

Chapter IV

BIOGAS TREATMENT AND PURIFICATION

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Introduction

The energy use of biogas in Brazil has been carried out for at least 40 years when it was initiated and integrated into the “green revolution” model in the 1970’s. Biogas has been used in the last decade as a national energy source, mainly due to the stimulus of the carbon credit market, which seeks to reduce methane emissions – a biogas component that contributes to the greenhouse effect. Currently, Brazil has 123 operating biogas plants used to produce thermal, electrical, and mechanical energy and biomethane/CNG (Figure 1) (CIBiogás, 2016). The substrates used in the biodigestion come from different industrial and agricultural sources.

The degree of purity and concentration of methane are the main factors to be considered in terms of biogas calorific potential, which varies between 15 MJ.Nm^{-3} and 30 MJ.Nm^{-3} (Abatzoglou; Boivin, 2009). Hydrogen sulfide (H_2S), carbon dioxide (CO_2), and ammonia (NH_3) stand out among the main contaminants that affect the energy potential

of biogas. The raw biogas may present H_2S concentrations ranging from 100 ppm to 10,000 ppm ($\text{mg}\cdot\text{m}^{-3}$) and, in extreme cases, up to 30,000 ppm, depending on the composition of the substrate used in the anaerobic digestion (Beil; Beyrich, 2013). H_2S is a gas that has a bad odor, in addition to being corrosive and toxic (Hendrickson et al., 2004; Ni et al., 2000). Regarding human health and toxicity, it is known that continuous exposure to low gaseous concentrations of H_2S (15 ppm – 50 ppm) results in mucosal irritation in the respiratory tract, which can cause headaches, dizziness, and nausea (MSDS, 1996). High concentrations between 200 ppm and 300 ppm result in respiratory arrest, and exposures to concentrations above 700 ppm for more than 30 minutes are fatal (MSDS, 1996). Despite being a flammable gas that contributes to the energy potential of biogas, the presence of H_2S causes corrosion in storage tanks, metallic pipes, and combustion engines, and results in the deterioration of the biogas production infrastructure (Garcia-Arriaga et al., 2010).

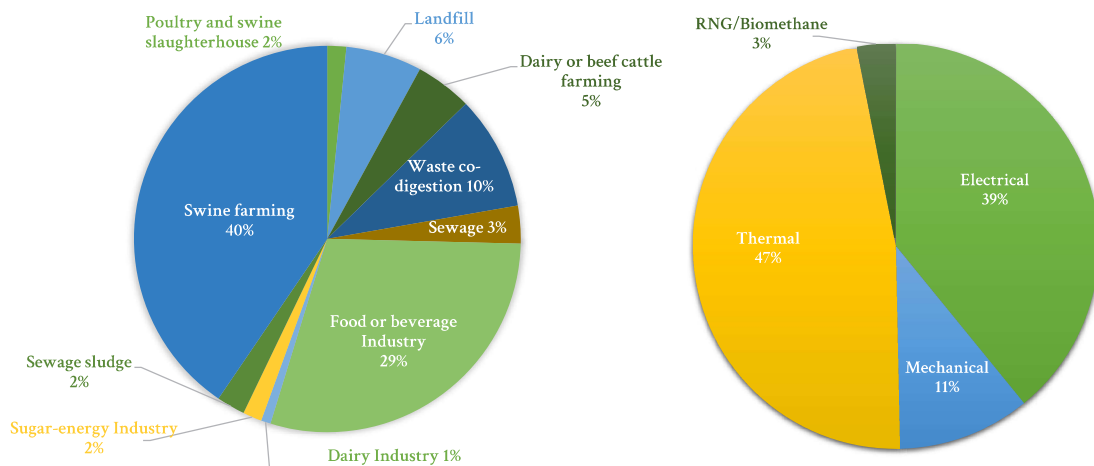


Figure 1. Distribution and variety of substrates used in anaerobic biodigestion (left) and energetic application of biogas use (right) in Brazilian operating plants.

Carbon dioxide (CO_2) is one of the main constituents of biogas, corresponding to a volume of 20% to 30% in substrates from agricultural residues (Wellinger et al., 2013). The presence of CO_2 directly interferes with the energy potential of biogas, as it is inert in terms of combustion and occupies a volume.

Ammonia (NH_3) is also another very common contaminant in biogas originating from agricultural residues, present at concentrations ranging from 50 mg.m^{-3} to 100 mg.m^{-3} (Wellinger et al., 2013). Ammonia has corrosive and toxic properties. The incomplete combustion processes in engines, for example, release nitrogen oxides (NO_x) into the atmosphere, which can contribute to the formation of acid rains and result in respiratory problems (Latha; Badarinath, 2004).

In addition to the mixture of gases, biogas also has water (moisture) in its composition at mean concentrations of 6% at 40°C . The water can accumulate in pipelines via condensation processes when not removed from the biogas, resulting in corrosion problems and/or clogging in the event of freezing. Table 1 shows the main problems caused by contaminants present in the biogas and the maximum concentration allowed according to the application.

In this context, implementing biogas treatment technologies to generate a quality fuel that can be efficiently converted into thermal, electrical, and/or mechanical energy is necessary. Currently, biogas treatment and purification processes are based on: (1) calorific value adjustment and removal of contaminants that affect the biogas quality and the useful life of system components; and (2) biogas purification and biomethane concentration for its insertion in biogas distribution and transport lines (Figure 2).

This chapter provides information on the most commonly used biogas treatment techniques, including the advantages and disadvantages of each process, as well as the basics of dimensioning. It is important to point out that the choice of treatment technology directly depends on the flow rate of the produced biogas, the biogas composition, and, mainly, the biogas purification level to be achieved (Figure 2). More complex and costly treatment systems to implement and operate will allow achieving higher biogas purification levels, as they allow the removal of contaminants more effectively and efficiently. However, conditioning biomethane with a high degree of purification is not always necessary. In this case, simpler and cheaper treatment systems can be used, as long as they meet the minimum requirements for each type of application (Table 1).

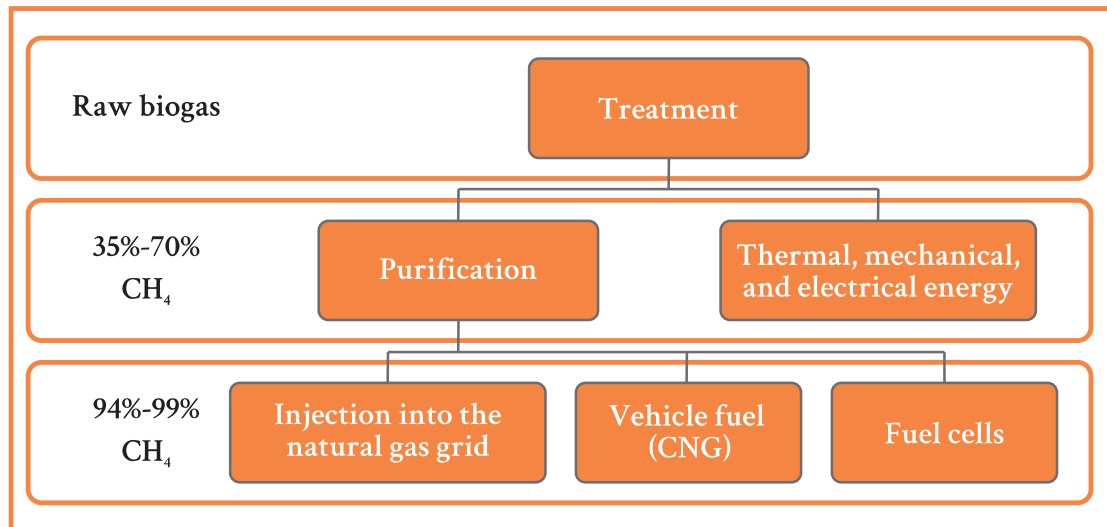


Figure 2. Biogas treatment and purification steps for biomethane concentration according to its final use.

The efficiency of removing contaminants in a treatment system is obtained through physicochemical analyses carried out to characterize the biogas at the entrance and exit of the treatment. In addition to specific analyses to determine contaminant concentrations, the Wobbe index, the relative density, and the calorific value of the biogas can also be calculated (Wellinger et al., 2013). The constituent concentrations must also be determined through specific analyses (e.g., BNT, ISO, and ASTM) in the case of conditioning or purifying the biogas for injection into the biogas network, in accordance with Resolution No. 16 of the National Agency of Petroleum, Natural Gas and Biofuels (ANP).

Table 1. Main biogas impurities, generated problems, and quality requirements for energy purposes.

Contaminant	Problems	Energy use requirements
Water	<ul style="list-style-type: none"> Corrosion of compressors, fuel tanks, and engines due to the formation of acids with H₂S, NH₃ and CO₂ Water accumulation in pipelines Condensation or freezing due to pressure 	Removal for performance in internal combustion engines, microturbines, molten carbonate fuel cells; conversion into biomethane
Particulate matter	Clogging by accumulation in compressors, fuel tanks and engines	
Oxygen	Danger of explosive mixtures due to the high O ₂ concentration in the biogas	
Ammonia	Corrosion by dissolution in water	
Hydrogen sulfide (H ₂ S)	<ul style="list-style-type: none"> Corrosion of compressors, fuel tanks, and engines Toxic concentrations in the biogas (>5 cm³ m⁻³) SO_x formation by combustion 	<ul style="list-style-type: none"> < 250 ppm for boiler heating 545 ppm – 1,742 ppm for internal combustion engines 2800 ppm for generators 10,000 ppm for turbines and microturbines 2 ppb – 15 ppb for injection into the biogas network 5 ppb for vehicle fuel 1 ppb – 5 ppb for fuel cells
Carbon dioxide (CO ₂)	Low energy value	< 2% in the conversion into biomethane
Siloxanes	<ul style="list-style-type: none"> Formation of SiO₂ and microcrystalline quartz by combustion Deposition on spark plugs, valves, and cylinders 	<ul style="list-style-type: none"> 9 ppm – 44 ppm for internal combustion engines 0.42 ppm for generators 0.05 ppm – 0.08 ppm for turbines and microturbines < 100 ppb for fuel cells
(Not generated by agricultural residues) Halogens	Corrosion in combustion engines	< 1 ppm for fuel cells

Source: Adapted from Ryckebosch et al. (2011) and Sun et al. (2015).

Water removal

The raw biogas obtained at the exit of the biodigester is saturated with moisture that must be effectively removed. The methods of water removal from the biogas generally also allow simultaneous removal of impurities such as particulate matter and foam (if any). Water removal is usually carried out at the first stage of biogas filtration to prevent corrosion of compressors and pipelines.

The physical separation of water by condensation or chemical drying are among the most used methods (Table 2). The main condensation techniques use cyclone separators, fine mesh screen demisters (porosity 0.5 μm - 2 μm), and pipes with a purge to separate and eliminate the condensed steam (Novak et al., 2016; Ryckebosch et al., 2011). Pipe cooling improves condensation and is generally more efficient in removing moisture from the biogas. However, the implementation and maintenance of this practice have a high cost, making it more complex with the installation of coolers and associated piping. Chemical drying includes the use of cylindrical reactors with absorbent materials in their internal volume, such as triethylene glycol or hygroscopic or adsorbent salts such as zeolites, silica gel, or aluminum oxide (Novak et al., 2016; Ryckebosch et al., 2011). Chemical drying is the predominant technique, but materials need to be changed and regenerated frequently to maintain the efficiency of moisture removal from the biogas (Table 2). Simultaneous removal of particles and hydrocarbons can also occur during the first step of the moisture removal treatment (Ryckebosch et al., 2011). Table 2 shows the advantages and disadvantages of conventional systems for removing the moisture from the biogas. Figure 3 shows a desiccator with absorbent material with the main function of removing water from the biogas.

Table 2. Advantages and disadvantages of techniques to remove water from the biogas.

Process	Technique	Advantages	Disadvantages
Adsorption	<ul style="list-style-type: none"> • Silica gel • Molecular sieve • Alumina 	<ul style="list-style-type: none"> • Adsorbent materials can be regenerated • They can be destined for any use of biogas, with low operating costs 	<ul style="list-style-type: none"> • Adsorption columns must be operated at a pressure of 6 bar – 10 bar • Particles and oil must be previously removed
Absorption	<ul style="list-style-type: none"> • Ethylene glycol • Selexol • Hygroscopic salts 	<ul style="list-style-type: none"> • Materials can be regenerated • Simultaneous removal of particles and hydrocarbons • They are not toxic compounds • High removal efficiency 	<ul style="list-style-type: none"> • Need for high temperatures and pressures for regeneration of the absorber solution • Need to treat high gas volumes (>500 m³ .h⁻¹) to be feasible economically
Cooling	<ul style="list-style-type: none"> • Cooling to 2 °C 	<ul style="list-style-type: none"> • Most efficient technique for removing moisture from biogas 	<ul style="list-style-type: none"> • High energy consumption to keep the system cool
Condensation	<ul style="list-style-type: none"> • Cyclone separator demisters • Pipe heat exchange systems • Piping with water vapor purge system 	<ul style="list-style-type: none"> • They can be applied as a pre-treatment in all biogas generation systems • Reduction of water vapor by up to 0.15% of the initial volume • Elimination of hydrocarbon and oil particles, simple technology 	<ul style="list-style-type: none"> • The pipes must be long and installed with a slope to allow purging of water vapor • The pipes must be resistant to freezing

Source: Adapted from Ryckeboesch et al. (2011).



Source: AVP, Air & Vacuum, Inc. (<http://airvacuumprocess.com>).

Figure 3. Example of a desiccator for water removal from the biogas: reactor filled with adsorbent material (zeolites).

H₂S removal

The H₂S removal can be carried out by biological, physical, or chemical processes. The desulfurization process is divided into two phases: (1) primary phase, which reduces H₂S levels to <500 ppm, achieving an efficient removal of approximately 100 ppm; and (2) precision phase, which adjusts the H₂S concentrations to specifications and requirements for injection into the natural biogas network. In this case, the H₂S concentrations are reduced to less than 0.005 ppm. In addition to this classification, desulfurization methods can be divided into internal or external methods when occurring inside or outside the biodigester, respectively (Figure 4).

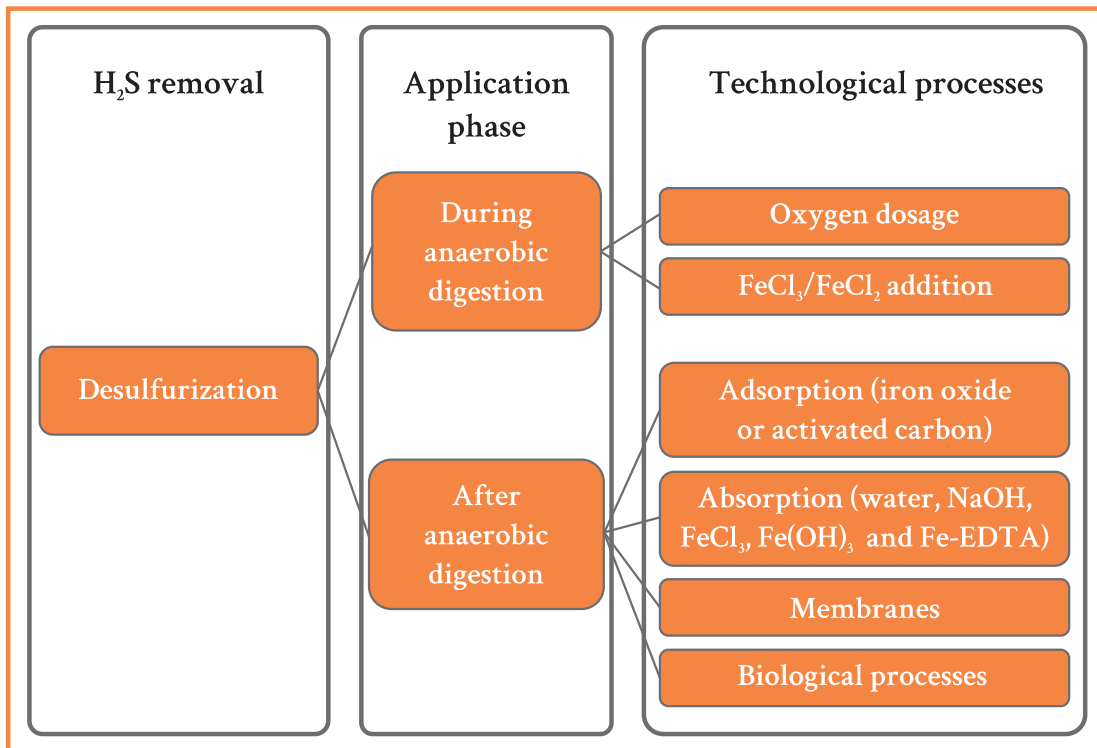


Figure 4. Most commonly observed technological processes for biogas desulfurization.

H₂S removal inside the biodigester

Oxygen injection

Desulfurization inside the biodigester occurs through micro-aeration or direct injection of air or pure oxygen through the use of special gas cylinders. The growth of bacteria that oxidize H₂S is stimulated in the presence of oxygen, occurring in the process of biological desulfurization of H₂S into elemental sulfur. Oxidation is carried out by the action of a specialized group of sulfide-oxidizing microorganisms, which are widely found in the anaerobic environment of biodigesters (e.g., *Thiobacillus* spp. and *Acidithiobacillus* spp.).

The oxygen supply needs to be carefully calculated and monitored to apply this technique. Sulfate (SO_4^{2-}) will be the main product to be formed if the molar ratio of oxygen consumption with sulfide (O_2/S_2^-) is higher than or equal to two (≥ 2). However, the products formed will be represented mostly by elemental sulfur if the ratio (O_2/S_2^-) presents values between 0.5 and 1.0.

Oxidation-reduction potential (ORP) meters are used to control the molar ratio between oxygen and sulfide (O_2/S_2^-) in the biodigester (Khanal; Huang, 2003). ORP values in the order of -100 mV to -400 mV indicate the formation of elemental sulfur as the main product, accounting for more than 80% of the removed H_2S (Janssen et al., 1998; Krishnakumar et al., 2005). A sensor for measuring the redox potential must be installed in the upper air part of the biodigester for the control of air injection provided by pumping (conventional injection pumps for aeration gases). An automatic controller triggers a solenoid valve to open or close the air injection system depending on the ORP setpoint.

However, there are disadvantages associated with the process despite the simple, efficient, and low-cost methodology for H_2S removal. Incorrect air dosing in the system can lead to potentially explosive mixtures (6%–12% v.v⁻¹ oxygen). The presence of oxygen in the biodigester can inhibit methane production, as methanogenic microorganisms are sensitive to the presence of oxygen. Furthermore, H_2S oxidation can generate elemental sulfur deposits inside the biodigester, increasing the sludge volume, which must be removed frequently. The presence of trace gases of oxygen and nitrogen resulting from the addition of air to the system may limit the biogas applicability.

Iron chloride addition

Iron chloride reacts with H_2S to form insoluble iron sulfide (FeS) through the precipitation reaction of the iron salt. Iron chloride addition (ferric chloride – $FeCl_3$, and ferrous chloride – $FeCl_2$) to the biodigester is carried out by direct dosing inside or externally, using a reactor installed in series in the biogas line. These chemical reactions are very efficient in reducing H_2S (Table 3), but the removal levels are not sufficient for limit concentrations established in fuel cells or injection in natural biogas pipelines. The concentrations achieved with this methodology are ≤ 100 ppm of H_2S (Ryckebosch et al., 2011), suggesting its application for biogas purification for use in boilers, engines, or turbines.

The sulfur precipitation reaction is pH-dependent despite being a low-cost and simple technique, with a lower efficiency under acidic conditions. However, methanogenic processes generally act to remove

the medium acidity (removal of H^+ , CO_2 , and organic acids used as biological substrates), which makes the medium naturally well buffered with pH ranging from 7 to 8. The lack of selectivity of reagents with sulfur enables parallel reactions to occur, resulting in reduced H_2S removal efficiency (Devai; Delaune, 2002; Speece, 2008). In this case, a higher concentration of oxidizing agent (Table 3) is necessary to guarantee the stoichiometric efficiency of the reaction with sulfur, which implies higher amounts of reagents to be used, thus increasing the costs and complexity of the technique. The formation of precipitates inside the biodigester is a potential problem.

The sediment formed must be frequently removed from the biodigester to avoid loss of internal volume and alteration in the biogas production capacity due to changes in the hydraulic retention time. Biodigesters that do not have a complete mixture may present an inefficient H_2S removal due to the lack of homogeneity necessary to favor an efficient chemical reaction.

The stoichiometric demand in the chemical treatment processes allows calculating the theoretical amounts of reagents and products to be added for desulfurization. Table 3 shows the amount of reagent to be used based on these calculations.

Table 3. Stoichiometric calculations and demand in the physicochemical and biological treatment processes for H_2S removal from the biogas.

Tratamento	Reações estequiométricas	Demanda química
$FeCl_3/FeCl_2$	$2FeCl_3 + 3H_2S \rightarrow 2FeS + S + 6HCl$	0.31 g $FeCl_3/g H_2S$
$Fe(OH)_n$	$2Fe(OH)_3 + H_2S \rightarrow 2Fe(OH)_2 + S + 2H_2O$ $2Fe(OH)_2 + H_2S \rightarrow FeS + 2H_2O$	0.16 g $Fe(OH)_3/g H_2S$ 0.19 g $Fe(OH)_2/g H_2S$
Iron oxides	$FeO + H_2S \rightarrow FeS + H_2O$ $Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$	0.47 g FeO/H_2S 0.64 g $Fe_2O_3/g H_2S$

Removal of H₂S downstream

Adsorption processes

Various adsorbent materials such as synthetic zeolites, activated carbon, silica gel, or alumina are used to remove H₂S, N₂, NH₃, and H₂O, among other compounds, from the biogas (Beil; Beyrich, 2013; Ryckebosch et al., 2011). Reactors with adsorbent materials are installed in series in the biogas line. These reactors in the form of columns operate at different stages, such as adsorption, depressurization, desorption, and pressurization. The adsorption of contaminants occurs under pressure (~800 kPa) and the desorption occurs by depressurizing the bed, allowing the removal of contaminants and regeneration of the adsorbent.

Although H₂S removal can be performed by this process, the recommendation is that it be previously removed through the other purification processes mentioned above, as the presence of H₂S can make the adsorption on the material irreversible (Ryckebosch et al., 2011). The presence of water in the biogas can also result in a rapid saturation of adsorbent materials and, therefore, water removal before the adsorption process is recommended. Gases such as O₂ and N₂ can be removed during adsorption, as long as the adsorbent material has selectivity to these elements and is applied under specific conditions of atmospheric pressure (Ryckebosch et al., 2011).

The most commonly used adsorbents consist of activated carbon and iron oxide (Abatzoglou and Boivin, 2009). Activated carbon can be impregnated with potassium permanganate (KMnO₄), potassium iodide (KI), potassium carbonate (K₂CO₃), or zinc oxide (ZnO), which act as catalysts, resulting in increased speed of the H₂S oxidation reaction (Pettersson, 2013). Activated carbon impregnated with metal salts with catalyst effect has a higher capacity for H₂S adsorption due to the combination of microporosity and oxidative properties. Examples of metal oxides also include Fe₂O₃, Cu₂O, and MnO (Wiheeb et al., 2013).

H₂S readily reacts with iron oxide, iron hydroxide, and zinc oxide to form iron sulfide or zinc sulfide, respectively. The method is commonly known as an iron sponge because it uses a solid base, in this case,

steel wool covered with iron filings to form the reaction bed (Figure 5). An alternative to the use of steel wool is wood chips impregnated with iron oxide, which have been preferably used as a reaction bed.

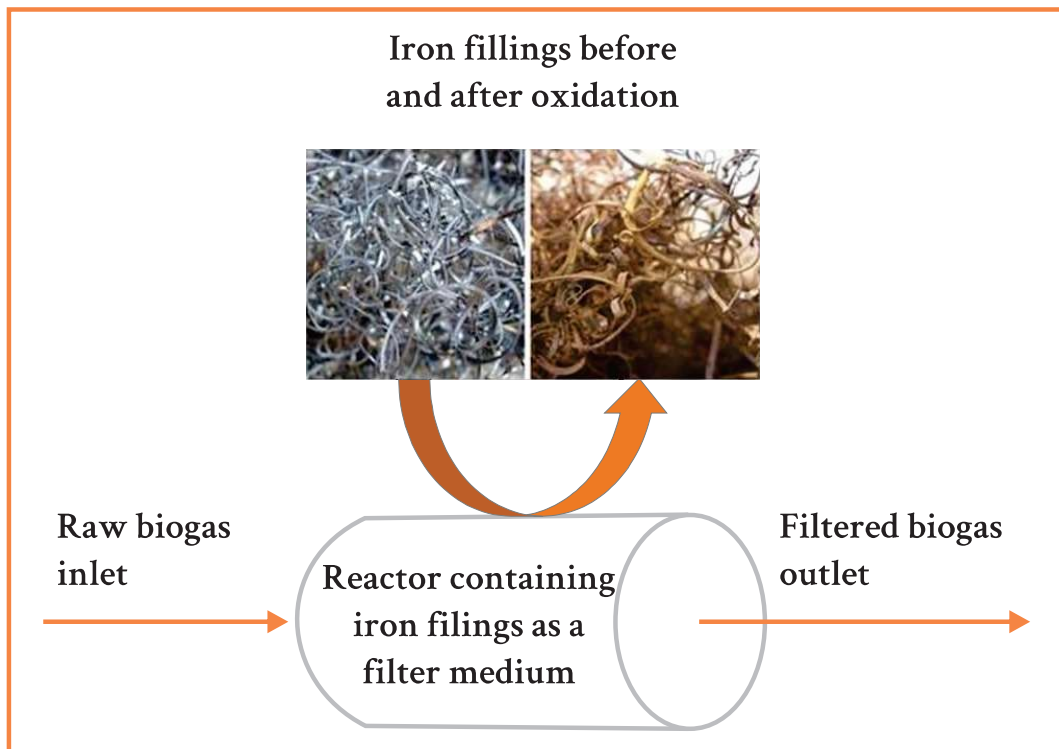


Illustration: Marcio Busi

Figure 5. Diagram of a filter installed in series in the biogas line containing iron filings as adsorbent material. Detail of iron filings oxidation.

Adsorption processes are extremely efficient in reducing H_2S (< 5 ppm) and are widely applied when there is a need to achieve low H_2S levels in the biogas, such as fuel cells and biomethane (Beil; Beyrich, 2013). One of the great disadvantages of this filtering practice is the accumulation of ferric sulfide, which is formed from the oxidation reaction of H_2S with iron, reacting exothermically in the presence of air and causing instantaneous ignition and risk of explosion. This is known as a pyrophoric process. The chemical equation for the ferric sulfide formation is shown in Equation 1:



Equation 1

Other disadvantages include the high cost of the system and difficulties in its operation and maintenance, which require regeneration or frequent exchange of adsorbent materials. There are also energy costs during the regeneration process, as high temperatures (450 °C) are required to achieve this goal. Neglecting rigorous maintenance results in a loss of contaminant removal efficiency, which compromises the quality and end-use of the biogas.

The adsorbent material is placed in a reactor installed in series in the biogas line to dimension the system. In general, these reactors are built using material inert to corrosion, such as PVC containers or even stainless steel, the latter presenting high costs. The quantity (or volume) of adsorbent material to be used is calculated according to the mass required to satisfy the reaction stoichiometry (Table 3). The use of activated carbon impregnated with oxidizing solution leads to an adsorption capacity of 150 milligrams of H₂S per gram of activated carbon. On the other hand, the adsorption capacity of non-impregnated activated carbon is reduced to 20 milligrams of H₂S per gram of activated carbon (Abatzoglou; Boivin, 2009). The activated carbon needs to be replaced after it reaches saturation and loss of adsorption efficiency and the consequent H₂S removal. The mass of activated carbon to be used per day (or months, according to the produced biogas flow rate and the adsorbent reactor size) can be estimated through the biogas flow rate (Q ; m³·d⁻¹) multiplied by the H₂S concentration found in the biogas (C ; kg·m⁻³). Based on the obtained result, the mass of activated carbon to be used is normalized by the maximum adsorption capacity mentioned above.

Absorption processes

Absorption processes encompass chemical methods using water, reagents, and/or organic solvents. Contaminants with a higher solubility are dissolved and removed along with water during biogas washing. The biogas washing to remove CO₂ can be carried out very effectively under high pressure (1,000 kPa–2,000 kPa). After decompression and desorption, CO₂ is released into the atmosphere, and water is regenerated. This simple, low-cost technology results in an efficient CO₂ removal (95%) (Beil; Beyrich, 2013; Ryckebosch et al., 2011). The final CH₄ concentrations range from 93% – 98%.

The presence of organic or chemical reagents has higher CO₂ absorption rates compared with water. Some examples of organic reagents include polyethylene glycol (Selexol®) and tetraethylene glycol dimethyl ether (Genosorb®) (Beil; Beyrich, 2013; Ryckebosch et al., 2011). Chemical solvents commonly used in the absorption process include aqueous amine solutions, alkaline salt solutions, or iron-containing solutions (Zhao et al., 2010). Chemical absorption uses low atmospheric pressure (50 mbar – 150 mbar), with the chemical solution being regenerated in the desorption column by heating processes (106 °C – 160 °C) (Beil; Beyrich, 2013). The treated biogas must undergo a drying process to remove the water vapor formed due to the heating of the desorption column (Beil; Beyrich, 2013).

The CH₄ recovery rates are high, reaching values close to 99.9%. Although it is a very efficient technique for removing H₂S (>97%), the disadvantages include costs with chemical-oxidizing agents, energy demand for continuous pumping of the solution to wash the biogas, and, mainly, the generation of a final liquid effluent that needs to be regenerated or properly treated before its final disposal.

Biogas washing is usually carried out using reactors with corrosion-resistant material (PVC or stainless steel). The reactors are usually cylindrical, and their internal volume is filled with water containing or not chemical solutions. The internal circulation of the washing liquid medium occurs through pumping. The reactors are generally built with a longer length and smaller diameter and arranged in a vertical position to optimize the reaction time and contact between CO₂ and H₂S. The biogas enters the bottom of the reactor and flows counter-currently to the liquid flow to the top of the reactor, where it is collected.

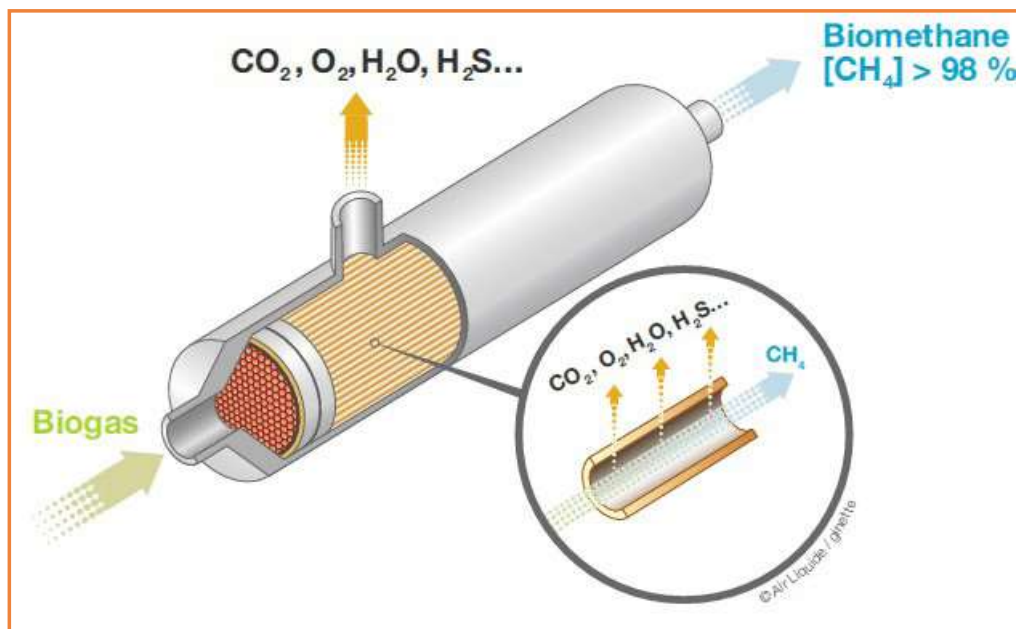
Selective membranes

The use of separation processes using membranes or gas permeation comprises the methane separation from other biogas contaminants by diffusion processes. The types of contaminants to be separated are associated with the type of membrane, structure, permeability, and lifetime. Polymeric or inorganic materials are the most used in the preparation of membranes for CO₂/CH₄ separation (Basu et al., 2010), and

polyimide and cellulose acetate are the most used (Budzianowski, 2016). Membranes composed of inorganic material have 5 to 10 times more selectivity than conventional polymeric membranes (Budzianowski, 2016).

Treatment using membranes (Figure 6) involves separation by high pressure (approximately 96% removal efficiency) or biogas-liquid absorption (98% efficiency) (Ryckebosch et al., 2011). The treatment process is performed in compact systems and generally does not require frequent maintenance (Zhao et al., 2010). Some examples of membranes available on the international market are PRISM[®], SEPURAN[®], Perm-Select[®], and Valopur[®].

One of the main disadvantages of the biogas treatment process using membranes is related to the high costs of the system. Therefore, this technique is only recommended when it is intended to obtain biomethane with a high degree of purity.



Source: <http://www.apsleyfarms.co.uk/gas-to-grid>

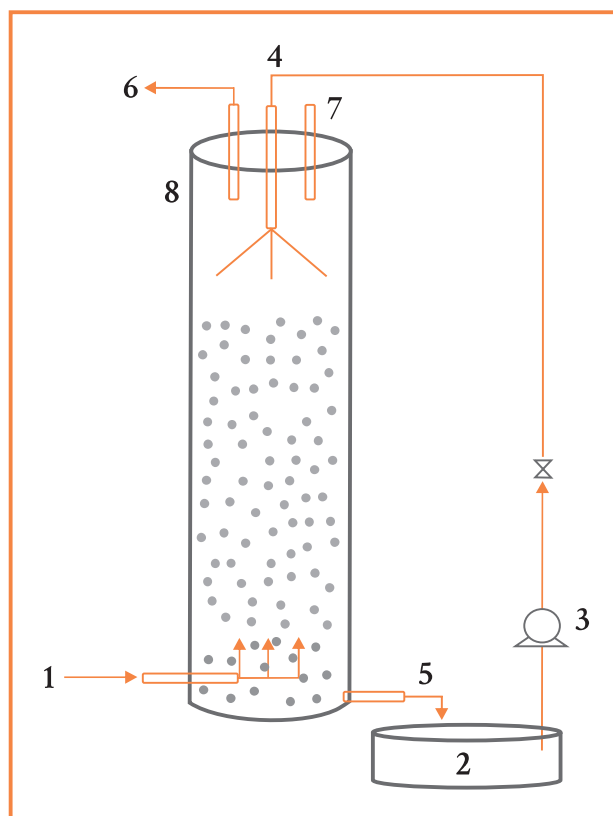
Figure 6. Representation of a biogas filtration system using membranes. The filter is installed in series in the biogas line.

Biological processes

The biological process is mediated by bacteria capable of oxidizing H_2S into sulfate (SO_4^{2-}) and/or elemental sulfur (S^0) in the presence of oxygen or nitrate as electron acceptors (Prescott et al., 2002). Examples of bacteria that oxidize H_2S are *Thiobacillus* sp., *Thermothrix* sp., and *Thiothrix* sp. (Stainier et al., 1986). These microorganisms are often found in various environments and are known as chemotrophs. The CO_2 present in the medium is used as a carbon source for cell multiplication. Therefore, the fortuitous CO_2 removal can also benefit from the use of a biofilter (Syed et al., 2006).

Biofilters are reactors usually made with corrosion-resistant materials with different configurations (Syed et al., 2006). In practice, these reactors are internally filled with porous materials (e.g., Bioballs®) (Pirulli et al., 2016), which have a high surface area for fixing microorganisms (biofilms), not restricting the biogas passage. A nutrient solution rich in nitrogen (preferably in the form of nitrates) and phosphorus is continuously pumped into the biofilter. This solution percolates on the internal porous material of the reactor to keep the population of bacteria metabolically active in the process of oxidizing H_2S . The sulfur removed by filtration, along with some nutrients still present in the liquid effluent, can be disposed of without the need for treatment and is also used as an excellent source of liquid fertilizer. Figure 7 shows a schematic illustration of the biofilter.

Biofilters are cost-effective in removing contaminants, being able to remove up to 100% of the H_2S present in the biogas. One of the drawbacks is the preparation of the nutrient solution, which needs to be changed regularly in the biofilter. However, the diluted effluent from the anaerobic biodigester can be used as a nutrient solution for the biofilter as a way to reduce labor and costs associated with nutrients (Pirulli et al., 2016). In this case, the digestate also serves as an excellent inoculum source for H_2S -oxidizing bacteria, which start to colonize the interior of the biofilter. Biofilters are generally limited by the low biological oxidation kinetics of H_2S . Thus, the process is mainly recommended for systems with low flow rates. The dimensioning of larger biofilters is possible to meet higher flow rates, but the costs become more significant.



Source: (Pirolli et al., 2016).

Figure 7. Representation of a biofilter. (1) Biogas inlet; (2) reservoir with a nutrient solution or diluted digestate; (3) circulation pump; (4) inlet of nutrient solution with an internal disperser to ensure uniform and homogeneous distribution across the entire surface of the internal porous material; (5) liquid nutrient solution outlet; (6) purified biogas outlet; (7) thermometer (not required); (8) PVC reactor with porous material for bacterial fixation (e.g., bio balls) inside.

The use of biofilters with microalgae has shown very promising results in the removal of CO_2 and H_2S from the biogas (Conde et al., 1993; Mann et al., 2009; Prandini et al., 2016). Usually, stabilization and treatment lagoons are used to treat the digestate produced by the biogas digester. The digestate is an effluent rich in nitrogen and phosphorus, which can lead to eutrophication processes when dumped in these lagoons due to the high growth of microalgae (Figure 8).

Microalgae use CO_2 during the biogas filtration process as a carbon source for cell growth through photosynthesis. The oxygen generated by photosynthesis serves as an electron acceptor, which is used by H_2S -oxidizing bacteria. Thus, 100% of the CO_2 and H_2S are removed from the biogas. The high CO_2 concentration in the biogas stimulates

the growth of microalgae and hence increases the nutrient consumption rate (phycoremediation) and the digestate treatment efficiency. The advantage of the technique of CO₂ removal by microalgae is the development of an integrated platform between digestate treatment and biogas filtration. In practice, the biogas can be bubbled in closed photobioreactors containing diluted liquid effluent and microalgae (Figure 8). The biogas flow rate (Q , m³.day⁻¹) to be used in the biofilter depends on the biological activity of removing contaminants by the microalgae. Kinetic tests are carried out in pilot systems to determine the biogas purification efficiency by microalgae.



Photo: Melissa Paola Mezzari

Figure 8. Eutrophication of treatment and stabilization lagoons due to the presence of microalga

Cryogenics

Biogas purification by the cryogenic process is a little-used technique and has been in continuous development (Ryckebosch et al., 2011). During the cryogenic treatment, the raw biogas is dried and compressed at high pressure (8,000 kPa) under controlled temperature conditions

(cooling), resulting in the separation of CH_4 (>97%) and CO_2 removal by condensation. Although the results obtained with cryogenic purification are very promising, the technology is unfeasible due to the high initial investment cost and high energy consumption (Budzianowski, 2016; Scholz et al., 2013).

Final considerations

Treatment or purification of biogas is a crucial process for its use as a source of biofuel. This chapter presents the processes most commonly used for the treatment and purification of biogas, including the removal efficiencies, as well as the advantages and disadvantages of each system. A correct dimensioning of the treatment and purification system requires the determination of the produced biogas volume, its physico-chemical characteristics, and, mainly, its degree of purity to be achieved. H_2O , H_2S , CO_2 , and NH_3 are among the main contaminants present in the biogas. Water is usually the first contaminant to be removed from the system, resulting in the minimization of corrosion of the entire infrastructure that composes a gas purification system, including compressors and pipelines. Water removal also reduces problems associated with the saturation of the filter material and adsorbents.

The removal of H_2S occurs inside or outside the biodigester through biological or chemical oxidative processes. The practice of injecting O_2 or air to remove H_2S must be considered carefully to avoid excess O_2 and the intrinsic risks of explosion. The amount of O_2 in the system must not exceed the maximum concentrations according to the rules and regulations in force for injecting biogas into the network. Biological processes are considered to have low implementation and maintenance costs and can significantly reduce H_2S and CO_2 sustainably. Furthermore, the integration of technologies in a modern biogas purification platform associated with the digestate treatment using microalgae has shown very promising results.

CO_2 can be removed during or after desulfurization processes by washing the gas with water and/or chemical reagents, using or not pressurized systems. The use of selective membranes for the removal of CO_2 and other contaminants such as H_2S and NH_3 can also be used.

Except for the cryogenic technique, all processes mentioned in this chapter have been used for biogas treatment and purification. The choice of the most appropriate technique to be used must consider the maximum levels of contaminants allowed in the biomethane composition, in addition to factors such as implementation and maintenance costs and the degree of complexity of the system and availability of parts and/or technical assistance.

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