[1.]Bianca Ştefania ZĂBAVĂ, [1.]Gheorghe VOICU, [1.]Nicoleta UNGUREANU, [1.]Mirela DINCĂ,
[1.]Gigel PARASCHIV, [1.]Mariana MUNTEANU, [1.]Mariana FERDES

METHODS OF BIOGAS PURIFICATION – A REVIEW

[1.]University Politehnica of Bucharest. Faculty of Biotechnical Systems Engineering, ROMANIA

Abstract: Biogas is a product of anaerobic ferment of organic products. Among the fuels from vegetal biomass, biogas has a great importance and can successfully replace fossil fuels for obtaining electricity and heat; the use of biogas exists for a few years also in the field of transport. Biogas formed in the methane fermentation process contains about 50÷60% of methane. Other ingredients such as carbon dioxide, hydrogen sulfide, water, water vapour and small amounts of nitrogen and oxygen are compounds that lower the energy value of biogas. In this paper are presented the main methods of biogas purification.
Keywords: biogas, purification, methane

INTRODUCTION

A major concern for most people these days is the use and availability of energy. People spend a large portion of their earnings on gas, propane and oil. These fossil fuels are being continuously used to a large extent. Because these forms of energy are non-renewable, their availability will continue to decrease and costs will continue to go up. This has led to a search for new energy sources. One excellent source of energy is *biogas*.

Biogas originates from bacteria in the process of bio-degradation of organic material under anaerobic (without air) conditions. The natural generation of biogas is an important part of the biogeochemical carbon cycle. Methanogens (methane producing bacteria) are the last link in a chain of micro-organisms which degrade organic material and return the decomposition products to the environment. In this process biogas is generated, a source of renewable energy.

Biogas is a mixture of gases that is composed chiefly of:
- methane (CH_4): 40-70 vol.%
- carbon dioxide (CO_2): 30-60 vol.%
- other gases: 1-5 vol.% including
- hydrogen (H_2): 0-1 vol.%
- hydrogen sulfide (H_2S): 0-3 vol.%

Like those of any pure gas. the characteristic properties of biogas are pressure and temperature-dependent. They are also affected by the moisture content. The factors of main interest are:
- change in volume as a function of temperature and pressure.
- change in calorific value as a function of temperature, pressure and water-vapor content and
- change in water-vapor content as a function of temperature and pressure

The calorific value of biogas is about 6 kWh/m^3 - this corresponds to about half a litre of diesel oil. The net calorific value depends on the efficiency of the burners or appliances. Methane is the valuable component under the aspect of using biogas as a fuel (*Thomas H. et al.*).

Biogas offers a diversity of options for use. e. g. the decentralised production of electricity and heat, the distribution via heat networks, the feed-in of upgraded biogas into the natural gas grid and its follwing use as a natural gas substitute for energy, as fuel or in the chemical industry – figure 1. Independently of the use selected, the objective is to make the energy utilisation as efficient as possible.

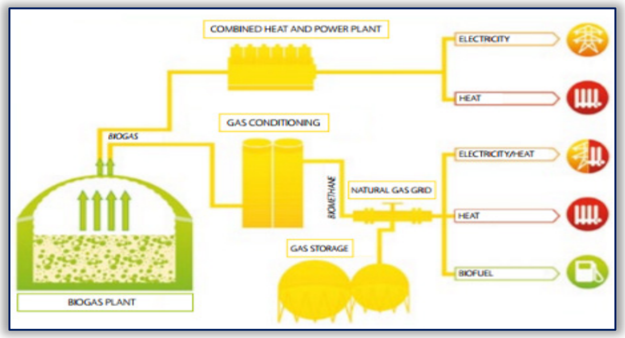

Figure 1 - Various options for using biogas

MATERIAL AND METHOD

Biogas is a product of anaerobic fermentation of organic products. Of the biomass fuel, biogas is of particular importance and can successfully replace fossil fuels for electricity and heat. In order to obtain biogas in a productive and profitable way, it must be processed before use. Thus, prior to use, raw biogas is subjected to conditioning (purification) operations, resulting in the properties required by users.

Biogas purification is the operation of retention of unwanted biogas components before it is used in the combustion process. Whatever the ultimate way of using biogas, it is impossible to use it in the raw state. The only recyclable component is methane. To enable the use of biogas by cogeneration, the substances to be eliminated are: water, organohalogen, carbon dioxide and sulfur *(Ioan B. and Minciuc E., 2003)*.

The most important reasons for improving the quality of biogas include the need to meet the requirements of the installations in which it is used (engines, boilers, fuel cells, etc.)

increasing its calorific value but also for standardizing the quality *(Krzysztof B. et al..2011).*

There are small amounts of biogas present in certain compounds that due to their oxidising or incombustible properties have to be eliminated to favor a good combustion process. During the conditioning process, these compounds that inhibit the combustion process are reduced in quantity or totally eliminated, depending on the final use of biogas.

Figure 2 shows the most commonly used methods of biogas conditioning: pressure adsorption, biogas purification with water under pressure, physical and chemical absorption, membrane separation and cryogenic separation. These methods largely involve the removal of hydrogen sulfide, carbon dioxide and water vapor.

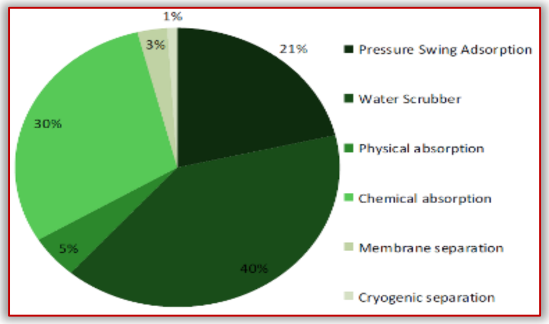

Figure 2 - Methods of biogas conditioning

Biogas can be used as a substitute for household and industrial gas or can be used as a renewable and sustainable energy source to produce heat or electricity in co-generation units (CHP) (*(Krischan J. et al.,2011).*

Table 1 highlights biogas components that are removed depending on how they are used.

Table 1. Removal of biogas components according to its final use

Use	H_2S	CO_2	H_2O
Gas station (boiler)	< 1000 ppm	No removal required	No removal required
Stove	Removal required	No removal required	Removal required
Cogeneration of heat and electricity	< 1000 ppm	No removal required	Removal required
Fuel for cars	Removal required	Removal required	Removal required
Fuel for the gas network	Removal required	Removal required	Removal required

The method of conditioning the raw biogas must be determined from the construction of the biogas plant for the fact that it may require some specific details in the construction of the plant.

RESULTS

Raw biogas needs to be cleaned to remove toxic and harmful constituents (e.g.. hydrogen sulfide, ammonia, VOCs. Halides, moisture, siloxanes, particulates, AB 1900 COCs, etc.) to meet regulatory and technical standards. The principle of cleaning techniques used currently includes adsorption, biofiltration, water scrubbing (an absorption process) and refrigeration.

— Biofiltration

Biofiltration relies upon the natural biological metabolism of sulfur-oxidizing bacteria species to convert hydrogen sulfide into elemental sulfur or sulfate. These systems are designed to ensure a high-density microbial community and maximize contact between the microorganisms and the feed gas *(Y. Zhu, 2001).*

A biological filter combines water scrubbing and biological desulfurization. As with water scrubbing, the biogas and the separated digestate meet in a counter-current flow in a filter bed. The biogas is mixed with 4% to 6% air before entry into the filter bed.

Biofiltration systems can be set up in three different configurations: bioscrubber, biofilter, and biotrickling filter (Figure 3).

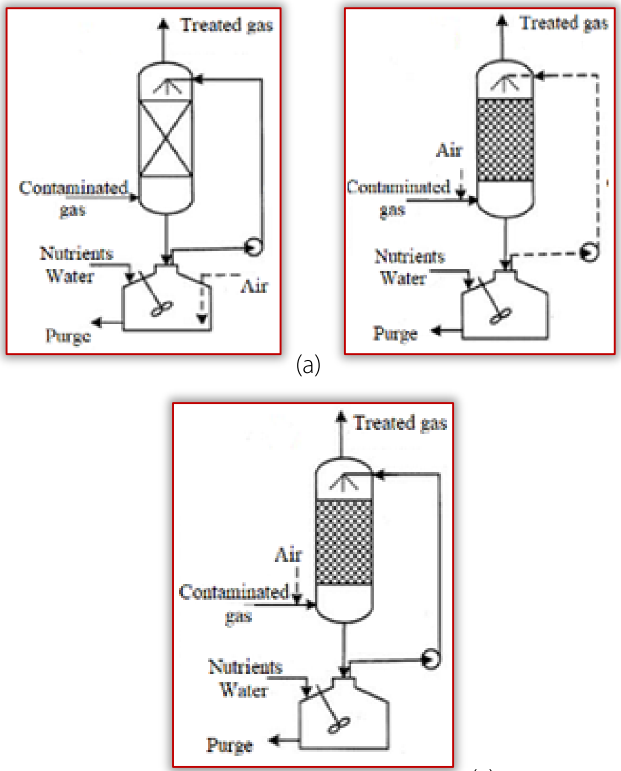

Figure 3 - Biofiltration Process Schematic

A) Bioscrubber. B) Biofilter. C) Biotrickling Filter

In a bioscrubber, pollutants are absorbed into liquid flowing counter-currently through an absorption column, similar to a water scrubber. The liquid is then sent to a bioreactor for microbes to degrade the contaminants.

A biofilter consists of a packed bed of organic material that stimulates biofilm growth through which humidified biogas is pumped. Contaminants in the biogas contact absorb and adsorb into the biofilm and interact with the microbes.

Biofiltration systems are effective for treating low and high H_2S concentrations from 50-100 ppm to 2000-4000 ppm, resulting in a H_2S removal of 89-99.9% at a rate of 20-125 g H_2S / m3 / h. Most bacteria grow and function optimally at a temperature of about 35 ° C and a neutral pH.

— Adsorption

Adsorption is the adhesion of compounds onto a solid surface. When biogas is flushed through an adsorbent bed, contaminant molecules will bind to the adsorbent's surface, removing the contaminants from the gas stream. Effective adsorbents are generally highly porous with high surface area which greatly increases their removal capacity.

Pressure swing adsorption (PSA) is a method for the separation of carbon dioxide from methane by adsorption/desorption of carbon dioxide on zeolites or activated carbon at alternating pressure levels. Commonly used adsorbents are zeolite, carbon molecular sieve, silicagel and activated carbon, due to their low cost, large specific area and pore volume and excellent thermal stability (*Siriwardane RV. Et al., 2003*). These adsorbents are designed to have a specific pore size thus enabling selective adsorption of molecules that are smaller than the designed pore size. Figure 4 shows a four-vessel swing adsorption adsorption system using carbon molecular sieves that circulate between absorption and regeneration *(Zhao Q. ei al.. 2010).*

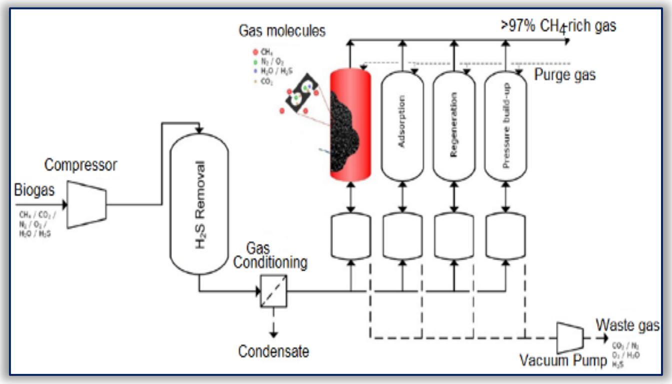

Figure 4 - Pressure Swing Adsorption Process Diagram

The adsorbent must be replaced once it is filled or can be regenerated a limited number of times. This contributes to operational cost.

— Pressurized Water Scrubbing

Purification of biogas by pressure water is one of the most widely used biogas treatment methods. Pollutant compounds can be physically adsorbed (or dissolved) in a liquid solution.

A schematic diagram of this method is shown in figure 5. To enhance the absorption of CO_2 and H_2S, biogas is usually compressed to 900–1200k Pa and a high surface area packing media is used.Inside the scrubber,biogas flows counter-currently to water that is sprayed from the top of scrubber and the absorption primarily occurs on the surface of the packing media. The raw biogas is introduced at the bottom of the column and flows upward, while fresh water is introduced at the top of the column, flowing downward over a packed bed. The packed bed (typically a high-surface-area plastic media) allows for efficient contact between the water and gas phases in a countercurrent absorption regime.

It is important that the H_2S be removed prior to the removal of the CO_2. as H_2S is highly corrosive and would result in decreased life and higher maintenance of the subsequent compressors required in the CO_2-removal step. Cleaned biogas can contain > 96% CH_4 after drying (*Liangcheng Y. et al., 2014*).

The disadvantage of water scrubbing is that it is less efficient than other processes, both in terms of CH_4 loss and energy. However, some of the energy inefficiency of the process may be offset by the use of a single-pass water scrubbing system, since other processes require a regeneration stage. Water scrubbing is the most applicable CO_2 scrubbing process for use in an agricultural setting because of its simplicity, low cost and low toxicity.

Another advantage of water scrubbing over some other processes is that water is fairly easy to dispose of whereas the chemicals used in some of the other processes may require special handling and disposal when spent.

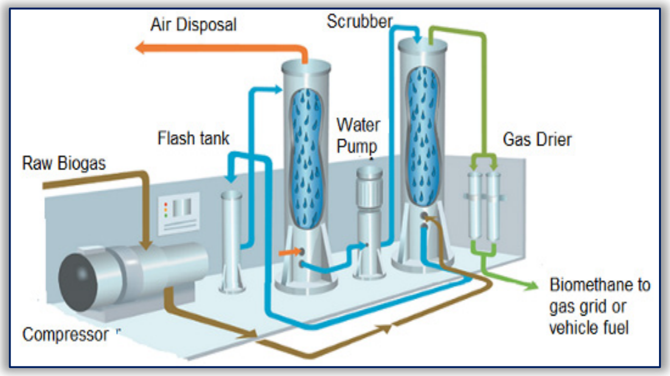

Figure 5 - The process of purifying biogas in a pressurized water system

— Refrigeration/Chilling

Refrigeration, or gas cooling provides a simple means for removing moisture from biogas. When the gas is cooled (typically to between -18 – 2 °C), water vapor condenses on the cooling coils and can be captured in a trap. Some ammonia will also be removed given the high solubility of ammonia in water. Insignificant trace amounts of other compounds may also be absorbed into the water. At lower temperatures of < -73 °C. VOCs will condense and can be removed too. At -70 °C. 99% removal of siloxane can be achieved as well, but it is costly to operate at such low temperatures.

H_2S should be removed prior to refrigeration to significantly lengthen the life of the refrigeration unit.

Raw biogas contains a variety of compounds aside from methane. These include hydrogen sulfide (H2S), oxygen (O2), nitrogen (N2), volatile organic compounds (VOCs), siloxanes and moisture (H2O). To remove these contaminants, adsorption, water scrubbing, biofiltration and/or refrigeration processes are employed *(Matthew D. et al.. 2014*).

Tabel 2. Contaminants removed by different biogas cleaning technologies

Biogas Cleaning Process	H_2S	O_2	N_2	VOCs	NH_3	Siloxanes	H_2O
Adsorption	**	/	-	**	*	**	**
Water Scrubbing	**	--	--	**	**	**	--
Biofiltration	**	--	--	**	/	/	--
Refrigeration	/	-	-	/	**	*	**

Legend: ** High removal (intended) * High removal (pre-removal by other cleaning technology preferred) / Partial removal - Does not remove -- Contaminant added R Must be pretreated

Next, a comparison is made between three methods of eliminating undesirable compounds from the biogas composition. Each of these technologies is able to treat different contaminants in different degrees (Table 2).

CONCLUSION

Biogas is a product of anaerobic ferment of organic products. Among the fuels from vegetal biomass, biogas has a great importance and can successfully replace fossil fuels for obtaining electricity and heat; the use of biogas exists for a few years also in the field of transport. Biogas formed in the methane fermentation process contains about 50÷60% of methane. Other ingredients such as carbon dioxide, hydrogen sulfide, water, water vapour and small amounts of nitrogen and oxygen are compounds that lower the energy value of biogas.

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Note

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