
Biogas Calorific Value Increasing Processes Using Different Techniques: A Review

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Abstract-The use of fossil fuel is increasing day by day and is going to deplete soon. Biogas is a clean environment friendly fuel. Biogas produced from anaerobic digestion of organic waste cannot be used directly as a vehicle fuel. The gases produced from anaerobic digestion are CH_4 and trace components like CO_2 , H_2O , H_2S , Siloxanes, Hydrocarbons, NH_3 , O_2 , CO and N_2 . To use biogas as fuel its CV should be nearly equal to CV of natural gas. Hence CV of biogas can be improved by removing CO_2 and trace components from biogas. These gases are not completely combustible and will harm engine parts. For transforming biogas to bioCNG two steps are performed:

(1) Cleaning process to remove trace components and

(2) Upgrading process to increase CV of biogas.

This paper reviews the attempt made to increase CV of a biogas by different methods for cleaning and upgrading.

Key words: fossil fuel, biogas, Calorific Value.

Nomenclature

CV-Calorific value

VSA-vacuum swing adsorption

PSA-pressure swing adsorption

I. Introduction

Anaerobic fermentation (AF) of organic waste produces a biogas with high concentration of methane (CH_4). The biogas formed in AF plants consists of 55–80vol% CH_4 , 20–45vol% CO_2 , 0–1.0vol% H_2S , 0–0.05vol% NH_3 and it is saturated with water [1]. Methane is the component chiefly responsible for a typical calorific value of 21–24 MJ/m³ or around 6kWh/m³. Biogas is often used for cooking, heating, lighting or electricity generation. Larger plants can feed biogas into gas supply networks. The activities of at least three bacterial communities are required by the biochemical chain which releases methane. Firstly, during hydrolysis, extracellular enzymes degrade complex carbohydrates, proteins and lipids into their constituent units. Next is acidogenesis (or fermentation) where hydrolysis products are converted to acetic acid, hydrogen and carbon dioxide. The facultative bacteria mediating these reactions exhaust residual oxygen in the digester, thus producing suitable conditions for the final step: methanogenesis, where obligate anaerobic bacteria control methane production from acidogenesis products. Anaerobic digesters are typically designed to operate in the mesophilic (20–40 °C) or thermophilic (above 40 °C) temperature zones. Sludge produced from the anaerobic digestion of liquid biomass is often used as a fertiliser [4]. The main impurities are CO_2 which lowers the calorific value of the gas and hydrogen sulphide (H_2S) which could cause several problem on the engine parts and on human health, in fact on the engine parts it causes corrosion (compressors, gas storage tank and engines), while it is toxic after its inhalation. Although CO_2 is a major problem in the biogas as its removal is useful to adjust the calorific value and the relative density according to the specifications of the Wobbe index [5, 6]. The unwanted CO_2 will reduce the quality of biogas and contribute to negative effect on biogas compression. After removing CO_2 , biogas can be used as renewable and low carbon fuel substituting natural gas for electricity generation and natural gas vehicle transportation. Methods for biogas upgrading are mainly focused on the removal of CO_2 with a little CH_4 loss [2]. After purification, the final product is referred to as

„bio methane“, typically containing 95-97% CH₄ and 1-3% CO₂. Bio methane can be used as an alternative for natural gas [7]. Biogas can be used for heat and steam production, electricity production and/or co-generation, vehicles fuelling, chemicals production and injection into the natural gas grid. However, using biogas as vehicle fuel or injecting it into the natural gas grid is applications that are gaining interest at international level. In both the last cases, an appropriate upgrading of the biogas i.e. removal of CO₂ and trace contaminants - is required. The output gas from the upgrading process is generally called bio methane and it is characterized by an increased content of methane with respect to the entering biogas [3].

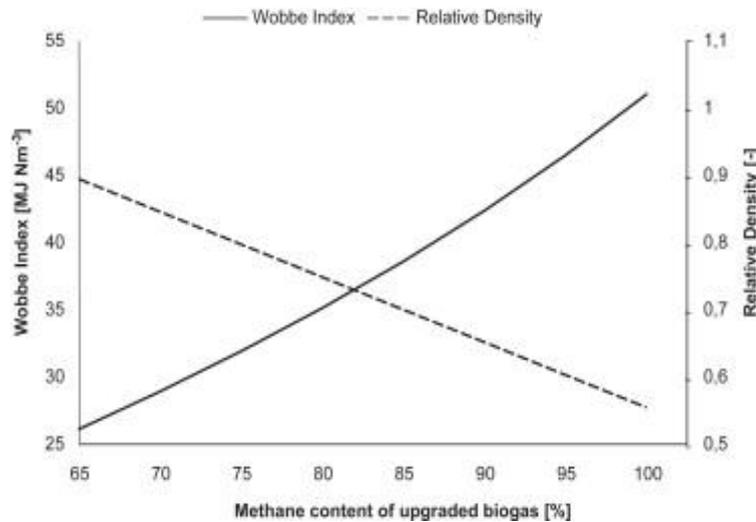


Fig. 1: Wobbe index and relative density as function of methane content of the upgraded gas [6].

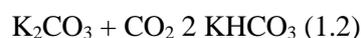
II. CO₂ removing

A. Chemical Absorption Process

Three agents NaOH, KOH and Ca(OH)₂ can be used in chemical upgrading of biogas [18]. The absorption process is based on using aqueous solutions of potassium hydroxide, with the final aim of producing potassium carbonate. The absorption reaction between KOH and the CO₂ produces an aqueous solution of K₂CO₃:



In this reaction, excess KOH leads to an increased production of potassium carbonate, while excess CO₂ leads to undesired chemical reaction as follows:



Potassium carbonate is a product which has many applications in the chemical industry if adequate quality is available (e.g., crystal industry, special glass production, potassium salts, inks and pigments, detergents, food industry, waste gas treatment). It can be sold as a pulverized solid, or in aqueous solution. The volumetric concentration of CH₄ significantly increases between 85-97%, similar to conventional natural gas quality [8]. This process may have higher energetic penalties since the CO₂ removal in biogas is a bulk removal process. The CH₄ purity in the range 97-98% is obtaining [19].

B. Physical absorption process

This is one of the easiest and cheapest method involves the use of pressurized water as an absorbent. The raw biogas is compressed and fed into a packed bed column from bottom and the pressurized water is sprayed from the top. The absorption process is, thus a counter-current one. This dissolves CO₂ as well as H₂S in water, which are collected at the bottom of the tower. The water could be recycled to the first scrubbing tower [18]. This is the simplest method for upgrading biogas. A continuous counter-current type scrubber with gas flow rate of 1.8 m³/h at 0.48 bar pressure and water inflow rate of 0.465 m³/h. It continuously reduced CO₂

from 30% at inlet to 2% at outlet by volume [18]. In this technique, H₂S is removed with CO₂. Also the purified CH₄ stream (with purity up to 98%) should be dried after leaving the scrubber [19].

C. Adsorption.

PSA and VSA are technologies that uses a column filled with a molecular sieves to separate some gas species from a mixture of gases under pressure [9,10]. To separate CO₂,

Activated carbon, silicagel, alumina or zeolites are typically used. The molecules are adsorbed in a reversible way in the cavities of the molecular sieve, so it is possible to create a cyclic batch process where the adsorber can be regenerated. Adsorption is performed on a relatively high pressure (800 kPa) while desorption is performed at lower pressure [11]. Usually three or four vessels are used, each working on a different stadium: adsorption, depressurization, desorption and pressurization [12]. Before the PSA or VSA unit, H₂S must be removed in order to prevent poisoning of the molecular sieve. In addition, the PSA process requires dry gas; so it is necessary to dry raw biogas before the upgrading process. PSA and VSA are similar systems, with the only difference that VSA requires a supplementary vacuum pump in this case the differential pressure is situated at lower absolute pressure [13].

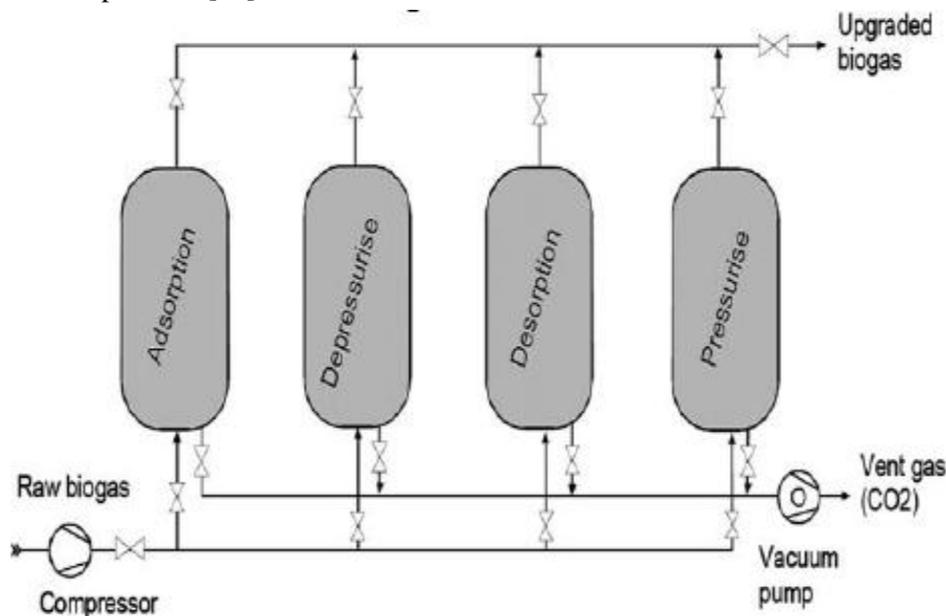


Fig. 2: Set-up of (vacuum) pressure swing adsorption [6].

The efficiency of this process is up to 98% [18]. One of the advantages of the PSA process is that it can be adapted to biogas upgrading in any part of the world since it does not depend on the availability of cold or hot sources [19].

D. Membrane separation

The use of membranes for gas cleaning is a well-established technology in chemical industries. The membrane is a porous material that let some gases permeate through its structure. The most commonly employed materials are hollow fibres made of different polymers [19].

1) Gas-gas separation

Gas is pressurized (2000 to 3600 kPa) and cleaned to remove hydrocarbons, H₂S and oil vapour. Acetate-cellulose membranes separate small polar molecules as CO₂, H₂S and moisture. With this technique, is possible to purify to maximum 92% CH₄ in one step. With more steps (two or three), a gas with even more than 96% CH₄ is achieved. The off-gas still contains 10-25% of CH₄, so has to be flared or used in a steam boiler [14,15]. Besides operation at high pressure, a pilot study has been carried out at low pressure (800 kPa) membrane separation system. Trace components need to be removed before the membrane-unit i.e. by an

active carbon filter. A 10% reduction by costs per m³ natural gas can be achieved, compared to high pressure membrane separation techniques [16].

2) Gas-liquid separation

Gas-liquid absorption membranes have been developed recently and they consist in a micro porous hydrophobic membrane that separates the gaseous from the liquid phase. The gas stream molecules which are able to diffuse through the membrane will be absorbed on the other side by the liquid. This process involves gas and liquid flowing in counter current. The gas is pressurized, so liquid is prevented to flow to the gas side. This process operate at atmospheric pressure (100 kPa), with advantages on the point of view of construction and operating cost. The removal of CO₂ is carried out with an amine solution and biogas with more than 96% CH₄ can be obtained in one step. Furthermore the amine solution can be regenerated by heating. During this process, a pure CO₂ flow is released and can be sold for industrial applications [14].

E. Cryogenic separation

It is possible to produce bio-methane by cooling and compressing the biogas, since different impurities liquefy at different temperature and pressure conditions. The raw gas is compressed in multiple stages, up to 8000 kPa. To prevent freezing during the cooling steps, the gas is dried before. After the compression, the biogas is cooled until -45 °C. The condensed CO₂ is removed and treated to recover the CH₄. The biogas is cooled further to -55 °C; afterward is expanded to 800-1000 kPa reaching the temperature of -110 °C. In this condition there is solid CO₂ and a gaseous phase with more than 97% CH₄, which is collected and heated before leaving the process [6, 12, and 18].

In the Netherlands, a cryogenic system to upgrade biogas to natural gas quality was implemented [15] in four steps. The incoming biogas is first compressed to 1000 kPa and cooled to -25 °C. Moisture, H₂S, SO₂, halogens, siloxanes and other trace components are removed from the biogas. From there, the biogas is further cooled till -55 °C.

Liquefied CO₂ is removed from the gas mixture so the calorific value is increased. The remaining gas stream is further cooled till -85 °C where CO₂ convert in to solid form. Three vessels are used: one is for upgrading the biogas, set at -85 °C, one is kept at intermediate temperatures (-85 °C to -60 °C) and one vessel is set at -60 °C to liquefy the CO₂. The gaseous phase is depressurized and can be injected after removing odour into the natural gas grid. The results show high efficiency and low methane losses [15].

F. Biological methane enrichment

In this experiment, different methanogens using only CO₂ as a carbon source and H₂ as an energy source were examined. The selection between mesophilic and thermophilic operation temperatures is typically based on whether the completion of reaction or the rate of reaction is of primary concern. Thermophilic methanogens exhibit rapid methanogenesis, while mesophilic bacteria give more complete conversion of the available CO₂. The organism works optimally at temperatures of 65-70 °C and has a specific requirement for H₂S, so both unwanted components are removed. A synthetic biogas of 50-60% CH₄, 30-40% CO₂ and 1-2% H₂S was mixed with H₂ to a final mole fraction of H₂: CO₂ equalling 0.79:0.21. The gas mixture was fed to the hollow fibers packed with organisms. This biological system can effectively remove CO₂ and H₂S, while approximately double the original CH₄ mass. Alternative physicochemical treatment methods only remove the contaminating gas components, without changing CH₄ mass. The purified biogas contains about 96% CH₄ and 4% CO₂, while H₂ and H₂S were not detected.

III. Removal of h₂S

A. Removal of H₂S during digestion

H₂S can be treated directly in the digester vessel and the most used techniques to interfere with its formation are adding air/oxygen or iron chloride [6, 12].

1) Air/oxygen dosing to the biogas system

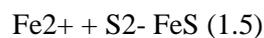
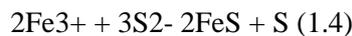
This technique is based on the biological aerobic oxidation of H₂S to elemental sulfur by a group of specialized microorganisms (autotrophic Thiobacillus). The following reaction occurs in the biogas:



Elemental sulphur and sulfate is formed, which cause corrosion in solutions. A small amount (2-6%) of O₂ needed for the reaction to occur, is introduced in the biogas system by an air pump. A reduction of H₂S concentrations down to 20-100100 cm³ /m³ and a removal efficiency of 80- 99% can be achieved [9, 14, 18]. Safety measures have to be taken to avoid overdosing of air in the biogas. Biogas in air (6-12%) is an explosive mixture. Care must be taken so that anaerobic conditions remain present in order to keep the digestion process from being inhibited [14, 18].

2) Addition of iron chloride into the digester

Iron chloride reacts with the H₂S present in the biogas to form FeS as solid precipitated particles. These are the chemical reactions:



The presence of H₂S in the biogas is avoided due to precipitation of FeS and therefore this method can achieve a reduction of H₂S concentration in the biogas down to 100 cm³/m³ at standard condition [17].

B. Removal of H₂S after digestion

1) Adsorption using iron oxide or hydroxide

Hydrogen sulfide reacts easily with iron oxide, iron hydroxide and zinc oxide and forms iron sulfide or zinc sulphide respectively. This process is often referred to as “iron sponge” because rust-covered steel wool may be used to form the reaction bed. Iron oxide and iron hydroxide react with H₂S in the biogas according to following reactions



The iron oxide can be regenerated with oxygen according to the following reaction:



This reaction is exothermic and therefore a large quantity of heat is released during regeneration. This may lead to self-ignition of the wood chips, if air flow and temperature are not carefully controlled. Typically two reaction beds are installed. One bed is regenerative while the other bed removes H₂S from the biogas [9]. The formed elementary sulfur remains on the surface and blocks the active iron oxide or hydroxide, restricting the number of cycles that can be performed [14].

2) Adsorption on activated carbon

H₂S can also be removed by using activated carbon often dosed with KI or sulfuric acid (H₂SO₄) to increase the reaction rate. In biological filters the H₂S is catalytically converted to elemental sulfur and water:



The biogas must have a certain amount of air before entering the carbon bed, therefore 4-6% air is added. The formed elementary sulfur is adsorbed by the activated carbon. Best efficiency is obtained at pressures of 700-800 kPa and temperatures of 50-70 °C. This temperature is easily achieved through heat generation during compression. If a continuous process is required the system can consist of two vessels [6, 12, and 14]: one vessel for adsorption and the other for regeneration. Regeneration can be performed with hot nitrogen (inert gas) or steam. The sulfur is vaporized and, after cooling, liquefied at approximately 130 °C. Typically, the activated carbon is replaced rather than regenerated [6, 7, and 12].

IV. Removal of water

A. Physical drying methods (condensation)

The simplest way of removing excess water vapor is through refrigeration. The minimum dew point reachable is 0.5 °C at atmospheric pressure due to freezing problems on the surface of the heat exchanger. To achieve

lower dew points the gas has to be compressed before cooling and then later expanded to the desired pressure [6,12]. The use of any kind of anti-freezing compound is not recommended. The chemical treatment itself is very complicated and adding other compounds would be too expensive and would involve more complexity in the system. In fact adding any chemicals in the gas requires a control injection system to ensure the correct composition and an absorption tower to re-separate the glycol from the biogas. Techniques using physical separation of condensed water include:

1. Demisters in which liquid particles are removed by wired mesh (micro-pores, 0.5-2 nm);
2. Cyclone separators in which water droplets are separated using centrifugal forces;
3. Moisture traps in which the condensation takes place by expansion. As consequence the temperature decreases and the water condenses;
4. Water taps in the biogas pipe from which condensed water can be removed [6,17].

B. Chemical drying methods

These techniques are usually applied at elevated pressures. The most common technique is adsorption by using alumina or zeolites/molecular sieves. Methods based on gas drying include:

1. Adsorption of water vapor on silica, alumina or equal chemical components that can bind water molecules (adsorption dryer). Two chemical columns are often used together in order to adsorb the water and to regenerate the adsorber;
2. Absorption of water in triethylene glycol. Regeneration of saturated glycol solvent is done in a specific unit operating at a temperature of 200 °C;
3. Absorption of water with hygroscopic salts. The salt dissolves as it absorbs water from the biogas. The salt is not regenerated and new salt granules have to be added to replace the dissolved salt [6,12].

V. Conclusion

Biogas produced from animal waste can be a valuable energy resource. By combusting waste methane (biogas), a powerful greenhouse gas is eliminated that would otherwise be released. One of the most interesting utilization of biomethane is as vehicle fuel. The substitution of conventional fossil fuels with biomethane can provide up to 80% less of greenhouse gases emissions. The cost of biomethane without incentives is generally not competitive compared with conventional natural gas. For increasing CV of biogas CO₂ must be removed from it and thus obtaining biomethane. Biomethane, due to its composition (97 to 99 % of CH₄), has all the good qualities that natural gas has: it is one of the most environmental friendly combustion fuel, it is easy to transport and it can be used as fuel for all sorts of vehicle.

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