molecular sieves

Under the category of molecular sieves, new types of zeolitic materials have been developed for CO_2/CH_4 separation. Guo et al.[278] developed a zeolite (NaTEA-ZSM-25) with a pore aperture size of 3.6 Å, which attracted a great deal of attention because of its CO_2/CH_4 adsorptive selectivity of 1.9–20 at high pressures, but the disadvantage was its low CO_2 working capacity in PSA applications (0.5 mmol/g from 10 to 1 bar)[278]. The low working capacity of NaTEA-ZSM-25 zeolites made the use of PSA impossible, and therefore, vacuum swing adsorption (VSA) would be required. However, VSA is energy-intensive, and thus may be seen as an unsuitable solution for the current limitations of benchmark biogas upgrading processes. To overcome this imperfection, Na-ZSM-25 was prepared by removing TEA from the zeolitic structure to obtain a higher CO_2 adsorption working capacity (1.5 mmol/g from 10 to 1 bar)[263]. Unfortunately, Na-ZSM-25 has a low kinetic rate which requires a long time to reach equilibrium conditions. Zhao et al.[265] solved this problem by injecting Li into the structure of ZSM-25, resulting in high CO_2 adsorption kinetics, which made its use possible in PSA-based CO_2/CH_4 separations.

Alonso et al.[84] studied the cleaning (H_2S removal) and upgrading (CO_2 removal) of biogas for two synthetic zeolites (5A and 13X) in comparison with a natural zeolite (clinoptiolit). They concluded that although synthetic zeolites have a better adsorption capacity for CO_2, natural zeolites have a better adsorption capacity for H_2S, making it possible to simultaneously target cleaning and upgrading of biogas in one step. Additionally, natural zeolites have good regenerability and a lower price, which makes them superior to synthetic zeolites[84].

3.2.4 Metal organic frameworks

MOFs are a novel family of adsorbents that have been developed with exceptional characteristics, such as extraordinarily high surface area, high CO_2 adsorption capacity, great stability against contaminants like H_2S or H_2O, high CO_2/ CH_4 selectivity, and tuneable pore size and shape by varying either metallic clusters or organic ligands[105]. Their structure is usually rigid, but some, such as MIL-53, have an incredibly flexible structure, which changes in response to the adsorption or desorption of some gases like CO_2[266]. In MIL-53, as $CO_{2,}$ is adsorbed, its structure shifts from large rectangular pores (0.85 × 0.85 nm), to narrow trapezoidal pores (0.26 × 1.36 nm)[266,279]. The tunability of MOFs permits the customisation of its performance for each application, this was demonstrated by Yan et al.[267], preparing amine-functionalised MOFs with tuneable porosity, that exhibited exceptional CO_2/ CH_4 selectivity of 931 at 1 bar and 25 °C.

Although providing a platform for the development of optimally performing adsorbents, developed MOFs from laboratory studies are mainly in powder form, while the consolidated industrial applied materials need to be in pellet form, to minimise the pressure drop across the vessel and avoid material carryover into the product or purge streams during each associated PVSA step. Yang et al.[280] investigated the effect of pelletisation on the adsorption capacity of MOF MIL-100(Cr) powder and observed it decreased from 5.8 for powder to 4.05 mol CO_2 / g for pellets. These results support the need of measuring the performance of laboratory studied materials in pellet form, to accurately assess their expected performance in industrial applications. They also investigated the effect of activation temperature on adsorption capacity and noticed that adsorption capacity of MIL-100(Cr) activated at 250 °C is 2.5 times higher than a sample activated at 150 °C. Designating a minimum activation temperature that maintains a material’s performance is important, and will contribute in the reduction of operating costs for the industrial scale production of a material.

The low recovery of PVSA processes for biogas upgrading can be addressed by development of materials that can simultaneously remove several impurities. Belmabkhout et al.[281] developed fluorinated MOFs like AlFFIVE-1-Ni for the simultaneous removal of H_2S and CO_2 from gas streams enriched with CH_4 like biogas. They tuned the intrinsic properties and functionalities of MOFs to produce SIFSIX-2-Ni-I, AlFFIVE-1-Ni, and NvOFFIVE MOFs with CO_2/H_2S selectivities of 0.3, 1, and 33 respectively.

The tunability of MOFs can be facilitated through molecular simulation techniques, allowing for the screening of a vast number of MOF designs or process conditions while minimising the amount of time and money that would be designated to laboratory synthesis and experimentation. Borges et al.[282] utilized grand canonical Monte Carlo (GCMC) simulations to calculate CO_2, CH_4, and N_2 adsorption isotherms then validated them with experimental results, finding good agreement between the two. He then used validated GCMC simulations to calculate the CO_2/N_2 and CO_2/CH_4 selectivities of 35 and 10 respectively at 1 bar on MIL-160 MOF. Pal et al.[283] could achieve higher CO_2/N_2 and CO_2/CH_4 selectivities of 51 and 36 respectively at 1 bar and 0 °C with Co-MOF, IITKGP-6 adsorbent, but used the using ideal adsorbed solution theory (IAST) instead.

Demired et l.[284] screened all 5109 available MOFs in the computation-ready experimental metal–organic framework (CoRE-MOF) database to shortlist the best MOFs for biogas upgrading. In the first screening step, they omitted 1710 MOFs due to their special geometry (pore diameter < 3 Å) or exceptional metal nodes. In the second screening step, GCMC simulations enabled them to omit MOFs that demonstrate a low selectivity of removing impurities from biogas in binary mixtures of CH_4/(CO_2 or H_2S or NH_3 or N_2). In the final screening step, GCMC simulations were performed for the simultaneous removal of 4 undesirable impurities, eventually narrowing them down to JOSNAG MOF as the ideal MOF for biogas upgrading.

3.2.5 Amine functionalised materials

A comprehensive study by Mafra et al.[275] was carried out on the use of primary, secondary and tertiary amines on mesoporous SBA-15 for the separation of CO_2/CH_4 gas mixtures. In their study, they revealed that the CO_2/CH_4 selectivity can reach extremely high values, especially for secondary (TMMAP) and mixed primary/secondary (N-3) amine-functionalised SBA-15, which have reported selectivity values of up to 1000 and 11000, respectively. The reason for such high selectivity is related to the reaction between CO_2 and surface amines, which, even at low pressures still have good adsorption capacities. The selectivity values for tertiary amines on SBA support do not show any significant improvement, but primary amines also have a positive impact on selectivity, albeit to a lesser extent. Although the selectivity of the adsorbent functionalised by primary amines are not as high as secondary or mixed amine adsorbents, their ease of regeneration makes them superior to others, with reported working capacities under vacuum and atmospheric desorption by Mafra et al.[275] showing higher values compared to TMMAP and N-3 [275].

The use of functionalised amine groups on different types of adsorbents has attracted a great deal of attention recently because of the high selectivity achievable by these adsorbents. Table 18 lists several adsorbent supports which have been loaded by various types of amines, and their CO_2 loading at different operating conditions. Amine loading has been shown to have a great importance on selectivity, and finding optimum amine loading for each adsorbent can be challenging. Although adsorbents functionalised by a high loading of amine groups (>30%) have very good selectivity and CO_2 uptake values, they do not have good chemical stability, and after several cycles and regeneration, their adsorption capacity decreases[285]. This problem has hindered their usage at an industrial scale[286]. The adsorption capacity of these adsorbents also decreases over consecutive cycles in a VSA process, consequently, temperature swing adsorption methods must be used[286–289].

Table 18. Comparison of various adsorbents modified with functionalised amines for biogas upgrading

Support	Amine type	wt.%	Adsorp. temp. °C	Pressure Bar	CO_2 loading mg.g^{-1}	Ref.
NKA-9	PEI	30	35	0.45	102.4	Meng et al.[285]
NKA-9	PEI	40	35	0.45	117.3	Meng et al.[285]
NKA-9	PEI	50	35	0.45	151.1	Meng et al.[285]
NKA-9	PEI	60	35	0.45	93.8	Meng et al.[285]
XAD-761	PEI	40	25	0.1	169.4	Liu et al.[286]
XAD-761	PEI	50	25	0.1	86.3	Liu et al.[286]
XAD-761	PEI	40	80	0.1	98.6	Liu et al.[286]
MgO			30	0.4	41.8	Kasikampha et al.[290]
MgO	TEPA	40	30	0.4	219	Kasikampha et al.[290]
SBA-15	PEI	50	75	0.15	139.9	Ma et al.[288]
KIT-6	PEI	50	105	1	136.4	Kishor et al.[289]
SiO_2	APTES	70	100	0.1	89.3	Quang et al.[291]
MMSV	PEI	60	90	1	208.1	Zhang et al.[292]

Table 19 summarises the most recent performance of cyclic adsorption units for biogas upgrading, all of which utilise a VSA process arrangement, which implies that vacuum conditions are mandatory for adsorbent regeneration. It can be deduced that equilibrium adsorbents cannot produce biomethane with a Purity>98% at an acceptable recovery (Recovery>90%). However, kinetic adsorbents show better potential in producing biomethane with the required specifications of biograde fuels while requiring less energy consumption. MOFs are newer adsorbents that are now being investigated for use in biogas upgrading due to their favourable characteristics, such as their lower energy consumption in comparison with existing industrial adsorbents. In comparison with zeolites and Carbon Molecular Sieves (CMS), the energy consumption of MOFs is the lowest, followed by CMSs, and then zeolites[293].

Table 19. Comparison of cyclic adsorption units for biogas upgrading

Feed CH_4/CO_2	Adsorbent Type	Adsorbent	Type	Beds	$P_{ads.}$	CH_4 Purity	CO_2 Purity	CH_4 Recovery	Power kW/Nm^3	Ref
(63/37)	Equilibrium	Zeolite 5A	VSA	4	6 bar	98.8%	78.5%	83.90%		Augell et al.[294]
(21/79)	Equilibrium	Zeolite 5A	VSA	4	6 bar	82%	99%	97%		Augell et al.[294]
(67/33) at 50 °C	Equilibrium	Zeolite 13X	VSA	2	4 bar	99%		85%	0.123 *	Santos et al.[89]
(60/40)	Kinetic	CMS	VSA	2	5 bar	97.5%		93.8%		Canevesi et al.[295]
(60/40)	Kinetic	CMS	VSA	2	5 bar	97.9%		91%		Canevesi et al.[296]
(55/45)	Kinetic	Silicagel	VSA	4	4 bar	98.0%	96.7%	97.3%		Shen et al.[297]
(55/45)	Kinetic	CMS-3K	VSA	2	8 bar	98.1%		79.7%		Grande et al.[298]
(55/45)	Equilibrium	Zeolite 13X	VSA	2	8 bar	98.0%		60.1%		Grande et al.[298]
(55/45)	Combined	CMS-3K/13X	VSA	2	8 bar	98.0%		80.3%		Grande et al.[298]
(67/33) at 50 °C	Equilibrium	Zeolite 13X	VSA	2		98.0%		85%	0.422	Wu et al. [293]
(67/33) at 50 °C	Kinetic	CMS-3K	VSA	2		98.0%		85%	0.214	Wu et al. [293]
(67/33) at 50 °C	Kinetic	MOF-508 b	VSA	2		98.0%		85%	0.185	Wu et al. [293]
(60/40)	Kinetic	CMS	VSA	2	5 bar	97.5%		90%		Canevesi et al.[296]

*kW/mol

The shape of the isotherm curve can give a good measure of the suitability of an adsorbent for a specific adsorption process for biogas upgrading. The development of new adsorbents with a linear CO_2 isotherm makes adsorbent regeneration feasible without the need for vacuum and, therefore, PSA can be used instead of VSA. This can become a key mode of minimising the energy consumption of biogas upgrading, since PSA processes have lower energy demands compared to VSA processes.

3.3. Membrane separation

Membrane separation for CO_2 removal is based on the selective permeation of CO_2 through porous membranes and the retention of CH_4 molecules. This technology is commercially available and already has an 8% share of the biogas upgrading market[4,281,282]. There are two types of membrane systems: (1) low-pressure liquid-gas modules, in which the diffused CO_2 is absorbed by a CO_2 solvent (mainly amine solutions) flowing on the outside of the membrane tubes; and (2) high-pressure-driven dense (gas-gas) module. Liquid-gas membranes operate at atmospheric pressure and can upgrade biogas to almost 96% methane purity. Afterwords, the CO_2-rich solvents can be regenerated through a thermal process to produce a pure CO_2 stream. In pressure-driven dense (gas-gas) membranes, the biogas is pressurised to 20-36 bar, although, few pilot cases have reported operation at lower pressures (around 8 bar)[7,46]. The gas-gas membrane units are manufactured as single-pass membrane, and multi-stage membrane with internal recirculation of permeates and retentates, presented in Figure 11. The single-pass and multiple stage membranes can purify the biogas to 92%-96% CH_4. However, the offgas contains 7-10% CH_4, and needs to be flared or post-processed. Membrane separation requires pre-treatment to remove water, H_2S, VOCs, NH_3, and siloxanes to avoid rapid deterioration and clogging of the membrane[18,46].

The investment cost of gas-gas membrane separation decreases from 4400 € $(Nm^3\ h^{-1})^{-1}$ for 250 $Nm^3\ h^{-1}$ to 2900, 2286, and 2000 € $(Nm^3\ h^{-1})^{-1}$ for 500, 700, and 1000 $Nm^3\ h^{-1}$ capacity, respectively, and remains almost constant at 1786 € $(Nm^3\ h^{-1})^{-1}$ for a plant capacity over 1400 $Nm^3\ h^{-1}$ [256]. The operational costs are around 0.13–0.22 € Nm^{-3}, and are mainly associated with membrane replacement (5-10 years lifetime), biogas compression costs (0.2–0.38 kWh Nm^{-3}), maintenance (3-4%), and any necessary biogas pre-treatment[18,46]. However, it should be noted that these operational costs are lower if the H_2S, water, and siloxane removal is performed by alternative processes. Over the last decade, developments in membrane separation have placed it in better economic standing, investment costs can range from 3500–7500 €/(m3/h) while having operational costs of 7.5–12.5 €/(m3/h).

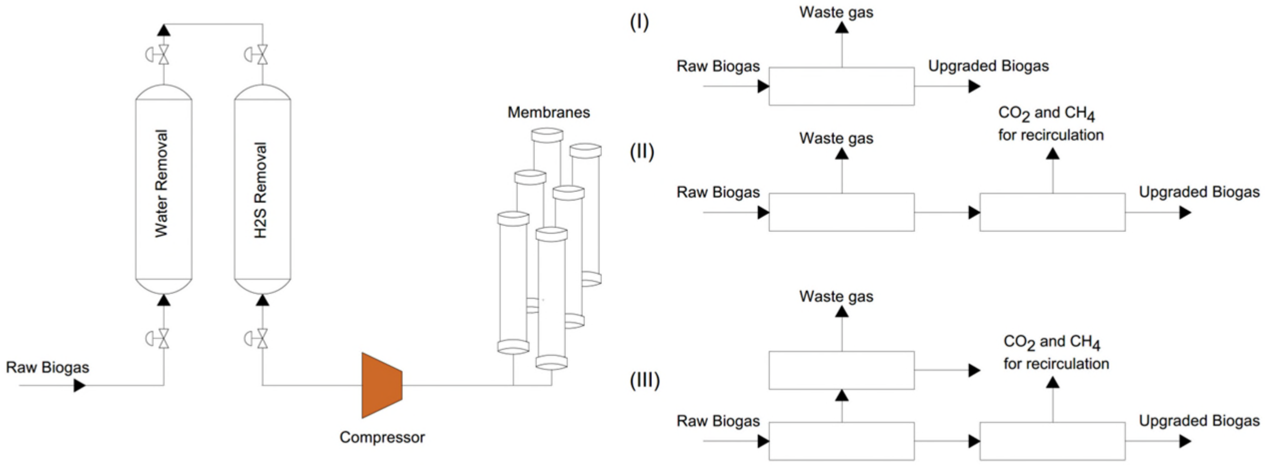


Figure 11. Decarbonisation of biogas using pressure driven dense (gas-gas) membrane separation: (I) single-pass membrane unit, (II) multiple stage membrane units with internal recirculation of permeate, and (III) internal recirculation of retentates[18,46].

The roll out rate of membrane technology for biogas upgrading in large-scale industrial plants continues to increase. The first biogas upgrading plant with 25 $Nm^3.h^{-1}$ capacity was built in the Netherland in 1993, but since then, its capacity has increased to 375 $Nm^3.h^{-1}$[9]. Esposito et al.[6] designed a large scale plant with biogas treating at an upgrading capacity of 6250 $Nm^3.h^{-1}$, producing biomethane with a purity of 96.3 vol% using Evonik's SEPURAN® membranes[299]. They also recovered waste CO_2 gas by enhancing its purity to 99.9 vol% through various purification steps to meet the required specification of the food and beverage industry. This project is the first industrial scale plant with simultaneous biomethane and food grade CO_2 production[6]. Some novel approaches have also been utilised with existing membrane materials for biogas upgrading, such as condensing-liquid membranes (CLM), which separate a gas mixture by using the solubility differences of the various components, across a thin layer of water covering a hydrophilic membrane[300]. They first saturate the biogas feed by a humidifier and then introduce it to the membrane, where temperature difference between the water saturated biogas and the cold membrane leads to the condensation of the water on the membrane, carrying with it any soluble impurities in the biogas, and thus upgrading the biogas stream [301]. This method has some major limitations though, such as the necessity of having sufficiently low temperatures in the membrane to facilitate the condensation of the vapour in the biogas being treated. The major drawback of CLM is the short residence time of biogas in the permeation cell, which causes the removal efficiency of impurities to decrease significantly. Poloncarzova et al.[302] demonstrated such limitations , enhancing the CH_4 purity in biogas from 67% to only 76% when using CLM. The membrane types can be classified into two major types, polymeric membranes and composite or mixed matrix membranes, and will be individually discussed in the following sections.

3.3.1 Polymeric Membranes

The superior mechanical behaviour of polymeric membranes compared to other membrane materials has made their fabrication technology versatile, evidenced by different forms such as spiral wound or hollow fibre membrane modules[303,304]. However, the plasticization of a membrane leads to significant loss in CO_2/CH_4 selectivity and permeability, and is considered a major pitfall that has hindered their widespread application, especially for high pressure conditions[305,306]. There are four types of commercial polymeric membranes that include; (i) thermally rearranged polymers (TR), (ii) polymers of intrinsic microporosity (PIM), (iii) polyimide membranes (PI), and (iv) poly ethylene oxide membranes (PEO)[307,308].

Although not mutually exclusive, there is an inverse relation between CO_2/CH_4 selectivity and the permeability of membranes, as the permeability decreases, the selectivity increases[309]. The majority of existing commercial membranes have selectivity values between 20 to 50, which coincide to a permeability that decreases from 4000 to 1 barrers[310]. The low permeability of existing commercial membranes has been addressed by ultrapermeable benzotriptycene-based PIMs that can achieve a permeability of 52,800 barrers at a CO_2/CH_4 selectivity of 7.28. However, due to the typical trade-off between permeability and selectivity, by increasing the selectivity of ultrapermeable benzotriptycene-based PIMs from 10 to 40, their permeability decreases from 40,000 to 4000 barrers[311].

TR and PIM membranes exhibit promising results for biogas upgrading due to a high portion of free volume in their structure that favours the diffusion of CO_2[312]. The thermal treatment of TR membranes at high temperatures (>350 °C) leads to the formation of insoluble rigid polymer backbones like polybenzimidazole (PBI), thus, creating a large free volume in the membrane structure[313]. For PIMs, the disrupted chain packing due to its contorted shape causes the large free volume in their structure[314]. Despite promising results in lab scale studies of TR and PIM membranes, their application for industrial purposes has not been achievable due to issues regarding their mechanical stability or loss of CO_2 permeability over time[315]. A comparison of different polymeric membranes for biogas upgrading is presented in Table 20.

Table 20: comparison of polymeric membranes

Type	Material	Pressure bar	Temp. °C	CO_2 permeability barrer	CO_2/CH_4 selectivity	Ref.
TR						
	TR HAB-FDA-6FDA	10	35	249	19	Sholes et al.[316]
	SPDA-SBF-PBO	2	35	1280	15	Ma et al.[317]
	TR-PBO-350(6FDA-HAB-allyl)	1	30	110	50	Tena et al.[318]
	(6FDA-SBF-PBO)	2	35	1160	20.7	Ma et al.[317]
PIM						
	BTrip	1	25	21500	12.7	Bibiana et al.[311]
	TMN-Trip	1	25	52800	7.28	Bibiana et al.[311]
	HMI-Trip	1	25	44200	9.08	Bibiana et al.[311]
	TFM-BTrip	1	25	33700	14.8	Bibiana et al.[311]
	DTFM-BTrip	1	25	42600	9.82	Bibiana et al.[311]
	PIM-7	1	30	1100	17.7	Bud et al.[319]
	PIM-1	1	30	2300	18.4	Bud et al.[319]
	TPE-PIM	2	35	862	21	Ma et al.[320]
	PIM-1	1	25	5120	15	Althumayri et al.[321]
	CoPI-TB-1	1	35	158	23	Zhuang et al.[322]
	DPPD-6F	3	30	392	16	Garcia et al.[323]
	CoPI-TB-6	1	35	330	17	Zhuang et al.[322]
	PI-TB-3	1	35	218	33	Zhuang et al.[324]
	TPE-75	2	35	977	16	Ma et al.[320]
	PIM-BTrip-TB	1	25	4150	15	Rose et al.[325]
	TPE-25	2	35	5203	13	Ma et al.[320]
	6FDA-DAT1	2	35	120	38	Alghunaimi et al.[326]
	DPPD-6F	3	30	261	20	Garcia et al.[323]

	DPPD-6F	3	30	1600	15	Garcia et al.[323]
	6FDA-DAT2	2	35	210	30	Alghunaimi et al.[326]
PI						
	Flurinated	3.5	30	480	7	Jusoh et al.[304]
	6FDA-DAM	2	35	681	24	Zornoza et al.[327]
	Matrimid	1	40	10	34	Gong et al.[328]
	6FDA-DAT	1	35	56	50	Bachmana et al.[329]
	6FDA-DAT (15%Ni_2)	1	35	64	52	Bachmana et al.[329]
	6FDA-DAM:DAT(1:1)	1	35	191	31	Bachmana et al.[329]
	6FDA-DAM:HAB (1:1)	10	35	54	18	Tien et al.[330]
	6FDA-durene	1	35	626	18	Bachmana et al.[329]
	6FDA-ODA:DAM (1:1)	10	35	54	24	Chen at al.[331]
	6FDA-ODA:DAM (1:4)	10	35	130	23	Chen at al.[331]
PEO						
	XLPEO	1	25	450	15	Gong et al.[332]
	PEO-PBT	0.5	25	150	17	Karunakaran et al.[333]
	Pebax	1	35	122	19	Beiragh et al.[334]
	PVC-g-POEM	1	35	70	14	Hwang et al.[335]
others						
	DBzPBI-BuI	20	35	26	16	Bhaskar et al.[336]
	Eva	4	25	19	6	Sadeghi et al.[337]
	PBI	20	25	0.03	6	Sadeghi et al.[313]
	PDMS	1.1	37	3020	4	Berean et al.[338]
	PEIm	3	25	4	27	Ozturk et al.[339]

3.3.2 Composite Membranes

The selection of membrane material for composite membranes is challenging since inorganic membranes, which showcase excellent CO_2/CH_4 selectivity and permeability, suffer from issues like low mechanical stability, short lifetime, and an especially low flexibility in forming hollow fibre or spiral wound membranes[340]. To address these issues, the development of composite membranes synthesized by integrating filler materials inside the structure of common polymeric membranes has become an increasingly attractive solution for biogas upgrading[341]. The fillers are classified as: (i) conventional fillers including; zeolites, metal organic framework (MOFs), zeolitic imidazolate frameworks (ZIFs), microporous organic polymers (MOPs), carbon based particles (CBPs), and mesoporous materials; (ii) two dimensional materials like; graphene-family materials (GFMs) and layered silicates (lamellar); (iii) one dimensional materials like carbon nano tubes (CNTs); and (iv) nonporous materials[342–347]. The fabrication of nano-fillers with diameters under 20 nm via innovative synthetic strategies will address particle agglomeration and non-ideal interfacial morphology issues of composite membranes[348,349]. Among current filler materials, two dimensional nanomaterials like 2D MOFs, GFMs and lamellar will play a major role in the fabrication of future composite membranes, due to the considerable enhancement in a membrane's selectivity even at filler loadings lower than 10 wt%[350,351]. Additionally, the diversity in shapes and morphologies of two-dimensional nano-filler materials will enable the large-scale fabrication of defect-free composite membranes[352]. This can also address issues with the loss in permeability of composite membranes, by permitting the tunability of the micropores' diameter and their orientation via various morphologies of 2-D nanofillers[353,354]. To achieve a significant enhancement in the performance of composite membranes, it is necessary to develop a comprehensive model at a molecular scale, to obtain valuable information that can improve the performance of composite membranes[257].

3.4. Cryogenic separation

In cryogenic separation, since CH_4 and CO_2 can be liquefied at different pressures and temperatures, biogas can be upgraded through cooling and compression. There are only a few available commercial cryogenic separation units, thus, their share in the biogas upgrading market is only 1%[4]. In this process, Figure 12, the untreated biogas is initially compressed to 80 bar. Afterword, the compressed gas is dried, to prevent any freezing during the cooling step, and incrementally cooled to -45 °C, whereupon the CO_2 is condensed. The biogas is then further cooled to -55 °C and expanded to 8-10 bar to drop the temperature to -110 °C to form a solid (CO_2)-gas (CH_4) phase. The gaseous CH_4 phase is then heated, or further cooled if liquefied biomethane (LBM) is desired. In this method, a biomethane with a CH_4 purity of 97% can be achieved[7,18].

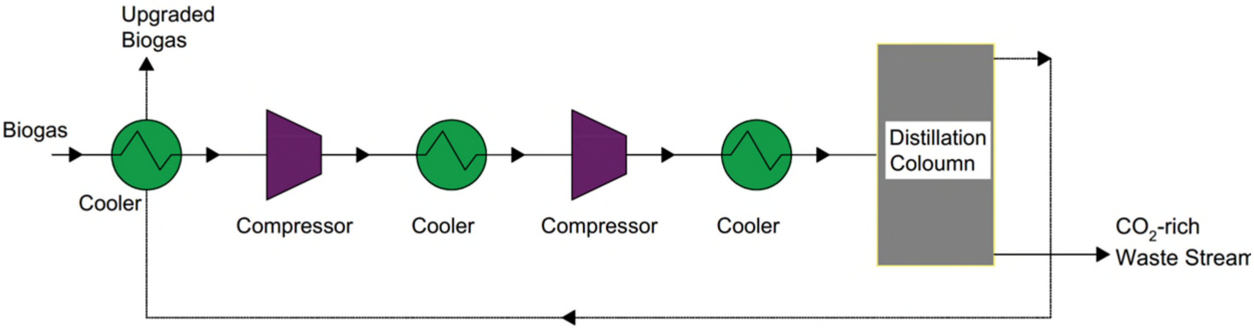


Figure 12. Process flow diagram of cryogenic separation[55].

New hybrid cryogenic separation technology has been developed for biogas upgrading and cleaning, through the simultaneous removal of water, H_2S, siloxanes, halogens, and CO_2. In this process, biogas is initially compressed to 10 bar and cooled to -25 °C, in which water, H_2S, dust particles, halogens, siloxanes, and other undesirable components are separated from the biogas. The biogas is then cooled to -55 °C, and at this point the CO_2 is liquefied and removed. The next step is to further cool to -85 °C, to solidify the remaining trace CO_2 compounds, and achieve a purified biomethane after a final depressurisation step[18,34].

3.5. Technology comparison and required investigations

The advantages and disadvantages of various biogas upgrading technologies are listed in Table 21.

Table 21. Advantages and disadvantages of technologies for biogas upgrading.

Method	**Advantages**	**Disadvantages**	**CH_4 loss (%)**	**CH_4 Purity (%)**
Water scrubbing	Most common technology, ideal for cold regions, high CH_4 purity and low CH_4 loss	The need for elevated pressures (6-20 bar) and a cooling unit before the absorption column (<20 °C), foam formation, accumulation of elemental sulphur, environmental issues such as global warming, acidification, and human toxicity	1-2	>97
Organic solvent scrubbing	Higher affinity towards CO_2, reduction in plant size and lower capital and operating costs, simultaneous removal of CO_2, H_2S and water, low desorption temperature of 40 °C	For high H_2S concentration, only steam or inert gas (not air) should be used for regeneration. It is recommended that H_2S be removed prior to organic solvent scrubbing	2	96-98
Chemical scrubbing	Low pressure in the absorption column and consequently lower capital costs, highest CH_4 purity and lowest loss	Foaming, high energy consumption for absorbent regeneration, poisoning by H_2S	0.1-1.2	>99
Adsorption	Low operating costs, environmentally friendly solution	Low CO_2/CH_4 selectivity and chemical stability of current adsorbents, the need for high vacuum or high temperature for adsorbent regeneration, VSA and TSA technologies can be used, low recovery, H_2S and water need to be removed before the decarbonisation step	>3	<98
Membrane	Commercial application, high mechanical stability, and flexible shapes for polymeric membranes, low energy consumption for gas-liquid membranes	Physical aging, plasticization, high pressure requirement (20-36 bar) for pressure driven dense (gas-gas) membrane, pre-treatment necessary to remove water, H_2S, VOCs, NH_3 and siloxanes to avoid rapid deterioration and clogging of the membrane	7-10	<96
Cryogenic	Simultaneous removal of all impurities	Highest energy consumption		97

Considering the reviewed technologies, the following recommendations can be drawn: (i) development of new packing material, capable of increasing the retention time of water within absorption columns, can reduce the required operating pressure; (ii) water scrubbers are the most common technology for biogas upgrading, and their environmental impacts, like hazardous effluent emissions, need to be addressed; (iii) future adsorbents should target a linear isotherm behaviour in order to reduce the energy demand for regeneration, and thus eliminate high vacuum levels or high temperatures during regeneration, and allow the transition from the currently used VSA processes arrangements to less energy demanding PSA processes; (iv) further developing adsorbents functionalised by amine groups, although they demonstrate superior selectivity, current studies of certain developed materials show low chemical stability or high regeneration demands, leading to a decrease in their adsorption capacity after several cycles, and therefore, limiting their use in VSA, PSA or TSA processes. This issue has hindered their usage at the industrial scale, and needs to be addressed; (v) further developing adsorbents which, in addition to high CO_2 adsorption capacity and CO_2/CH_4 selectivity, have an acceptable kinetic rate; (vi) the development of new adsorbents and absorbents capable of operating at temperatures as high as 50 °C is necessary; (vii) Building on the designs of composite membranes by integrating engineered sub 20 nm filler materials into the structure of polymeric membranes, to become a viable alternative for current commercial membranes that suffer from physical aging, particle agglomeration, and plasticisation; (viii) the development of pilot plants and applying their results into the development of theoretical models to provide valuable insight for future improvements of the performance of composite membranes; (ix) Further investigation into the development of 2-D nanofillers like MOFs, lamellar, and GFMs is required, due to their promising performance in comparison to other filler materials; (x) The necessity of developing engineered filler materials with tuneable control of its micropores' diameter and orientation to address issues of permeability loss in composite membranes; (xi) The facilitation in further improving composite membranes' performance through the use of comprehensive models at a molecular scale to provide valuable information unachievable from just lab experiments.

3.6. Methane leakage in biogas upgrading plants

The global warming potential (GWP) of CO_2 is set at 1 and considered as a reference value, while the GWP of CH_4 is 28 times more than CO_2[296,355]. It is therefore essential to distinguish and eliminate any source of methane leakage in the discussed biogas upgrading and cleaning technologies. Table 22 presents methane leakage (CH_4 loss) associated with each biogas upgrading technology, as well as calculated GWP.

The highest GWP is attributed to membrane separation, due to its high methane loss if not flared. However, if the waste gas is flared, membrane separation has the lowest GWP. Flaring can be potentially used when the CH_4 content in waste gases is 5-15%; therefore, it is only possible for membrane separation. In all cases, it is important to note that there are strict regulations for gas flaring in several countries, such as the UK, and waste gas flaring may not be an option.

Table 22. Comparison of various technologies for GWP for a biogas mixture of CO_2/CH_4: 55/45 mol%

Method	CH_4 loss (%)	CH_4 Purity in product (%)	CH_4 purity in waste (%)	GWP of CH_4 in waste gas	GWP* before flare	GWP after flare (if permitted)
Water Scrubbing	1-2	>97	0.8-1.6	18-32	121-143	121-143
Membranes	7-10	<96	5.6-7.8	62-70	251-310	100
Chemical Scrubbing	0.1-1.2	>99	0.1-1	2-22	102-127	102-127
Adsorption	>3	<98	<2.4	40	165	165
Organic Physical Scrubbing	2	96-98	<1.6	31	143	143

$$\mathrm{CH_4\ purity\ in\ waste\ gas\ (\%)} = \frac{\mathrm{CH_4\ in\ waste\ gas}}{\mathrm{CH_4\ in\ waste\ gas + CO_2\ in\ waste\ gas}}$$

CH_4 in waste gas = CH_4 loss × CH_4 content of biogas (45%)

CH_4 in biomethane product = CH_4 content of biogas (45%) - CH_4 in waste gas

$$\mathrm{total\ moles\ of\ biomethane\ product} = \frac{\mathrm{CH_4\ in\ biomethane\ product}}{\mathrm{CH_4\ purity\ of\ biomethane}}$$

CO_2 in biomethane product = total moles of biomethane product - CH_4 in biomethane product

CO_2 in waste gas = CO_2 content of biogas (55%) - CO_2 in biomethane product

* GWP = CH_4 purity in waste gas (%) × 28 + [100- CH_4 purity in waste gas (%)]

The GWP data from Table 22 have been calculated without considering the energy consumption for the separation process, however, this term has a significant impact on GWP, since approximately

38%[356] of the CH_4 produced is required to meet the energy demand of each separation process; this will indirectly enhance the GWP due to the indirect increase of CH_4 loss (decrease of CH_4 recovery). However, within the literature, the CH_4 recovery or loss reported just considers the net CH_4 produced, but works should account for the CH_4 required to produce the required electrical energy for the process, as it will significantly enhance CH_4 loss (or reduce the calculated recovery). This can be directly seen in Table 23, which summarises the GWP values considering the energy consumption of each separation process. The CH_4 loss value reported in literature for water scrubbing is 1-2%, but considering the high energy consumption of this technology, the real loss value is 17-18%. Chemical scrubbing has the lowest GWP if no flaring occurs, followed by membranes, adsorption, and physical scrubbing. In all the cases presented in table 23, the GWP data has not considered the energy consumption of pre-treatments steps, but accounting for them would lead to higher CH_4 losses, and consequently a much higher GWP. Water scrubbing has the highest GWP, but it only has 1 pre-treatment step for siloxane removal, while membrane or adsorption technology require almost all pre-treatment steps for H_2O, H_2S, and siloxane removal. A life cycle assessment for biomethane production from raw biogas can contribute significantly on this discussion comparing the exact GWP of each technology, and is a task that must be undertaken for a more accurate analysis.

Table 23. Comparison of various technologies for GWP considering the required energy for separation for a biogas mixture of CO_2/CH_4: 55/45 mol%

Method	Energy consumption (kWh/Nm^3)	CH_4 loss (%)	GWP* before flare[355]	GWP after flare (if permitted)
Water Scrubbing	0.67[6,46]	17-18	448-462	448-462
Membranes	0.21-0.3[357]	12-15	364-415	364-415
Chemical Scrubbing	0.3[6]	7-8	259-279	259-279
Adsorption	0.46[6,357]	14	385	385
Organic Physical Scrubbing	0.49[6,46]	14	382-387	382-387

Note: The heat of combustion of CH_4 assumed 890 kJ/mol, burning efficiency 95%[358]

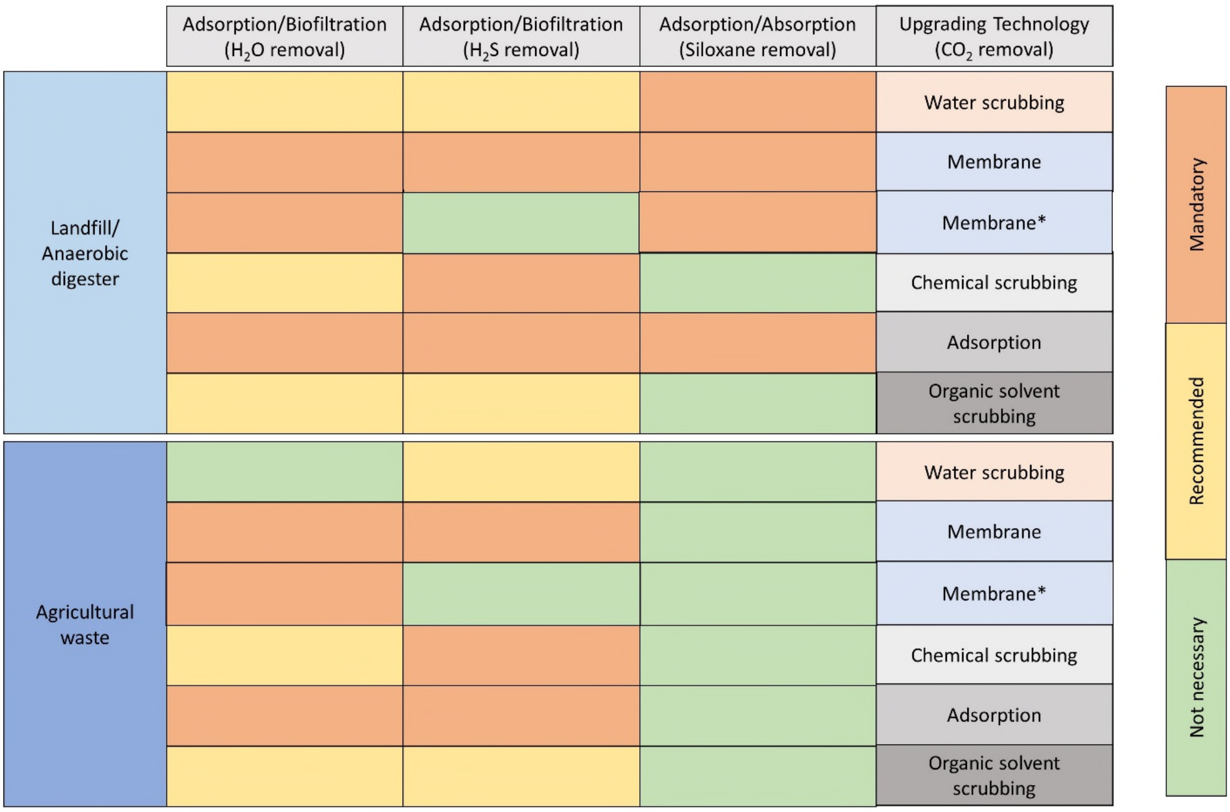
4. Proposed scheme for production of biomethane from biogas

The existence of various impurities in biogas brings up key considerations related to the order of removal of each impurity, and will influence the choice of process scheme for biomethane production. The removal efficiency of H_2S and siloxane in dried biogas is much higher than wet biogas; therefore, biogas drying is recommended as the first pre-treatment step in the biomethane production chain. H_2S is highly corrosive; therefore, corrosion-resistant material is required when it exists in the gas stream. Additionally, health, safety and environmental considerations must be factored in, as it is toxic and can be fatal once the concentration exceeds 800 ppm; it is therefore recommended that H_2S be removed directly after the drying step. With respect to current absorption techniques, the high amount of CO_2 in biogas and high CO_2 absorption capacity of amines puts their use for H_2S removal in question. The low purity and recovery of membranes confirm the lack of maturity of membrane technology for H_2S removal, and further research in this subject is required. Thus far, adsorption and biofiltration methods are good choices, with proven performance by industrial plants currently using them for H_2S removal. However, when considering biofiltration methods for H_2S removal, it should not be used for streams with high concentrations of H_2S (>15000 ppm_v).

After H_2S removal, siloxanes become the major impurity which needs to be removed. Absorption and adsorption are technologies that are currently used for siloxane removal, but adsorption is the more commercially viable technology. Membrane separation is not suggested for siloxane removal due to high methane loss, and low material sensitivity to other biogas impurities. The use of biofiltration leads to a low removal efficiency (max 74%), making it an inadequate solution for siloxane removal. The most common technologies which are used today for biogas upgrading, in decreasing order, are water scrubbing, membrane technology, organic solvent scrubbing, and PSA.

Figure 13 depicts proposed pathways for the production of biomethane, in response to different biogas sources. Water scrubbing can remove all impurities except siloxanes (H_2S, CO_2, and VOC). However, it is highly recommended that H_2S be removed prior to CO_2 to reduce the capital cost of the project, and to prevent the formation of elemental sulphur in the stripping column. For water scrubbing, if the biogas is sourced from anaerobic digestion (AD) or landfill gas, the siloxane removal step becomes mandatory. In employing membrane technology, their sensitivity to impurities necessitates their removal, and all the pre-treatment steps need to be taken, except for biogas sourced from agricultural waste, in which no siloxane would be present in the stream. For chemical scrubbing, H_2S must be removed prior to decarbonisation steps, as it poisons the amine. For organic solvent scrubbing, though this method enables simultaneous removal of H_2S, CO_2, and H_2O, it is highly recommended to remove H_2S and H_2O beforehand, to reduce the required regeneration temperature, and associated energy penalties. The simultaneous removal of H_2S and CO_2 can embody a promising solution in enhancing CH_4 recovery, however, for water, organic solvent, and chemical scrubbing, and adsorption, it is not recommended. On the other hand, recent developments of composite membranes at laboratory scale have been able to remove both impurities simultaneously[359–361].

Referring to Figure 13, biogas upgrading is the last step of biomethane production. However, to significantly reduce CH_4 loss and global warming potential (GWP), this stage of the process must be redesigned, to target the simultaneous production of biomethane and ultra-pure CO_2. Esposito et al.[6] reported the results of a first large scale industrial plant that produces biomethane at a purity of 96.3%, and produces CO_2 with a purity of 99.9%, permitting its use for food and beverage applications. They used membrane technology for the biogas upgrading step, followed by the use of cryogenic distillation for further purification of the CO_2 waste gas stream to the required purity of the European Industrial Gas Association and International Society of Beverage Technologists (EIGA/ISBT). Although with exceptional product quality at both ends of the biogas upgrading step, the cryogenic distillation technology used by Esposito et al.[6] is a highly energy demanding technology. In comparison, Rosaria et al.[294] used a 2 PVSA configuration for the simultaneous production of high purity CH_4 and CO_2. The first PVSA unit produces high purity biomethane and a waste gas with low purity CO_2, this stream is directed to a second PVSA unit that both recovers the remaining CH_4 and enhances the CO_2 purity to above 99% becoming suitable for reuse. This technology has a lower energy demand and does not impose a high capital investment as in cryogenic technology. However, the vacuum requirement in a 2 PVSA configuration increases the energy consumption. To address this additional energy penalty, Golmakani et al.[362] developed a polymeric adsorbent with a practical working capacity achievable at above atmospheric pressure, and a cyclic performance that enables biogas upgrading by PSA without vacuum desorption required. They used a twin double-bed PSA unit to produce biomethane with a 91% recovery, and a CO_2 tail gas purity >90% from the second PSA unit, thus suitable for geological storage. The simultaneous purification of CH_4 and CO_2 can have a big impact on the progress towards a sustainable society, specifically when the supplied biogas is from organic household waste, or organic wastes from farming, or the agricultural industry. These sources would lead to the production of a negative emission CH_4 stream, thus lowering the overall impact of human activities on the environment.



	Adsorption/Biofiltration (H_2O removal)	Adsorption/Biofiltration (H_2S removal)	Adsorption/Absorption (Siloxane removal)	Upgrading Technology (CO_2 removal)
Landfill/ Anaerobic digester	🟨	🟨	🟧	Water scrubbing
	🟧	🟧	🟧	Membrane
	🟧	🟩	🟧	Membrane*
	🟨	🟧	🟩	Chemical scrubbing
	🟧	🟧	🟧	Adsorption
	🟨	🟨	🟩	Organic solvent scrubbing
Agricultural waste	🟩	🟨	🟩	Water scrubbing
	🟧	🟧	🟩	Membrane
	🟧	🟩	🟩	Membrane*
	🟨	🟧	🟩	Chemical scrubbing
	🟧	🟧	🟩	Adsorption
	🟨	🟨	🟩	Organic solvent scrubbing

🟧 Mandatory
🟨 Recommended
🟩 Not necessary

Figure 13: Proposed schemes for various upgrading technologies. * Simultaneous removal of H_2S and CO_2 with recent state of the art membranes.

5. Biogas utilisation

Biogas has the potential to play the role of a multi-purpose solution, with versatile utilisation in different sectors, such as heat and steam production, electricity generation and vehicle fuel. Currently, biogas shares in the world energy market is limited, but its environmental benefits make it a noteworthy means for energy supply[363–365]. In the following sections, biogas utilisation in combined heat and power (CHP), combined cooling, heat and power (CCHP), microturbines, micro humid air turbines (mHAT) and solid oxide fuel cells (SOFC) will be discussed.

5.1. Combined heat and power systems

The total amount of waste heat and energy losses in conventional power plants is estimated to be around 44%[366–370]. Figure 14 depicts various sources of waste heat in conventional power plants. The stack of boilers, the stack of power generation units and the hot air exiting the cooling tower packages are major sources of heat waste in conventional power plants.

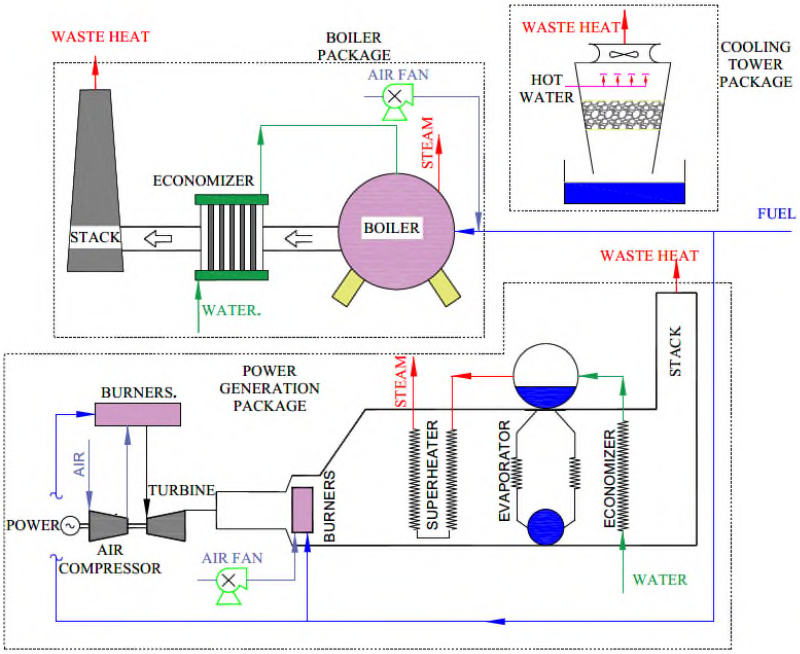


Figure 14. Waste heat sources from conventional power plants[366,371–373].

Large heat and power losses of conventional power plants has resulted in widespread research on the application of CHP systems. CHP addresses heat loss problems by capturing its energy for building heating, while also eliminating transmission losses from the power plant to the point of consumption; in this manner, on-site power generation efficiency can be up to 80%[366,371–373].

The only drawback in the use of biogas for CHP systems is the low efficiency of turbines. Consequently, the emergence of micro turbine power generators resulted in a remarkable jump in the use of biogas in the production of electricity by CHP systems[40,374–377].

5.2. Combined cooling, heat and power systems

Combined cooling, heat and power can be of several types, one of which is tri-generation. This system is similar to the CHP system, but with the waste heat being used to improve the efficiency of a plant. CCHP uses the waste heat from the CHP system to supply the required power for chilled water generation by absorption chillers, to be used for air conditioning purposes or refrigeration[378–381]. The CCHP system can also be referred to as an on-site generation method. This set-up allows for a much more efficient production of energy due to the lack of transmission losses; in fact, efficiencies up to 90% can be obtained. Another type of CCHP system is quad-generation, i.e., a carbon-neutral CCHP by means of CCHP with carbon capture, utilisation and sequestration (CCUS), in which the captured CO_2 can be sequestered or utilised[382]. The captured CO_2 can be used in the food industry for drinks and food manufacture, such as a carbonation source in the soft drinks industry, or other industrial processes. It can also be used in sequestration processes such as in the horticultural industry, in which the produced CO_2 is consumed by the plants in the photosynthesis process. The CO_2 becomes a physical part of the plant, hence, removing it from the atmosphere and reducing carbon emissions[383]. Quad-generation not only encompass the advantages of high efficiency generation, it also uses more than 90% of the energy which exists in the gas, and also proposes a means for zero carbon emissions by utilising carbon dioxide, a by-product of the combustion process in industrial processes[384–387].

5.3. Fuel for vehicles

The ongoing debate over finding promising decarbonised solutions for the abatement of global warming naturally leads to the enhancement of the use of renewable energy in the transport sector[388]. Biogas is a promising solution that can contribute a small portion to the renewable energy within the transport sector. Some countries have released decrees to enhance the use of biomethane as a decarbonisation solution[389]. Sweden is one country in which approximately half of the biogas produced is used for vehicle fuel. Germany is the another country, in addition to the Netherlands, Denmark and South Korea which have moved toward using biomethane as an automotive fuel[4]. Jo et al.[390] found that 25% of natural gas used in the transport sector can be substituted by biomethane produced from the organic wastes of a South Korean urban area. The main obstacle for widespread use of biomethane in the transport sector is the availability of biomass to produce biogas. There are numerous sources for biogas production such as food wastes, food waste-recycling wastewater, sewage sludge, livestock manure, animal and plant residues[390]. However, the availability of each source is dependent on the geographical location and available landmass. For instance, livestock manure or plant residue does not exist in urban areas.

5.4. Micro turbines

Micro gas turbines were developed according to principles of larger power generation systems. The essential need to produce electricity at a small scale (kW-scale) was a great motivation toward development of micro turbines. The main obstacle in converting industrial gas turbines to micro turbines was the decrease in turbine efficiency with decreasing gas flowrate or power output. The high pressure requirement of combustion chambers (20-30 bar) was another challenge[11]. New micro turbines with blades the size of a few millimetres could tackle the challenges associated with increasing turbine efficiency . The concept of micro turbines was inspired by small compact high-speed turbo generators, which simultaneously generate heat and power. They can work under low gas flowrates with acceptable efficiencies. A basic micro turbine cycle (Figure 15) comprises a compressor coupled to a generator, turbine and combustion chamber[391]. The power supply efficiency is about 30% with a recuperator, and half of that without a recuperator. The total efficiency of heat and power generation in CHP systems is in the range of 75-85%[11,392,393].

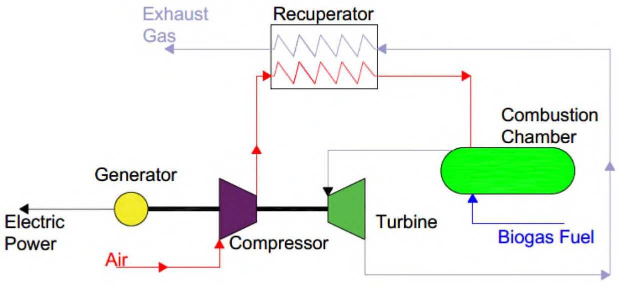


Figure 15: Sample schematic of a micro turbine cycle powered with biogas[303,304,389,390].

Micro gas turbines benefit from fuel flexibility and can be fed with gaseous fossil fuels and biogas. The specifications from some of the providers of micro turbine technology is presented in Table 24. With new micro turbines, a minimum power output of 12 kW can be generated, but they still suffer from low efficiency values. In addition, there are micro turbines which can produce electricity from biogases with low methane purity (40%) or fuel with lower heating values (LHVs) as low as 12 MJ/Nm^3. The small scale of turbine blades causes their speed to be very high (up to 135000 RPM), and this speed increases if lower electrical energy production is required. In other words, by decreasing power output, the micro turbine speed increases. Backman et al.[11] investigated the feasibility of micro turbines for CHP systems (< 100 kW$_{el}$) and obtained efficiency values of 80-90%. They concluded that higher efficiency values of the micro-scale CHP systems guarantee energy security, as well as long-term sustainability of energy resources.

Table 24: Micro turbine technology providers and specifications

Model	Turbine Inlet temp. (°C)	Speed (RPM)	W_{net} (kW)	Elec. efficiency %	CHP efficiency %	Exhaust Temp. (°C)	CH_4 min (%)	Fuel LHV (MJ/Nm^3)	Fuel press. (barg)	Ref.
Bladon		135000	12	25		250				Bladonmt[394]
AnsaldoT100	950	70000	100	30		270	>90	27-40	0.1	Ansaldo[395]
AnsaldoT100B	950	70000	105	30		270	>40	18-25	6-8	Ansaldo[395]

FLEX GT250	913	45400	250	30		256	12-22	0.06-9	FlexEnergy[396]
Aurelia A400			400	40		185		7-8	Greenray[397]
Capstone C30			30	26	Max 90	275			Capstone[398]
Capstone C65			65	29	Max 90	309			Capstone[399]
Capstone C200			200	33	Max 90	280			Capstone[400]

5.5. Micro humid air turbines

One of the main challenges of utilising biogas in micro gas turbines is associated with the low energy density of biogas. Micro humid air turbines, Figure 16, have solved this problem by increasing the mass flow rate of gas in the micro turbine[12,401,402]. In this technology, the heat recovered from the exhaust gas is used to produce hot water[403–407]. Produced hot water is injected in a saturator that humidifies the air entering the combustion chamber to increase the mass flowrate to the turbine, which leads to an increase in power output and efficiency.

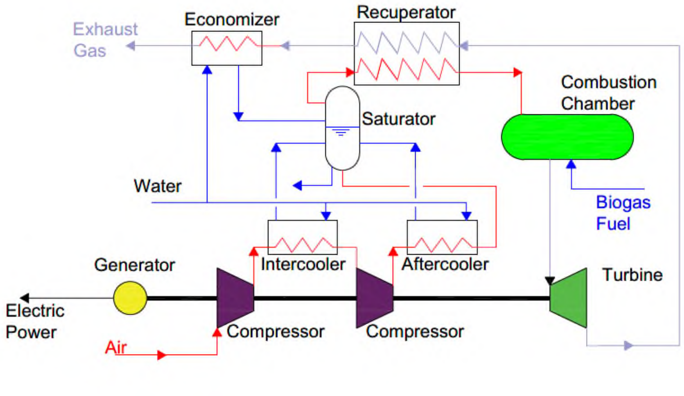


Figure 16: Sample schematic of mHAT cycle powered with biogas[403–407].

HAT cycles were originally employed in large power installations, but current researchers have focused on the use of HAT cycles in decentralised applications to avoid transmission losses and high capital costs, reduce SO_x and NO_x emissions, while improving reliability of these systems[408–411]. HAT-based plants have already been demonstrated in large scale applications, including a 3 MW unit in Hitachinaka (Japan), developed by Hitachi[412], and a 0.6 MW unit in Sweden, developed by Volvo[413]. A comprehensive study on mHAT-based CHPs was conducted by Mosayebnezhad et al.[40], in which they used biogas from waste water treatment plants (anaerobic digestion) as feed. In their work, they reported an electrical efficiency of 46.6% with a CHP efficiency of 81.2%[40,414].

5.6. Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) benefit from fuel flexibility, and so, can be directly (internal reformimg) and indirectly (external reforming) fed with biogas. SOFCs can achieve up to 50% electrical efficiencies, and up to 85%-90% efficiency in CHP and CCHP modes[168]. The electrical efficiency of fuel cells is higher than micro turbines and mHAT turbines making them superior to other methods. However, they suffer from high degradation rates due to their operation at elevated temperatures of 600-1000°C[415]. The high degradation rate reduces the life of fuel cells, and imposes large capital and operating costs on the plant[13,416–418]. The target value for the degradation rate of fuel cells is 0.2%/1000 h[419–421]. Fuel cell life is directly linked with the concentration of impurities in biogas. Therefore, efficient removal of impurities such as H_2S and siloxanes helps improve the life time of SOFCs[415,422–424]. Figure 17 presents a solid oxide fuel cell combined with a CCHP system. As shown, biogas (after cleaning) enters the reformer to produce hydrogen (syngas), which then enters the anode to produce electricity. The exhaust gas then moves toward the catalytic afterburner (OXICAT) unit and the burner. This exhaust gas is used to preheat the air and supply the heat required for the absorption chiller. Heat from the exhaust gas may also be utilised to further increase the efficiency of the system[168].

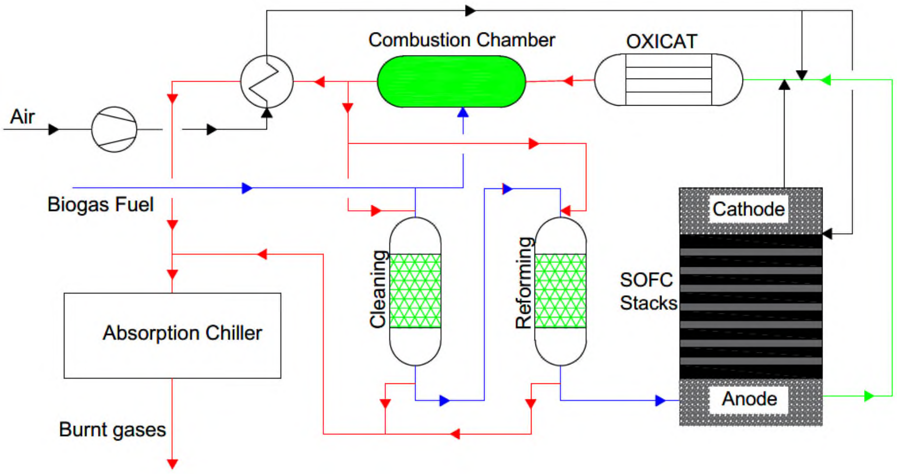


Figure 17: Sample schematic of biogas-powered solid oxide fuel cell (SOFC) CCHP[168].

5.7. Hybrid SOFC-micro turbine

The electrical efficiency of SOFCs can be further increased when combined with micro gas turbines. In such hybrid system, the SOFC is pressurised by the micro gas turbine, thus increasing its electrical efficiency. Figure 18 shows a hybrid SOFC-micro gas turbine. Air is compressed and purges the pressure vessel containing the fuel cell stacks. The SOFC is fed by a pressurised mixture of fuel and recycle stream (anode inlet), and air (cathode inlet). The unused fuel in the anode along with the cathode off-gases are then fed to the combustion chamber to be utilised in the micro gas turbine to generate further power[14].

Chan et al.[14] simulated a 2.1 MW_{el} hybrid SOFC-micro turbine, achieving an electrical efficiency of 62%. In comparison, Veyo et al.[425] simulated a 0.22 MW_{el} hybrid SOFC-micro turbine and obtained a lower electrical efficiency of 55%. This indicates that the size of the hybrid SOFC-micro turbine unit can significantly affect its electrical efficiency.

Kaneco et al.[426] achieved efficiency of 56% in a 35 kW_{el} unit. The reason for such a high efficiency at low electrical output is that their novel design consists of two turbines. The first one is directly connected to the air compressor, while the other turbine is joined to the generator. The SOFC is located between the first turbine and compressor; therefore, it works under an elevated pressure which causes the efficiency to increase. Westinghouse[427] developed a 220 kW_{el} hybrid SOFC-microgas turbine plant and achieved an efficiency of 53%. Similarly, Mitsubishi[428] has developed a 200 kW_{el} unit which achieves an efficiency of 54%.

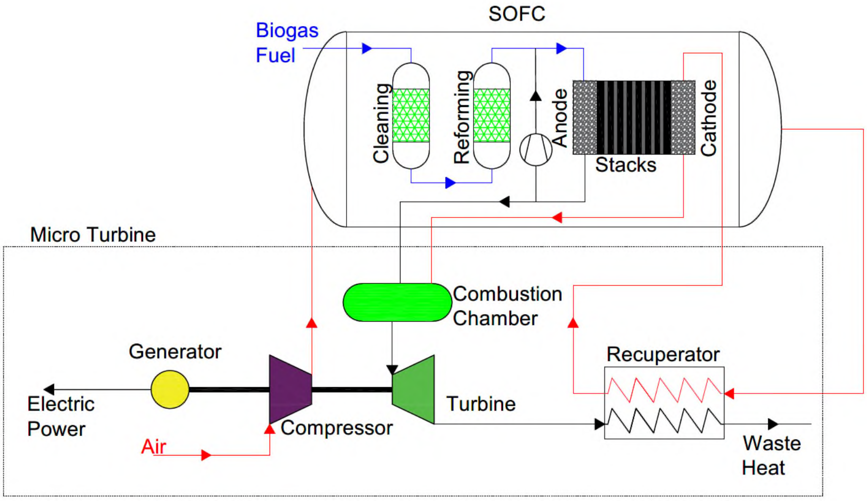


Figure 18: Hybrid SOFC with micro turbine[14].

5.8. National grid injection

The utilisation of biogas is not limited to onsite consumption, it can instead be upgraded to the required specifications for injection into the national gas grid. The lack of a unique international standard or regulation on biomethane quality has led to the development of individual national standards by each country, dictating the requirements for the injection of biomethane into the national gas grid[18,429–431]. Table 25 summarizes the required specifications of upgraded biogas by various countries. The diverse range of guidelines on the compositional makeup for grid injection by each country allows flexibility in the choice of the ideal biogas upgrading scheme, and it should guide future studies on the optimisation of individual technologies presented in this work.

Table 25: required specifications for grid injection on a per country basis[18,429–431]

Country	Wobbe index $MJ.Nm^{-3}$	CH_4 vol%	CO_2 vol%	H_2S ppm	Sulfur ppm	Mercaptans ppm	Si $mg.m^{-3}$	NH_3 ppm	H_2 vol%
California	47-52	--	3	88	265	106	0.1	<10	--
Spain	48-58	>95	2.5	15	50	17	<10	<3	--
Netherland	43-44	>85	<6	<5	<45	<10	<6.2	<3	<12
Germany	38-56	--	<6	<5	<30	<15	--	<20	<5
France	42-56	>86	>2.5	<5	<30	<6	--	<3	<6
Switzerland	48-56	>96	<4	<5	<30	<5	--	<20	<4

Sweden	43-47	>97	<3	<15.2	<23	--	--	<20	<0.5

6. Conclusions

This review summarises state-of-the-art developments in biogas cleaning, upgrading and utilisation technologies. It identifies key research problems by determining the present status, current challenges, and impediments for future deployment and commercialisation. Considering the above sections of this review, it can be concluded that:

(a) Adsorption is the most commercialised technology for H_2S removal from biogas.

(b) Water scrubbing is the best option for H_2S removal on a large scale, facilitated by cold weather conditions.

(c) Physical and chemical absorption of H_2S are associated with a high consumption of water and/or chemical reagents. Therefore, this method is not economically feasible on a small scale.

(d) Membranes are currently not a developed technology for H_2S removal from biogas, due to the low purity values and the material's sensitivity to sulphur species.

(e) Biofiltration is an efficient method for H_2S removal, especially using aerobic biofilters (RE>98%), but there is a possibility of the formation of an explosive environment if an incorrect dosage of oxygen is introduced. In comparison, the anoxic method has a lower efficiency but is safer and produces less biomass.

(f) Among various absorption methods for siloxane removal from biogas, Selexol is currently the sole method that is accepted from a commercial and industrial standpoint. Other methods such as acid or alkaline solutions, or water scrubbing, have not produced acceptable results.

(g) Adsorption is the most commercialised technology for the removal of siloxanes from biogas, however, it requires the pre-drying of the biogas for better adsorbent performance. Activated carbon cannot be regenerated and must be replaced after saturation, but silicagels or activated alumina can be regenerated several times.

(h) The use of cryogenic condensation for siloxane removal is not recommended because it needs a great amount of energy, instead, it can be a better choice for biogas drying.

(i) The amount of impurities in biogas that can damage membranes is high, and it is recommended to avoid the use membranes for siloxane removal.

(j) Low mass transfer rates from the gas into the microorganisms' cells in biotrickling filters lowers their removal efficiency for siloxanes. Their maximum siloxane removal is 74%, which renders this method unfeasible for siloxane removal.

(k) Adsorption is the most common technology for biogas drying. At water partial pressures below 1 kPa, zeolites have better water loading values than silicagels, but at pressures above 1 kPa, the performance of silicagel is superior to other zeolitic adsorbents. The achievable dew points using the adsorption method for biogas is as low as -40 °C.

(l) Water scrubbing is the most common technology for biogas upgrading on a large scale, especially for cold regions, which can achieve methane purities above 97% with just 1-2% methane loss. Although it is stated that water scrubbing can tolerate H_2S concentrations as high as 2500 ppm_v, it is highly recommended to remove H_2S prior to water scrubbing to prevent the accumulation of elemental sulphur.

(m) Organic solvent scrubbing is a physical absorption method that can produce 98% purity methane with about 2% loss. Like the water scrubbing method, at high concentrations of H_2S only steam or inert gas should be used for stripping.

(n) Chemical scrubbing can produce biogas with more than 99% CH_4 purity and typically 0.1-1.2% CH_4 losses. The presence of H_2S in biogas poisons the amine, and H_2S must be removed beforehand.

(o) Among various upgrading methods, membrane technology has the highest GWP due to its high methane loss, but if coupled with flaring (where permitted) it has the least GWP.

Although a lot of valuable and high-quality research has been conducted on issues regarding biogas, there are some challenges which require further study:

(a) Improving the surface chemistry and low kinetic rate of adsorbents for H_2S removal, as well as addressing environmental issues like SO_2 emissions. Zeolites are a potential candidate for H_2S removal, but their regenerability and stability should be improved.

(b) There is a necessity of developing new materials with non-wetting properties, for the prevention of liquid penetration into membranes used for H_2S removal. The developed membrane materials should also be able to withstand the presence of humidity or sulphur species.

(c) The possibility of an explosion by aerobic biofilters used for H_2S removal should not be ignored, and the development of anoxic biofilters which can handle biogas with high H_2S concentrations or volatile organic carbon are required. Also, improved designs for packing are required to alleviate their clogging problems.

(d) The removal efficiency of siloxane by adsorbents decreases considerably in the presence of moisture; therefore, feed drying should always be carried out prior to their removal by adsorption. The further development of materials that are able to remove siloxane in the presence of water or remove both simultaneously can make a significant impact on the efficiency of this process.

(e) When studying the adsorption capacity of various adsorbents for siloxane removal, it is suggested that L2 removal be studied first because it is the lightest and smallest gas that elutes from the bed. When studying the regeneration properties of adsorbents, it is recommended that heavier siloxanes be studied, as they have stronger adsorption bonds to adsorbents.

(f) It is important to establish microorganisms compatible with high concentrations of siloxanes or H_2S. Identifying the bacteria appropriate for the biodegradation of siloxanes with enough growth on related packings can considerably improve their removal efficiency.

(g) Although water scrubbing is currently considered the top choice for biogas upgrading in cold regions, it is recommended that the pressure inside the absorption column be reduced to lower the electrical energy consumption. This can be accomplished through the development of novel packing that increases the retention time of water in the packed bed.

(h) Chemical scrubbing is a technology which has the highest methane purity (>99%) and lowest methane loss (0.1-1.2%), but problems of degradation, amine loss, and high energy requirements need to be addressed before they can become a more widespread solution.

(i) The majority of existing biogas upgrading units using adsorption need vacuum for adsorbent regeneration. Adsorption technology for biogas upgrading has the potential to become the best upgrading method, if a new adsorbent with a linear isotherm behaviour for CO_2 at pressures above 1 bar can be developed for use in PSA processes. The novel adsorbent should have a high adsorption capacity for CO_2, high CO_2/CH_4 selectivity, and a high kinetic rate of adsorption.

(j) The current issues with existing commercial membranes such as physical aging, particle agglomeration, and plasticisation should be addressed by the development of composite membranes that insert sub 20 nm filler materials into the structure of polymeric membranes.

(k) The development of pilot scale membrane biogas plants and applying their results in theoretical models will provide valuable insight for future improvements of the performance of composite membranes.

(l) Further investigation into the development of 2-D nanofillers like MOFs, lamellar, and GFMs is required due to their promising performance in comparison to other filler materials for biogas upgrading using composite membranes.

(m) The development of engineered filler materials with tuneable control of its micropores' diameter and orientation is in dire need in order to address issues with permeability loss in composite membranes.

(n) The development of a comprehensive model at a molecular scale provides valuable information in improving the performance of composite membranes.

(o) The development of MOFs with high mechanical, thermal and chemical stability in order to be able to work at severe conditions (high temperature and pressure, moisture, acidic or basic environments, etc.) will contribute to their commercial application in industrial plants.

(p) The poor cyclic and structural stability of MOFs needs to be addressed by the smart selection of metal-organic linker combinations, the synthetic procedure used, and the development of composite materials.

(q) As lab-based materials need to be in pellet form to prevent the escape of material from the bed during PSA operation, and to minimise the pressure drop across the bed, further investigation into the drop in performance of powder materials reported in laboratory studies after their formation into pellets is necessary.

7. Abbreviations

AC	Activated carbon
APTES	Aminopropyl-triethoxysilane
ASU	Air separation unit
BTF	Biotrickling filter
CA	Cellulose acetate
CCUS	Carbon capture, usage and sequestration
CCHP	Combined cooling heat and power
CHP	Combined heat and power
CFS	Coagulation-flocculation sludge
CLM	Condensing-Liquid Membrane
CNG	Compressed natural gas
DEA	Diethanolamine
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexasiloxane
DMSD	Dimethylsilanediol
EBRT	Empty bed retention time
EC	Elimination capacity
6FDA	2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane
FW	Food waste
GCMC	Grand canonical Monte Carlo
GRT	Biogas Retention Time
GWP	Global Warming Potential
L2	Hexamethyldisiloxane
L3	Octamethyltrisiloxane
L4	Decamethyltetrasiloxane
L5	Dodecamethylpentasiloxane
LHV	Lower heating value
MDEA	Methyldiethanolamine
mHAT	Micro humid air turbine
MOF	Metal organic framework
N-PSAC	Nitrogen-enriched palm shell activated carbons
PAN	Polyacrylonitrile
PDI	Pressure differential indicator
PDMS	Polydimethylsiloxane
PEG	Polyethyleneglycol
PESf	Poly(ether sulfone)

PIM	Polymer of intrinsic microporosity
PPO	Poly(2,6-dimethyl-1,4-phenylene oxide),
PPY	Polypyroll
PI	Pressure indicator
PP	Polypropylene
PSA	Pressure swing adsorption
PSV	Pressure safety valve
PTMSP	Poly[1-(trimethylsilyl)prop-1-yne]
PUU	Poly(urethane-urea)
RE	Removal efficiency
SOB	Sulphide-oxidising bacteria
RGE	Regeneration efficiency
RGT	Regeneration time
SOFC	Solid oxide fuel cell
SP	Sample point
TI	Temperature indicator
TMMAP	Trimethoxy[3-(methylamino) propylsilane]
TMS	Trimethylsilanol
UWP	Used wood pallets
VSA	Vacuum swing adsorption
WG	Waste gases
WWTP	Waste water treatment plant

Conflict of Interest:

There are no conflicts of interest to declare.

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