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Upgrading Strategies for Effective Utilization of Biogas

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Production of biogas is based on anaerobic digestion of different renewable raw materials including human, animal, agricultural, industrial, and municipal wastes. In addition to methane content, biogas contains carbon dioxide along with water vapor, hydrogen sulfide, ammonia, and depending on the raw materials siloxane can be present. Thus, different purification and upgrading strategies are necessary in order to enhance the methane content; this review presents some of the upgrading technologies for practical removal of major contaminants in biogas. Recent development in membrane technology with high selectivity and permeability could serve as a boost in search for the most efficient biogas upgrading process capable of meeting the requirements for its use in vehicle fuel as well as incorporation in the natural gas grid. © 2015 American Institute of Chemical Engineers Environ Prog, 34: 1512–1520, 2015

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INTRODUCTION

Rapid increment in agricultural, municipal, and industrial wastes needs appropriate management strategies to reduce their effects on environment. Anaerobic digestion has been found to be an effective and sustainable method in reducing the harmful effects of these wastes in the environment, where the organic components are utilized by microorganisms resulting in the production of biogas [1].

Biogas is a renewable energy source which consists of 50–70% CH_4, 25–50% CO_2, 1–5% H_2, 0.3–3% N_2, and some notable impurities such as NH_3, H_2S, siloxane, and halides [2]. The concentration of each of these compounds depends on the composition of the raw materials used for the production. Biogas is basically generated through a multistage reaction process where different microorganisms utilize the available energy stored in complex polymers (polysaccharides, lipids, and proteins) under anaerobic condition for their metabolism [3].

Consortia of microorganisms (anaerobes and facultative anaerobes) participate in transforming complex nutrients in a three-step reaction into biogas; these include: hydrolysis–acidogenesis, acetogenesis, and methanogenesis [4,5].

Energy from biogas can be obtained in a cost-efficient way by making it free from all impurities, including H_2S which is corrosive with intent possibility of damaging energy co-generation equipment; CO_2 needs to be eliminated particularly if the biogas is to be upgraded to standard natural gas and removal of water prevents the accumulation of condensate in the pipeline [6]. Thus, after elimination of the impurities, the methane has calorific value of 37,781.6 kJ/Nm^3 with energy generation capacity of 5 kWh/Nm^3 [6,7].

Generally, methane has been utilized in various applications associated with heat and electric power generation through a relatively easy to handle processes. Purification and compression of the gas aid in its utilization as fuel for internal combustion engines and automobiles [4,8] as indicated in Figure 1.

Biogas upgrading as well as enrichment is a crucial downstream process which accounts for the overall success of the production. The processes used for biogas purification can be physical, chemical, and biological [9]. Removal of impurities from biogas increases the Wobbe Index (the acceptable representation of the heating value of natural gas) as well as reducing some of the adverse effects associated with acid gas and overall increases the biogas utilization as a potential energy source [10]. Renewable residues ranging from agricultural, municipal and industrial have been used for biogas production. However, the utilization of these residues individually tend to affect the digestion process resulting in accumulation of ammonia due to low carbon to nitrogen (C/N) ratio; as such addition of external nutrient and buffering agent to serve as co-substrate has been considered to be a reliable option [11,12]. Several researches on the digestion of one or more substrates for achieving higher biogas yields are available in the literature [1,6,11–14].

Despite the increasing number of publications on anaerobic digestion of different substrates for biogas production and utilization, attempts have been made for upgrading and elimination of impurities and trace compounds found in biogas which can be corrosive, odorous and hazardous and overall affect its final application. This article is aimed at reviewing some of the general techniques that prove effective and can easily be applicable for biogas upgrading even at small scale levels. This is due to the rapid development of bioenergy sector which accounts for about 3% of US energy production with marked prediction of 10% by 2030 in Europe [15].

TECHNIQUES FOR UPGRADING AND PURIFYING BIOGAS

Abatzoglou and Boivin [16] showed the currently employed processes for biogas purification are chemical

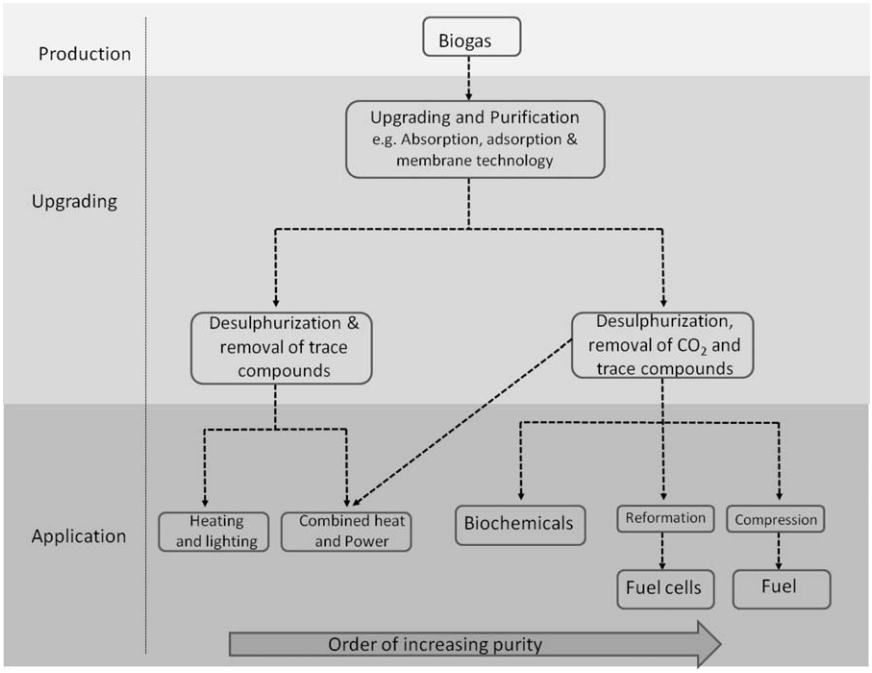

Figure 1. Schematic showing the processes for biogas utilization.

absorption, adsorption, cryogenic separation, catalytic oxidation, membrane separation and scrubbing. In most countries and for application purposes, recommended limits of the biogas constituents are set by the major producers as shown in Table 1. The notable compounds that need to be eliminated in biogas are H_2S and CO_2 and in most cases specific techniques aimed at reducing these two compounds help in eliminating the other trace compounds such as ammonia, siloxane, water and other organic matter. Globally, biogas upgrading plants reported by IEA Bioenergy task 37 were 347; Germany as the main player in the field has the largest number followed by Sweden. The list of countries and the number of upgrading plants available in the world are represented in Table 2.

Removal of Hydrogen Sulfide

Removal of H_2S from biogas has been faced with numerous challenges and its removal contributes to the total production cost. Efforts by researchers have been fruitful where different methods used in removing H_2S and CO_2 resulted in enhancement of methane content as shown in Table 3. Some of the methods used in removal of H_2S include adsorption, absorption, and biological techniques.

Adsorption Process

Activated carbon and carbon molecular sieves are the major adsorbents used in most adsorption studies. Cebula [32] showed that the activated carbon developed by Silesian University of Technology Poland proved effective in removing major impurities including H_2S and CO_2, making the produced biogas suitable for direct use in solid oxide fuel cells.

Micoli *et al.* [33] studied the use of Cu and Zn modified 13 × zeolites as adsorbent for H_2S removal in biogas. The adsorption of H_2S was based on its interaction with the cations present in the zeolite and basic oxides (CuO or ZnO) as represented in the equations:

$$CuO + H_2S \rightarrow CuS + H_2O \quad (1)$$

$$ZnO + H_2S \rightarrow ZnS + H_2O \quad (2)$$

Cations present in the zeolite could be in form of K^+, Na^+, Ca^{2+}, or Mg^{2+}, and in all cases acid–base interaction between the zeolite and H_2S can occur.

$$Zeolite{-}K + H_2S \rightarrow Zeolite{-}H + KHS \quad (3)$$

Based on their findings, the presence of basic oxides improved the adsorption properties of 13 × zeolite with a breakthrough time of 580 min at 0.5 ppm H_2S, which was found to be 12 times longer than the unmodified zeolite [33].

Also, adsorbents containing ferric oxide or hydroxide are called iron sponge, and beds containing these compounds aid in removing H_2S [32]. The interaction between H_2S and iron oxide or iron hydroxide is indicated in the equation:

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad (4)$$

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O \quad (5)$$

Under a controlled condition, presence of oxygen results in regeneration of iron oxide/hydroxide from insoluble sulfide, this allows repeated use of the bed as shown in the equation:

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S \quad (6)$$

The work of Cherosky and Li [34] uses the iron sponge technology, where various biodegradable wastes (ground garden waste, digested garden waste, and spent tobacco) as the supporting materials were used in developing the adsorbent. Both the ground and digested garden waste showed excellent removal efficiency of 89–92% of H_2S which was comparable with the commercial adsorbent (SulfaMaster™). Also, several commercially available iron sponges are marketed worldwide including Sulfur-Rite™, Media-G2™ and SulfaTreat™ [35].

Table 1. Some of the biogas quality requirements of different countries for grid injection [17–20]

Parameter	Germany	Denmark	Austria	Sweden	Switzerland	Nertherland	France	USA
Wobbe Index (MJN m^{-3})	37.8–46.8*; 46.1–56.5**	51.9–54.9	47.9–56.5	45.4–48.6	47.9–56.5	43.46–44.41	43.2–46.8*; 49.1–56.6**	–
Fuel Value (kWh m^{-3})	8.4–13.1	11.1–12.3	10.7–12.8	–	–	–	–	9.8–11.4
Methane (vol %)	87.0–98.5	87–91	>96	95–99	>50	>80	—	—
Carbon dioxide (vol %)	<6	1.4	≤2	≤3	<6	—	<2	<2–4
Oxygen (vol %)	<3	—	≤5	<1	<0.5	—	—	<0.2–1
Hydrogen (vol %)	≤5	—	≤4		<5	<12	<6	—
Water vapor dew point (°C)	<*t*	<–5	<–8	<*t* – 5	—	–10	<–5	—
Total sulfur (mg/m^3)	30	—	10	23	30	45	30	0.37†

*Low calorific value gas.
**High calorific value gas, *t* = earth temperature.
†mmol %.

Table 2. Number of biogas upgrading plants across the world [21]

Country	No. upgrading plant
Germany	144
Sweden	55
USA	49
Netherlands	21
Switzerland	20
Austria	12
Japan	6
United Kingdom	6
Finland	5
France	5
Canada	4
Norway	4
South Korea	4
Brazil	3
Luxembourg	3
China	2
Spain	1
Denmark	1
Iceland	1
Hungary	1

Biofiltration Process

Biofiltration is another method of choice for biological removal of H_2S which is less capital intensive with good removal efficiency. Hydrogen sulfide was effectively removed using biofiltration by Degorce-Dumas *et al.* [36] using biogas to air ratio of 2:1. Empty bed retention time (EBRT) has been described as the key factor affecting the efficiency of biofilters. Chaiprapat *et al.* [37] found that increase in EBRT from 78 to 313 s resulted in corresponding increase in H_2S removal efficiency from 86 to 95%.

The packing material of a biofilter must contain the required nutrient to support microbial growth. Other properties of interest include its high porosity, high water holding capacity and its adsorbing properties. Thus, chemotrophic bacteria (*Thiobacillus* sp., *Thermothrix* sp., and *Thiothrix* sp.) are widely used for the biofiltration processes [38].

Namgung *et al.* [39] studied the removal of H_2S from biogas using *Acidithiobacillus thiooxidans* seeded aerobic biofilter. Removal efficiency of 30–60% was observed when the in-let concentration of H_2S was 180 ppm. Increase in removal efficiency was observed following a decrease in pH from 6.3 to 1.5 which coincided with increase in optical density of the bacteria (OD_{600}) from 0.05 to 0.4. From day 8 onward, the removal efficiency was found to be greater than 97% even after the increment of inlet concentration of H_2S to 400 ppm. This confirmed that the growth as well as metabolism of the bacteria was sufficient to handle the high loading rate of H_2S. The oxidation of H_2S under the aerobic and anaerobic conditions can be represented by the equations:

$$H_2S + {}^1/_2O_2 \rightarrow S + H_2O \quad (7)$$

$$H_2S + 2O_2 \rightarrow SO_4^{-2} + H^+ \quad (8)$$

$$12H_2S + 15NO_3^- \rightarrow 6S + 6SO_4^{-2} + 5NO_2^- + 5N_2 + 2OH^- + 4H^+ + 9H_2O \quad (9)$$

Based on this, Montebello *et al.* [40] reported the rate of removal of H_2S at neutral pH under aerobic and anaerobic biotrickling filters. Maximum elimination capacities for aerobic and anaerobic biofilters were found to be 100 $gH_2S\ m^{-3}$

Table 3. Biogas enrichment based on CO_2 and H_2S removal by different upgrading methods

Method	Methane enrichment (%)	Percentage removal (%)		Reference
		CO_2	H_2S	
Membrane technology (Polyimide)	94	81	53	[22]
Reverse osmosis membrane	>80	77	80	[23]
Composite membrane (zeolite within polyimide and polyetherimide)	90–95	75–85	–	[24]
Absorption (scrubbing using NaOH, $Ca(OH)_2$, and mono-ethanolamine, MEA)	96 (NaOH); 95 ($Ca(OH)_2$); 98 (MEA)	3.2 (NaOH); 4.0 ($Ca(OH)_2$); 1.3 (MEA)	>99 (NaOH); > 99 ($Ca(OH)_2$); > 99 (MEA)	[25]
Absorption (alkali with regeneration process)	88	91	–	[26]
Absorption (lime reaction, stripping & acid absorption)	68	<20	90	[27]
Biofiltration (*Acidithiobacillus* sp.)	>83	–	95	[28]
Biofiltration (*Chlorella* sp.)	93	85	–	[29]
Adsorption pressure-swing (aluminium terephthalate–MIL-53(Al))	99	95	–	[30]
Adsorption pressure-swing (Zeolite 13X)	99	96	–	[31]

h^{-1} at EBRT of 120 sec. and 140 $gH_2S\ m^{-3}\ h^{-1}$ at EBRT of 90 sec. respectively.

The potential of *Azospirillum*-like anaerobic phototrophic bacteria consortium for H_2S removal from swine waste biogas was found to be more than 97%. Rapid decrease in concentration of H_2S from 1200 to 30 ppm was observed within 3 h. The removal efficiency remains unaffected when the experiment was repeated, indicating the robustness of the biofiltering process [41].

Absorption Process

The classical wet techniques for removal of H_2S are based on transferring the biogas to the gas/liquid interface, and then to the bulk of the liquid phase, for reactions to occur. The compounds with practical applications for H_2S removal include alkaline solution, ferric chloride, soda ash and hydrogen peroxide as indicated in the following equations:

$$H_2S + 2NaOH \rightarrow Na_2S + 2H_2O \quad (10)$$

$$3H_2S + 2FeCl_3 \rightarrow Fe_2S_3 + 6HCl \quad (11)$$

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3 \quad (12)$$

$$H_2S + H_2O_2 \rightarrow S + 2H_2O \quad (13)$$

Chelate complexes of polyvalent metals are also used in removing H_2S from biogas. Chelate complex reacts with H_2S according to the equation:

$$H_2S + EDTA{-}Fe^{3+} \rightarrow EDTA{-}Fe^{2+} + S + 2H^+ \quad (14)$$

Separation of the elemental sulfur from the EDTA-Fe^{2+}solution can be done using Sedimentation or filtration, while oxygenation results in regeneration of the EDTA-Fe^{2+} into its Fe^{3+} active form. Using this technique, removal efficiency of 90–100% could be achieved in biogas containing $\geq$2% H_2S at gas flow rate, chelate complex solution rate and inlet pressure of 1 $dm^3\ min^{-1}$, 84 $cm^3\ min^{-1}$ and 220 kPa, respectively [42].

Removal of Carbon Dioxide

Absorption-Based Process

This involves passing a stream of biogas into the liquid phase, for reactions to occur. Compounds with broad application for CO_2 removal include alkaline and alkanolamines as presented in the equation:

$$CO_2 + 2OH^- \rightarrow CO_3^{-2} + H_2O \quad (15)$$

$$CO_2 + CO_3^{-2} + H_2O \rightarrow 2HCO_3^- \quad (16)$$

$$CO_2 + R{-}NH_2 + H_2O \rightarrow R{-}NH_3^+ + 2HCO_3^- \quad (17)$$

Several amine containing compounds have been reported to have practical application in removal of CO_2; these include mono-, di-, tri-ethanolamine, diglycolamine (DGA), diisopropanolamine (DIPA), methyldiethanolamine (MDEA), and a mixture of glycol and monomethylamine, which in addition to removal of CO_2 has gas dehydration properties [32].

Packed column reactor was used to study the absorption of CO_2 using NaOH, $Ca(OH)_2$ and mono-ethanolamine (MEA) solution. Through counter current flow, liquid phase became in contact with the biogas and maximum CO_2 removal efficiency was achieved, generating CH_4 enriched fuel. Thus, saturation was reached after 50 min for $Ca(OH)_2$, and 100 min for NaOH and MEA [25].

Adsorption-Based Process

This involves adsorption of CO_2 on solid surfaces under specific conditions. Several kinds of activated carbon or molecular sieves (zeolites) are used as adsorbents. These adsorbents could be selective for CO_2 and thus enriching the methane content of biogas.

Tufo Giallo Napoletano (TGN) is an adsorbent made up of alumina and silica with high potential to remove CO_2 from biogas under controlled pressure and temperature. Lastella *et al.* [43] evaluated the biogas produced from recycled digested sludge for CO_2 removal using TGN by a two-step adsorption-desorption cycle. Chromatographic analysis of the biogas before and after the adsorption process showed the efficiency of $\leq$98%.

Similarly, Alonso-Vicario *et al.* [44] carried out comparative studies of two synthetic zeolites (molecular sieves 13 × and 5A) and one natural zeolite (Clinoptilolite) as adsorbents based on pressure swing adsorption technique for upgrading biogas. Maximum removal of CO_2 was found using natural zeolite (Clinoptilolite) with CO_2 adsorption capacity of 173.9 mg CO_2/g Clinoptilolite. The method is cost effective with high stability through adsorption–desorption cycles.

Modification of mesoporous silica (SBA-15) with methyldiethyl-amine (MDEA) and piperazine (PZ) proves successful for removal of CO_2 from biogas. Characterization of the adsorbent by X-ray diffraction (XRD) showed that loaded amines did not affect the structure of SBA-15, despite the improvement in its adsorption capacity. The developed adsorbent was found to be seven-fold more specific to CO_2 than CH_4. Also removal of CO_2 was further enhanced by mixed-amine (MDEA + PZ) modification. The regeneration by purging the adsorbent with purified gas and its stability through several adsorption cycles were found to be excellent [45]. Additionally, polymer resin show the ability to adsorb CO_2 from biogas with high potential for continuous usage based on desorption experiments. Following the optimization of process conditions in a continuous lab-scale plant, methane purity of 98% was realized [46].

Other adsorption techniques used for removal of CO_2 from biogas are temperature- and vacuum-swing adsorption processes.

Biological-Based Process

This method is based on sequestration of CO_2 by autotrophic organisms where CO_2 is fixed via photosynthetic reactions during growth and metabolism. Cyanobacterium *Arthrospira platensis* uses CO_2 present in biogas as sole carbon source for its growth as reported by Converti *et al.* [47]. Linear relationship exists between the rates of *A. platensis* growth and CO_2 removal from biogas. The experiment was carried out with an initial biomass concentration of 0.105 g/L and light intensity of 35.6 μmol photons/m^2/s without addition of any carbon source; the organism being a photoautotroph, utilizes the available CO_2 which corresponds to the increase in biomass concentration of 2 g/L and the biogas contains appreciable amounts of O_2.

Similarly, CO_2 biofixation of biogas by microalgae *Scenedesmus* sp. was carried out; increase in biomass concentration (1.23 g/L) and growth rate (0.2715 g L^{-1} day^{-1}) resulted in 27% increment in calorific value of methane (from 6104.904 kcal/m^3 to 7767.268 kcal/m^3) [48].

In case of mutant *Chlorella* sp. MB-9, which has high tolerant to CH_4 and CO_2; 70% of the CO_2 in biogas was utilized by the organism for growth. This resulted in increment of CH_4 content to ∼90% [49].

Removal of Trace Components

Siloxane

Biogas produced from sludges contains siloxanes; which are used in the manufacture of different house-hold products including cosmetics, deodorants, shampoos and food additives. The presence of these compounds in biogas poise a serious problem in combustion facilities. Depending on the raw materials used for biogas production, siloxane concentration could be between 3 and 25 mg/m^3 [50].

Siloxanes can be removed from biogas using absorption processes but the major challenge is the safety. About 95% removal efficiency was obtained using Nitric acid (>65%) and sulfuric acid (>48%) for volatile methyl siloxanes (hexamethyldisiloxane and decamethylcyclopentasiloxane) [51].

Wheless and Jeffrey [52] reported about 99% siloxane removal using Selexol^{TM} which contains dimethyl ethers of polyethylene glycol. Combined effect of adsorption and drying was found to be economical as it removed siloxanes almost completely. Rossol *et al.* [53] evaluated the combined effect of adsorption on activated carbon and pre-drying steps based on cooling (5 °C) and re-heating (15 °C) with biogas flow rates of 750 m^3/h and 20 mg/Nm^3 total siloxane content. At the end of this experiment, complete removal of siloxane was achieved.

Bacteria sp. isolated from activated sludge from a municipal waste water plant was found to degrade Hexamethyldisiloxane (D3) and Octamethylcyclotetrasiloxane (D4). The set up was cultured for 90 days and D4 was degraded to dimethylsilanediol via hydrolysis. In case of D3, 10–20% removal efficiency with EBRT of 3.6 min and feed concentrations of 46–77 mg/m^3 was established [54].

Ammonia

Depending on the substrates, ammonia is found in trace amount in biogas at <100 ppm concentration [55]; thus routine cleaning process results in its complete removal as such additional process is not required. Ammonia is characterized with high solubilty in water and most technologies for removal of CO_2 can equally be used. High concentration of ammonia above 100 ppm exerts a serious problem to traditional gas engines. During combustion of ammonia, a greenhouse gas nitrous oxide is formed. Based on this, more stringent requirements are set by many Countries in which ammonia concentration in biogas should not exceed 20 mg/m^3 [56]. Thus, the main approaches that effectively remove ammonia from biogas are stripping, adsorption and precipitation.

Stripping is widely used but formation of scales in packed reactors and fouling are its major challenges. Thus, the rate of removal of ammonia is dependent on pH as a result of its exchange between the two forms i.e. ammonium ion and ammonia. Sometimes stripping is combined with absorption such that the ammonia released into the air from the waste stream is absorbed by strong acid (e.g. sulfuric acid), forming an ammonium salt that can be crystallized [57].

Zhang *et al.* [58] linked the removal of ammonia by stripping technology with methane production. The removal was found to be dependent on pH and aeration rate, which follows the pseudo-first-order kinetics. Increment in methane production of 69% and 59% were reported when the stripping was carried out at pH 9.5 and pH 10, respectively.

Moreover, washing of biogas with water results in removal of ammonia as well as dissolution of carbon dioxide, this on the other hand favours salification of ammonia as described by Jiang *et al.* [27]. This appears to be advantageous, as not only ammonia, CO_2 and H_2S in biogas could be reduced.

The highest ammonia adsorption capacity of 260, 280, and 230 mg g^{-1} were obtained when ammonia scrubbing material called N-TRAP adsorbents impregnated with 75, 80, and 65% sulfuric acid were used. The adsorbents which were made up of waste wood shavings and biosolids developed by Guo *et al.* [59] showed excellent ammonia removal efficiency from air stream and biogas. Also, clinoptilolite tuffs both natural and acid impregnated were used as adsorbents for removal of ammonia from air stream by Ciahotny *et al.* [60] and maximum adsorption capacities were found to be 12.7 and 31.5mgg^{-1} for natural and acid impregnated clinoptilolite, respectively.

Water

Biogas contains small amounts of water that needs to be eliminated before it can be used. Temperature tends to influence the water content; at 35 °C the water could be as high as 5%. Water content of 100 mg m^{-3} was considered to be the optimum for pipeline quality standards. Excess water from biogas can be removed through refrigeration by lowering the dewpoint to 0.5 °C. This is achievable only by compressing biogas before cooling and pressure could be applied to expand it. Through this, the condensate can be completely entrapped and removed. Silica, triethylene glycol, magnesium oxide, activated carbon, and aluminum oxide can be used to absorb/adsorb water from gas stream [61].

Membrane: An Emerging Upgrading Technology

This is a well developed technology and widely applicable in different purification processes. All major pollutants

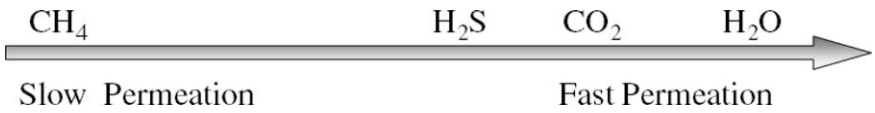

Figure 2. Schematic showing relative permeation across a membrane [58].

present in biogas (e.g. CO_2, H_2S, siloxane, etc.) can be eliminated using this method. It is evident that this technology offers both technical and economic justification to be a better method of upgrading biogas from all contaminants than absorption and adsorption processes [18]. Thus, membranes are continuously produced with higher selectivity and higher permeability at cheaper manufacturing costs for biogas upgrading [62].

Most upgrading processes aimed at establishing a very high methane content of 97–98%. Membranes from Air Liquide Medal™ were among the first to grace the market and since then many selective membranes of suitable designs have been established. The major manufacturers of highly selective membranes for biogas upgrading are Air Liquide Medal™, Evonik Sepuran®, and MemfoACT AS [63].

During biogas upgrading using membrane technology, the components of biogas show different permeabilities as indicated in Figure 2. CO_2 and H_2S permeate through the membrane faster than CH_4; thus cellulose acetate membrane for example found to be 60 and 20 times more permeable to H_2S and CO_2, respectively than CH_4 [19].

Kim *et al*. [64] developed fixed-site carrier membranes by casting polyvinylamine (PVAm) on four different supports (poly (ether sulfone) (PES), polyacrylonitrile (PAN), cellulose acetate (CA), and polysulfone (PSO)). Crosslinking of the cast PVAm on the support was achieved by reacting with four solvent systems (glutaraldehyde, hydrochloric acid, sulfuric acid, and ammonium fluoride). Of all the tested membranes, the PVAm cast on polysulfone and crosslinked by ammonium fluoride showed highest selectivity for CO_2 over CH_4 with a ratio of $1:>1000$. The developed membrane can be used for efficient removal of CO_2.

In order to increase the calorific value of biogas, polyimide membrane was used. The membrane was found to have higher permeability to CO_2, water vapor and H_2S; this aids in separation of the biogas from all contaminants. The raw biogas with initial methane content of 55–65% was enriched to 91–94%. Thus, single operation module of polyimide membrane resulted in complete elimination of all the contaminants with marked enrichment in methane content [22].

Similarly, Chmielewski *et al*. [65] demonstrated the efficiency of polyimide hollow fiber membrane for biogas purification using a raw biogas from Polish two-stage agricultural biogas plant that contains about 70% CH_4, the remaining percentage was majorly CO_2 and up to 250 ppm of H_2S. The authors reported that the membrane selectively enriched the methane content to 90% CH_4 and all the contaminants (CO_2, H_2S, and H_2O) were found in the permeate stream with limited loss of CH_4.

A water-swollen thin film composite membrane proposed by Kárászová *et al*. [66] could be effectively utilized for upgrading of raw biogas to pseudo natural gas quality. Maintaining the temperature below the dew point of raw biogas causes condensation of water on the membrane, which results in the formation of a very thin selective water layer. As CH_4, CO_2, H_2S, and other impurities have different solubility and permeability in and through the water layer, effective separation of the components could be established. Using this new approach, biogas methane enrichment from 63 to 95% was obtained.

Despite the high selectivity of membrane technology in upgrading biogas from all contaminants; the technology may go a long way in taking over from conventional technologies for removal of CO_2 and H_2S. However, a continuous improvement and development in membrane technology would make the process to be the best and cost-effective for biogas upgrading.

COST IMPLICATIONS OF BIOGAS UPGRADING

Depending on the intended applications, intensive upgrading of biogas paves a way for its utilization in novel processes including vehicle fuels and fuel cells as well as its inclusion in natural gas grid. Thus, Lie [67] suggested that performance and cost-effectiveness of biogas upgrading process depend on the capacity of the operation plant, technology to be employed, location, and the recommended quality intended to achieve. The cost of biogas upgrading is deriven from the total cost of investment and operation as well as maintenance.

Based on these, De Hullu *et al*. [68] carried out comparative cost analysis of different biogas upgrading techniques and estimated that the upgrading costs were within the range of 0.13 €/Nm^3 to 0.44 €/Nm^3 biogas; and lower operating cost of 0.12 €/Nm^3 biogas could be achieved by membrane technology, despite the initial capital cost and membrane fouling. Similarly, many researchers quoted the costs of biogas upgrading processes within the range of 0.11–0.25 €/Nm^3 biomethane for the treatment of 100 to 1000 m^3/h raw biogas [69,70]. In case of Linkoping, Sweden; the upgrading facilities for treating biogas obtained from slaughterwaste was reported to be about 0.876 €/Nm^3 biomethane [69]. Lombardi and Carnevale [71] obtained a specific upgrading cost of 0.72–0.73 €/Nm^3 biomethane based on their developed methods called absorption with regeneration methods.

Carborex® PWS absorption technology developed by Dirkse MilieuTechniek was reported to be efficient in upgrading biogas for higher methane content >97%, when applied to a plant of >250 Nm^3/h biogas. The total cost of the upgrading process was found to be between 0.08 and 0.05 €/Nm^3 biogas [72].

Biogas upgrading to ~99% CH_4 content was achieved using polyvinylamine/polyvinylalcohol (PVAm/PVA) membrane based on a 1000 Nm^3/h biogas facility. The cost of the upgrade and the possible compression to natural gas network pressure was found to be 0.17 \$/Nm^3. This value was lower than the price of the international market for natural gas which fluctuates up to 0.55 \$/Nm^3 [10].

One of the specific factors affecting biogas upgrading plant is the cost of electricity associated with compression, cooling and pumping. This is because during the process, methane loss can be minimized at the expense of energy consumption. Many upgrading process reported the economic analysis in terms of functional unit of €/kWh.

The estimated cost of 1–1.5 €ct/KWh was quoted for upgrading facilities of 200–300 m^3/h raw biogas and down sizing the facility to < 100 m^3/h raw biogas resulted in increase in the total cost to about 3−4 €ct/KWh [73]. This accounts for 3–6% of the energy requirements when compared with the total energy content in the upgraded biogas. Thus, upgrading of biogas becomes necessary in a cost effective way so as to ensure its efficient utilization, reduction in

the emission of greenhouse gas and commitment towards both Kyoto and EU greenhouse gas targets.

CONCLUSION

Biogas as a second-generation biofuel with high potential for future development requires the most efficient technology for freeing it from all contaminants so as to meet the quality as well as the calorific value of natural gas. Development in biogas production offers good sustainability and environmental benefits by treating various human, animal, agricultural, industrial and municipal wastes, and overall improves life by curbing the concentration of one of the greenhouse gases. Different upgrading strategies using conventional technology for freeing biogas from CO_2, H_2S, siloxane, and ammonia proved successful; this aids in increasing the wobbe index and preventing the release of unwanted exhaust gases (e.g. sulfur dioxide and dioxins) and corrosion of internal combustion engines. Cost-effectiveness, reliability, and robustness should be kept in mind when selecting any upgrading methods. The new approach for developing highly selective membranes should be attentive on the membrane compatibility with different biogas components not limited to enhancing the membrane selectivity. Full adoption of these technologies requires governmental support policies, incentives and benchmarking of the upgrading processes. It is envisaged that implementation of the technologies will offer a sustainable future in the development of bioenergy, environment and waste management.

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