BIOGAS PURIFICATION BY SORPTION TECHNIQUES

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Abstract
A number of research centres are interested in uncontrolled release of methane into the atmosphere. This results from the concern for the atmosphere and hope of obtaining power and chemical resources. The production of biomethane from biogas offers the possibility of acquiring chemical resources, fuel for combustion engines, gas turbines and fuel cells. However, each biomethane application necessitates its specific treatment. The study shows methods of biogas treatment which ensure its purity so that it could be used as engine fuel, network gas, CNG and in fuel cells. It also demonstrates sorption techniques of biogas treatment described in the literature and results of the author's research.

Streszczenie
Niekontrolowanym uwalnianiem się metanu do atmosfery interesuje się wiele jednostek badawczych. Spowodowane to jest troską o ochronę atmosfery jak również nadzieją na pozyskanie surowca energetycznego i chemicznego. Otrzymanie biometanu z biogazów stwarza nadzieję na pozyskanie surowca chemicznego, paliwa do silników spalinowych, turbin gazowych i ogniw paliwowych. Jednak każdy rodzaj użycia biometanu wymaga jego odpowiedniego oczyszczenia. W publikacji przedstawiono sposoby oczyszczania biogazów do takiej czystości, żeby nadawały się do wykorzystania jako paliwo silnikowe, gaz sieciowy, CNG oraz do ogniw paliwowych. Zaprezentowano metody sorpcyjne oczyszczania biogazów opisane w literaturze oraz wyniki badań własnych.

Keywords: **Biogas; Sorption; Purification.**

1. INTRODUCTION

Biomass is more and more frequently used as a raw material to produce biomethane and synthetic liquid fuel. The increasing energy problems in Poland and the promotion of electrical power production from renewable sources attach a special significance to biogas. The potential for agricultural biogas production in Poland equals the amount of biogas imported currently from Russia. Meeting Poland's obligations stated in the National Plan of Waste Management also necessitates the implementation of digestion techniques of selected organic waste. However, the biogas needs to be treated prior to its use. Basic impurities present in biogas include: carbon dioxide, hydrogen sulfide, nitrogen, oxygen, ammonia, chlorinated organic matter, silanes, siloxanes [29, 30], volatile phosphorus substances and other volatile trace compounds. The techniques of carbon dioxide and hydrogen sulfide removal from biogas are very important for many reasons. After carbon dioxide, hydrogen sulfide and moisture are removed from biogas, it can be compressed and used as CNG, especially during the operation of agricultural and landfill biogas plants outside the peak time of power consumption. Further removal of the impurities makes the biogas suitable for gas piping. The removal of trace impurities, notably phosphorus compounds, enables biogas to be used in the production of hydrogen for fuel cells [25-28, 37].

The real significance of biogas is proved by the fact that currently there are about 5000 agricultural biogas plants in Germany and by 2020 the German government is planning to replace 6% of natural gas with biogas produced through digestion [1]. About several hundred agricultural biogas plants operate in Austria

Table 1.
Chemical composition of biogas

Biogas	CH_4 %	CO_2 %	O_2 %	N_2 %	H_2S ppm	Benzene mg/m^3	Toluene mg/m^3
Landfill [2, 3]	59.4 – 67.9	29.9 – 38.6	1-5	10 - 25	15.1 – 427.5	21.7 – 35.6	83.3 – 171.6
Landfill [4]	37- 62	24.9	<1	-	-	<0.1 – 7	10 – 287
Landfill [5]	55.6	37.14	0.99	-	-	3.0	55.7
Landfill [6]	44	40.1	2.6	13.2	250	-	65.9
Wastewater treatment plant [7]	57.8	38.6	0	3.7	62.9	-	-
Wastewater treatment plant [8]	62.6	37.4	0.5	3.4	<8000	0.1 – 5.0	0.1 – 5.0
Wastewater treatment plant [9]	58	33.9	0	8.1	24.1	-	-
Agricultural biogas plant 10,19]	45 -75	25 -55	0.01 –2.0	0.01 – 5.0	10 - 30000	< 300	<300

and several dozen in the Czech Republic. Millions are located in India and China. So far, despite repeated attempts, not a single agricultural biogas plant has been operating in Poland. Perhaps a new agricultural biogas plant which is currently being built in Studzionka will start the trend for biogas technology in the country.

2. CHEMICAL COMPOSITION OF BIOGAS

The biogas produced in municipal wastewater treatment plants differs greatly in the chemical composition from landfill and agricultural gases [Table 1].

Generally, the composition of agricultural biogas is more homogenous and has less impurities. The landfill biogas contains more nitrogen and oxygen compared to other biogas types. The quantity and quality of volatile trace chlorinated organic compounds are also higher. The biogas in a municipal wastewater treatment plant contains less organic matter characterized by higher boiling point compared to the agricultural biogas [20-24].

3. BIOGAS TREATMENT

The first stage of biogas preparation for use involves sulfur removal. It is carried out because most processes of carbon dioxide separation act antagonistically towards hydrogen sulfide; the smaller concentration of hydrogen sulfide, the better effects of carbon dioxide removal from biogas. Hydrogen sulfide removal can be performed in the same process line used for carbon dioxide, but it should be done first. Fuel cells, due to the high quality of their components, require the highest standards as far as biogas quality is concerned [Fig. 1].

4. HYDROGEN SULFIDE REMOVAL

The removal of hydrogen sulfide from biogas posed a serious problem in the past [36]. Like the cost of biogas storage, the cost of sulfur removal reached 1/3 of an entire biogas installation. Those costs fell enormously following the introduction of new technologies and cheap materials.

4.1. Adsorption techniques

The removal of impurities by adsorption is usually performed, using activated carbon, carbon molecular sieves and molecular sieves. The Polish activated carbon used and our own apparatus [Fig. 2] produced biogas suitable for combustion engines. Tests carried out in the Institute of Combustion Engines at the Silesian University of Technology proved the effectiveness of the treatment [Fig. 3]. According to the specialists from the Fraunhofer Institute in Dresden, the biogas thus treated is suitable for direct use in SOFCs.

One of the ways that could be used to purify biogas from hydrogen sulfide is passing it through a bed filled with iron oxides. The reaction of hydrogen sul-

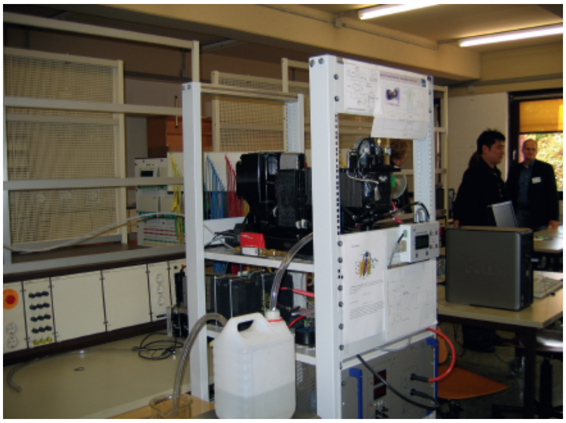

Figure 1.
Use of biogas in fuel cells in FH. Braunschweig/Wolfenbuttel

Figure 2.
PSA installation used to investigate the treatment of biogas in the Institute of Water and Wastewater Engineering at the Silesian University of Technology

Figure 3.
Investigation into the suitability of biogas for combustion engines in the Institute of Combustion Engines at the Silesian University of Technology

fide with iron oxides forms insoluble sulfides that are deposited on the bed.

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3\downarrow + 3H_2O$$

Figure 4.
Installation used to investigate the effectiveness of hydrogen sulfide removal from biogas on different sorbents developed in the Institute of Water and Wastewater Engineering at the Silesian University of Technology

After the entire bed has been covered with iron sulfides, it is regenerated producing a lot of heat. One of the popular techniques involves the deposition of hydrated iron oxides on the surface of wooden shavings. The bed is capable of sorbing considerable amounts of hydrogen sulfide. Hydrated iron oxides also sorb other sulfur compounds, such as mercaptans. Oxides of other metals, like manganese, cobalt, nickel, lead, copper and zinc behave similarly [Fig. 4].

4.2. Absorption techniques

One of the classical techniques used in sulfur removal from biogas is so-called "wet technique" in which the following reaction takes place in a solution of sodium hydroxide:

$$2\,NaOH + H_2S \rightarrow Na_2S + 2H_2O$$

Sodium sulfide reacts with sodium carbonate present in the solution, forming sodium hydrosulfide as described by the reaction:

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3$$

The hydrated iron oxide introduced into the solution reacts as follows:

$Fe_2O_3 \cdot 3H_2O + 3NaHS + 3NaHCO_3 \rightarrow Fe_2S_3 \cdot 3H_2O + 3Na_2CO_3 + 3H_2O$

This technique has certain disadvantages. Firstly, the resulting sodium sulfide and hydrosulfide can not be regenerated, and thus must be regarded as waste that needs to be utilized. Secondly, the process necessitates the use of large amounts of water at low hydrogen sulfide concentrations. Therefore, iron(III) chloride added directly to the digested matter is recommended in small biogas plants where the amounts of hydrogen sulfide in the biogas produced are relatively small.

$3H_2S + 2FeCl_3 \rightarrow 6HCl + Fe_2S_3\downarrow$

Another technique of sulfur removal from biogas involves oxidizing hydrogen sulfide with atmospheric oxygen. A small amount of air (2-6% volume of produced biogas) is introduced directly into a bioreactor filled with digested matter. It is done by pumps that supply suitable amounts of air [Fig. 5, 6]. Originally, normal aquarium pumps were used to carry out the task. The oxidization process results in elemental sulfur. The reaction looks as follows:

$2H_2S + O2 \rightarrow 2S + 2H_2O$

The precipitated elemental sulfur is disposed in a field along with used digested matter. This technique can be recommended because it is cheap, does not require additional chemicals and is extremely effective. 95% of hydrogen sulfide concentration can be reduced, depending on the temperature, reaction time and the place air is supplied into the bioreactor.

The removal of hydrogen sulfide can also be carried out by hydrogen peroxide solution, and the following reaction of hydrogen sulfide oxidization to sulfates takes place:

$H_2S + 4H_2O2 \rightarrow H_2SO4 + 4H_2O$

Since the 1960s, chelate complexes of polyvalent metals have been protected by patents as catalysts of hydrogen sulfide removal from biogas. In practice, the only processes that became significant were those which employed iron chelate complexes containing organic NTA (nitrilotriacetic) and EDTA (ethylenediaminetetraacetic) acids as ligands. The essence of hydrogen sulfide removal from biogas is described by the following reactions:

$2\,Fe(III)L + H_2S \rightarrow 2Fe(II)L + S + 2H^+$

$2Fe(II)L + H_2O + 1/2O_2 \rightarrow 2Fe(III)L + OH^-$

$H_2S + 1/2\,O_2 \rightarrow S + H_2O$

L-organic ligand

Fe(III)L i Fe(II)L- iron chelates

One of the techniques of hydrogen removal from biogas involves passing it through a solution of amino alcohols. The research into the effectiveness of landfill biogas treatment is shown in Fig. 7.

4.3. Biological techniques

Another way of removing hydrogen sulfide from biogas is of biological nature, using bacteria and algae [Fig. 8, 9] [11].

Algae are uni- and multicellular organisms of vast difference in size – microscopic or several centimeters (thalli). Algae used to remove hydrogen sulfide from biogas are grown in a washer that works as an absorber which has a specific construction. The algae must have favourable conditions for their fast growth. A properly prepared installation can remove 100% of hydrogen sulfide from biogas [Fig. 10].

5. REMOVAL OF CARBON DIOXIDE

The removal of carbon dioxide is carried out primarily for energy and technological reasons. Sorption techniques are found to be the most popular in this field [13, 14, 16].

5.1 Adsorption techniques

Common techniques used to separate carbon dioxide from biogas include those based on adsorption on the surface of a solid [15, 17]. They involve the separation of methane from impurities at the phase boundary.

The techniques include:

- PSA – Pressure Swing Adsorption,
- TSA – Temperature Swing Adsorption,
- VSA – Vacuum Swing Adsorption,
- ASU – Air Separation Units.

It is worth mentioning that the selection of a bed regeneration technology depends on the concentration of the main mixture component planned to be adsorbed.

Pressure Swing Adsorption is a process which involves separation of gases from a mixture under pressure taking into account the molecular characteristics and similarities of the material a given adsorbent is made of. Materials that meet the requirements include zeolites [35], carbon molecular sieves and activated carbon. The use of carbon molecular sieves is characterized by high effectiveness, low start-up and technological costs, as well as simplicity of operation [34].

Figure 5.
Aquarium pump supplying air to oxidize hydrogen sulfide in biogas

Figure 6.
Air pump used in a large agricultural biogas plant

Figure 7.
Research into biogas treatment, using a column filled with monoethanolamine. The tests were carried out at a municipal landfill site in Knurów, Poland

Figure 8.
Deposition of elemental sulfur in a bioreactor during removal of sulfur compounds from biogas

Figure 9.
Installation for biological removal of hydrogen sulfide in a biogas plant using bird droppings and corn silage in digestion process

Figure 10.
Installation used to remove hydrogen sulfide, using algae (Freising, branch of Technical University of Munich)

Table 2.
Comparison of physical properties of amine alcohols

Property	MEA	DEA	TEA	MDEA	DIPA	DGA
Molar mass	61.09	105.14	149.19	119.17	133.19	105.14
Specific gravity	1.0179	1.0919	1.1259	1.0418	0.9890	1.0550
Boiling point	171		360	247.2	248.7	221
Freezing point	10.5	28	21.2	-21	42	-9.5
Water solubility %	100	96.4	100	100	87	100
Heat of vaporiza-tion	355	288	230	223	184.5	219.1

Temperature Swing Adsorption deals with the difference in bed's absorption capacity against temperature. The lower the temperature, the greater absorption capacity of an adsorbent for a given component. When the adsorbent becomes fully saturated, the bed is regenerated. It involves increasing temperature which causes the component adsorbed on the bed to be released again. However, the flaws of this techniques hamper its global use.

Another technique of carbon dioxide separation from biogas is adsorption on an activated bed, followed by its regeneration which involves passing neutral gas through it. Each of those techniques has its advantages and disadvantages. In order to improve their effectiveness and reduce the disadvantages, their complementary combinations are used.

5.2. Absorption techniques

Cheap and effective techniques of impurity removal from biogas have been being looked for all the time. So far, the sorption techniques may be regarded as those having the above characteristics.

5.3. Carbon dioxide absorption, using amino alcohols

Carbon dioxide absorption involves passing a stream of biogas through a water solution of a substance in which carbon dioxide dissolves better and at the same time methane does not react with the absorbent [12]. The effectiveness of carbon dioxide depends greatly on biogas pressure. Separation of hydrogen sulfide and carbon dioxide in a solution of dimethyl ether and ethylene glycol is an example of such absorption.

Another method involves a chemical binding of carbon dioxide. Since the reaction is reversible, the adsorbent can be recovered again. The use of methanolamine to remove carbon dioxide provides an example of reversible absorption [18].

Carbon dioxide can be removed from biogas, using another absorption technique which involves an irreversible chemical reaction e.g. absorption of carbon dioxide in lime milk.

The amines used in carbon dioxide separation from biogas include:

– monoethanolamine – MEA,
– a mixture of glycol and monomethylamine,
– diethanolamine – DEA,
– triethanolamine – TEA,
– diglycolamine – DGA,
– diisopropanolamoine – DIPA,
– methyldiethanolamine – MDEA,
– amine mixtures.

Amines bind effectively not only carbon dioxide, but also hydrogen sulfide, the latter being bound permanently.

The general schematic of the reaction is as follows:

$$\mathbf{RNH_2 + CO_2 \rightarrow RNHCOO^- + H^+}$$

The resulting carbamate can be then decomposed by temperature.

The characteristics of selected amine alcohols are shown in Table 2.

Monoethanolamine is commonly used to remove carbon dioxide and hydrogen sulfide from biogas. However, its large amounts are lost during hydrogen sulfide removal. Acid gas absorption involves passing a mixture of gases through an amine stream in which acid gases are "caught up" by alkaline particles of the amine. This technique is applied at a normal temperature. If an amine solution is to be regenerated, it should be boiled for 5 min at 105°C. As a result, the bound particles of carbon dioxide are released and the solution reused. A mixture of glycol and monoethanolamine was used to remove carbon dioxide and dry it at the same time. The system is effective because of economical power consumption. The biogas can be dehydrated to 5% moisture.

Diethanolamine was used for many years to purify gas in refineries, primarily from carbonyl sulfide and carbon disulfide.

Triethanolamine was the first amine used to purify gases from carbon dioxide and sulfur substances on an industrial scale as early as the 1930s. As organic chemistry developed, it was replaced with monoethanolamine and diethanolamine.

Diglycolamine is a primary amine and thus the separation of gases from a mixture follows the procedure for MEA.

Other amine alcohols, such as diisopropanolamine (DIPA) and methyldiethanolamine (MDEA), are selective amines used to separate sulfur compounds mainly in the treatment of natural gas. If an effective removal of carbon dioxide is required, a mixture of the amines mentioned above is used.

5.4. Adsorption techniques in the solutions of inorganic bases

Organic compounds are not the only ones employed to remove carbon dioxide from biogas. In some cases sodium, potassium and calcium hydroxides are sufficient. Sometimes hydrogen carbonates are used. The process necessitates the formation of basic medium in the solution. The dissolved carbon dioxide reacts with water as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Carbon acid forms a hydrogen carbonate ion in the basic medium.

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$$

Carbon dioxide is removed from biogas in the form of hydrogen carbonates.

The process involves passing raw gas at a lowered temperature through a column containing potassium hydroxide which makes carbon dioxide present in the biogas react and form potassium hydrogen carbonate. The resulting sediment is then regenerated. An increase in temperature returns the recovered hydroxide into the purifying column. The technique produces biogas with an 80-85% methane concentration.

An application of arsenic trioxide to carbon dioxide removal is also an interesting suggestion. Its stoichiometric amounts in sodium hydroxide and potassium carbonate markedly increase the sorption and desorption coefficients of carbon dioxide. Such a solution does not only cause a considerable decrease in heat during regeneration, but also produces gas of much higher purity than that resulting from a normal hot carbon dioxide removal with potassium carbonate.

$$6CO_2 + 2K_3AsO_3 + 3H_2O \rightarrow 6KHCO3 + As_2O_3$$

The reaction is completely reversible.

5.5. Techniques for leaching carbon dioxide from biogas with water

The main advantages of this technique include the simplicity of operation, low operating costs and possibility for carrying out the process at low gas flow. Apart from carbon dioxide, water is capable of removing other impurities, such as hydrogen sulfide, ammonia, hydrogen phosphide, chlorinated hydrocarbons and others. Biogas is introduced at the bottom of the column while water sorbing the impurities is introduced at the top, sprinkling the column. Gases, except for methane, form a strong “complex” reacting with water which is broken down by decreasing pressure. In time, the columns overgrow which reduces their efficiency and therefore an occasional use of disinfectants is recommended. Various technological solutions are suggested. The differences lie in the use of scrubbers of different parameters of gas pressure, water flow or water purity [31-33].

6. RESUME

Purification and application of biogas requires full scale researches. Country like Poland posses huge biogas production possibilities however, it is not fully used. Depending on local conditions biogases could be applied in fuel cells, compressed natural gas, raw material for chemistry and for heating and electricity production. Development of purification methods for all biogases is required. Those methods need to be technologically and constructionally investigated and described.

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