Review of technology for cleaning biogas to natural gas quality

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Introduction
Biogas formed in the methane fermentation process contains about 50-60% of methane. Other ingredients such as carbon dioxide, hydrogen sulfide, water, water vapor and small amounts of nitrogen and oxygen are the ballast lowers heating value of biogas. The calorific value of raw biogas is much lower than natural gas or compressed natural gas used as motor fuel CNG.

Biogas most of fen is used for processing into electricity and/or heat. Purification of biogas for these applications is reduced mainly to remove hydrogen sulfide and water, which negatively affecting the functioning and viability of power equipment, causing them to corrode.

Due to the efficiency of energy conversion processes, preferred are processes involving the purification of biogas to natural gas quality and use it directly as an energy source - the fuel for combustion engines. Due to the expanded distribution gas grid in Poland, it becomes possible to transport the purified biogas and biomethane to be more localized service stations or to the industry. Currently in Poland we have 31 compressed natural gas stations, and there are technical possibilities to build many more of these stations, depending on the potential market of customers. Processes use of biomethane as a direct energy source in combustion engines and industrial processes is becoming increasingly important. They are carried out in these scope European projects such as: „Baltic Biogas Buses”, “Biogas Highway”, „Biogas Fuel Eureka”, in which Poland is one of the main contractors. It is believed that, the use of biogas as a fuel to power internal combustion engines driving electric generators is much less energy-efficient and adverse environmentally than direct the fuel supply of traction motors, because at every stage of energy conversion are entropic “losses”, regardless of the difficulties related to the connection Local power to power grids. Therefore, work is being done to ensure the effective purification of biogas to raw biomethane that is to receive of quality equivalent to natural gas quality. Due to the chemical composition of biogas, natural, raw biogas purification technologies rely primarily on the removal of carbon dioxide, hydrogen sulfide, and water siloxane. It is obvious that the chemical composition of biogas depends not only on methanation processes, but mainly on the type of raw materials and process conditions. Selection of the optimum material and process conditions is the subject of many ongoing research and development, in which one of the goals is to develop even more accurate „biogas calculators” that help determine not only the composition of raw materials and process parameters, but also economic efficiency. An example of this calculator could be extended calculator „Falköpping Calculator” developed by the project Biogas Max.

I. Technical standards for biogas injected to the natural gas grid

Biogas injected into the gas grid must fulfill the relevant quality requirements. Adaptation of biogas takes place through the installation procedure for standardizing treatment. The quality parameters that must be fulfill by natural gas in Poland have been defined in two standards:
• PN-C-04752:2002 – Natural gas. Gas quality in transmission grid
• PN-C-04753:2002 – Natural gas. The quality of gas delivered to customers from the distribution network.

Currently there are no unified, European technical standards, which regulate the conditions for injections biogas into the gas grid. The European Commission is currently working on developing standards determining the quality parameters for biomethane. Also in Poland, in the website of the Ministry of Economy is a draft regulation on the confirmation of data on quantities produced agricultural biogas injected into gas distribution grid. Article 3, paragraph 1 of the Regulation sets out the quality parameters of biogas for putting it into the distribution grid.

Similar Regulations are already in other European Union countries. Thus, in Germany the quality parameters for the biogas (biomethane) are based on those defined for natural gas. The legislator allows for injection into gas grid two types of biogas: Type „H”(High), a gas having a high calorific value and type „L” – (Low) – having a low heating value. Table 1 shows German quality requirements for biogas injected into gas grid.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wobbe index</td>
<td>MJ/nm³</td>
<td>46.1-56.5 dla gazu¹ H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37.8-46.8 dla gazu² L</td>
</tr>
<tr>
<td>Relative density</td>
<td></td>
<td>0.55-0.75</td>
</tr>
<tr>
<td>Dust</td>
<td></td>
<td>Technically free</td>
</tr>
<tr>
<td>Water dew point</td>
<td>°C</td>
<td>&lt;t¹</td>
</tr>
<tr>
<td>CO₂ Vol-%</td>
<td></td>
<td>&lt;6</td>
</tr>
<tr>
<td>O₂ Vol-%</td>
<td></td>
<td>&lt;3 (in dry distribution grids)</td>
</tr>
<tr>
<td>S</td>
<td>mg/nm³</td>
<td>&lt;30</td>
</tr>
</tbody>
</table>

¹ concern >97.5% methane
² concern>87.98.5% methane
¹ – earth temperature

2. Removal of water

One of the main stages of the production of biomethane from biogas is its drying. Relative moisture of raw biogas in digester is 100% which means that it is saturated with water vapour. Removal of water mainly requires biogas received during the wet fermentation and after treatment processes using water. The drying process usually takes place during the cooling and it is possible in all production lines. Some water vapor is isolated in the form of condensate accumulated in the dephlegmators. During the process of removal of water, along with water can also be remove other undesirable components of biogas, mainly water-soluble gases and aerosols.

3. Pressure Swing Adsorption - PSA

Pressure swing adsorption is one of the most frequent techniques of biomethane production. In this technology, carbon dioxide is removed from the biogas by adsorption onto activated carbon surface or on a zeolite molecular sieve at increased pressure. On activated carbon can also occur for the adsorption of hydrogen sulphide and water vapour, which could result deactivation of the bed, however, it is advisable to...
pre-treatment of the biogas from these compounds before giving it to the adsorption column. In order to maintain continuity of the process, the upgrading plant is usually equipped with four, six or nine columns working in parallel.

Adsorbent material, after exploited its adsorption capacity can be regenerated and using another again. Regeneration is conducted by heating the adsorbent, or by passing it through a stream of inert gas. However, the most frequently used method is heating gas to the boiling point of the adsorbent. In case when there is a probability of decomposition of substance, this method may also be accompanied by lowering the pressure in the system. During the regeneration pressure is reduced gradually. The gas that is desorbed can be returned into the tank with the raw biogas inside, because it contains yet certain recoverable quantities of methane, which was adsorbed together with carbon dioxide. Gas for the desorption process; if it no longer contains methane, it is released to the atmosphere.

In case of desorption with using of inert gas impurities pass from the adsorbent to gas and then they are burn.

Schematic operation of the PSA system is shown in Figure. 1.

4. Absorption

The absorption as a process of diffusion moving of gas particles into a liquid caused gradient difference in both phases is divided into three basic steps:

- Moving gas to the liquid surface
- Dissolution of gas in the boundary layer
- Move the gas absorbed into the liquid

Absorption processes conducted in scrubbers serve primarily to remove carbon dioxide, but with their participation is also removed hydrogen sulphide. This technology uses the phenomenon of increased solubility of CO in water than methane. Therefore, the liquid leaving the column contain a higher concentration of carbon dioxide, but gas contains more methane. In installations which upgrading raw biogas using absorption technology, the column in which this process proceed is filled by sealing material mainly made of plastic (to increase contact surface and ensure optimum contact time of gas and liquid phase).

5. Water scrubbers

Carbon dioxide as already mentioned has a higher solubility in water than methane. This gas will be dissolved to a higher extent than methane, especially at lower temperatures. In the scrubber column, carbon dioxide is dissolved in water, while methane concentration in the gas phase increases. Gas leaving the scrubber has a much higher concentration of methane. The water leaving the absorption column goes to the storage tank. The gas, which contains certain recoverable amount of methane is recycled back to the inlet of the raw gas. If the water should be recycled it is transferred to a desorption column filled with plastic material. Water is cooled down to a temperature in which will be possible to achieve a significant difference between the solubility of carbon dioxide and methane before it is recycled and returned to the absorption column.

Water scrubber is a technique, which is the most popular for upgrading biogas, and installations using this method are widely available on the market. Therefore, there are also many suppliers of this technology and the necessary equipment. For example, the company „Biorega AB” developed a water scrubber, which is designed for small installations with a small flow of raw gas. In the system proposed by Biorega, carbon dioxide is desorbed using a vacuum pump connected to the desorption column. In 2004, established a pilot plant with a capacity of 12 Nm³/h of raw biogas. The second demonstration plant with a capacity of 15 to 18 Nm³/h is currently under construction.

Alternative water scrubber was developed by Finnish company called Metener. In this process, biogas is at the same time upgrading and subjected to a pressure of about 150 bars in batch mode. The installation consists of two columns working in parallel in several stages (while one column is filled, the other is emptied). The raw biogas is compressed and injected into the column. The column is then filled with water using a high-pressure water pump. Carbon dioxide and sulphur compounds are dissolved in water. After the cleaning process at a pressure gas leaves the column, while water is regenerated in a special tank.

The Metner technology is most effective for the flow of biogas within the limits of 30÷100 Nm³/h.

Pic. 1. Installation for biomethane upgrading working in PSA technology, Helsingborg, Sweden

Pic. 2. Installation of biogas purification using water scrubber technology, Stockholm, Sweden. Sources: http://www.biogas.org.nz
Water scrubber with a capacity of 75÷800 m³/h has been installed in many plants in Sweden. One of them is the installation located in Stockholm presented in Picture 2.

6. Organic scrubbers
Organic scrubbers work in a similar manner as the water scrubber with the difference that carbon dioxide is absorbed in an organic solvent such as polyethylene glycol, which has greater than the water solubility of CO₂. A solution of polyethylene glycol is regenerated by heating and/or a gradual reduction of pressure. Together with carbon dioxide can be removed also hydrogen sulphide, water, oxygen and nitrogen. However, they are usually removed before the purification process. Organic scrubbers are much less using than the water scrubber. Installations where this technique has been used are mainly located in Germany (Schwandorf).

7. Chemical scrubber
Chemical scrubbers, in other words amine work on the principle of chemical reaction of carbon dioxide with monoethanolamine (MEA) and dimethylethanolamine (DMEA). Reaction is very selective, so that methane losses are insignificant (<0.1%). Some liquid is lost during the process due to evaporation and must be supplemented. The liquid in which carbon dioxide is chemically bound is regenerated by heating. If hydrogen sulphide is present in raw biogas, it will be absorbed in the solution contained in an amine scrubber, which means that you will need higher temperatures to regenerate this solution. Therefore, it is advisable to remove hydrogen sulphide before the absorption process in the scrubber amine. Examples of plants containing chemical scrubbers are located among others in Sweden (Goteborg), Germany (Jameln) or in Switzerland (Obermeilen).

Using a chemical scrubber is also possible to remove H₂S. The process of chemical absorption of hydrogen sulphide using iron compounds is a process which have a high removal efficiency of H₂S. However, they are usually removed before the purification process. Organic scrubbers are much less using than the water scrubber. Installations where this technique has been used are mainly located in Germany (Schwandorf).

8. Membrane techniques
Membrane techniques allow the separation of pollutants mainly carbon dioxide and hydrogen sulfide. This processes are still relatively new but growing up very rapidly. The advancement of research in the field of membrane technology and their results indicate the technical and economic justification for their use as one of the best methods for cleaning biogas from pollutants.

Membrane is a filter through which can pass without any obstacle, at least one of the components of the separated mixture, while others are stopped by it because of their size or affinity. It is associated with different permeability of the membrane. Transport through the membrane occurs thanks to an appropriate driving force, i.e. the chemical potential difference in both sites of the membrane. This potential may be cause, inter alia, by difference in pressure, concentration, temperature or electrical potential occurring on both sides of the membrane. It depends closely on the type of membrane (a porous or diffusion membrane). In membrane techniques transport of molecules is cause by chemical potential difference in both sites of membrane, and separation occurs due to the difference in the rate of transport of various substances, components and solutions or mixtures.

The membrane is the continuous phase with a symmetrical or asymmetrical build. In the asymmetric membrane is a fine-porous layer covering the macroporous substrate or microporous, relatively compact (un-porous) layer formed separately imposed on the porous substrate (the so-called. composite membranes). Membranes are most common in form of so-called capillary fiber. These fibers have a very small diameter, thus forcing the solution flow through the membrane requires the use of high pressure. High pressure are forcing a large mechanical strength of the membrane, it may be very easy to block the capillary channels. The result is a significant increase of the cost of running the process.

Dry membrane used for upgrading biogas is made of materials that are permeable to carbon dioxide, water and ammonia (Azan). Compounds such as hydrogen sulfide and oxygen permeate through the membrane only in a certain extent, while the permeability of nitrogen and methane is slight. The purification process runs with membranes often occurs in two stages. Before the gas pass through the membrane it passes first through a filter that retains water and oil droplets and aerosols, which would otherwise negatively affect the membrane performance. Membrane separation is one of the main methods of treatment of landfill gas. The first plant was built in the late 1970s in the U.S., and then in the Netherlands.

9. New developments in biogas upgrading technologies
9.1 Cryogenic separation
In addition to the continuous improvement of already existing biogas purification technology are developed also new technologies. One of them is a cryogenic purification of biogas. This process takes place under very low temperatures (about -100°C) and high pressure (40 bar). The raw biogas is cooled down to a temperature at which the carbon dioxide is condensed or sublimation, and can be separated from the biogas in liquid or solid fraction, while the methane accumulates in the gas phase.

The principle of operation of cryogenic separation process is shown in Figure 3.
Raw biogas stream passes through the first heat exchanger that cools the gas to a temperature of -70°C. The next stage of the process is passing cooled biogas by a series of compressors and heat exchangers, which additionally cool the gas and cause the compression it to about 40 bar before entering the gas to the distillation column. The last step of cryogenic separation process is the separation of CH₄ from the other impurities, mainly H₂S and CO₂.

The main advantage of cryogenic separation is possible to obtain biogas with high methane content of up to 99%. The main disadvantage is that to the upgrading process is necessary to use many of technological equipment, especially compressors, turbines and heat exchangers. This significant demand for equipment makes cryogenic separation extremely expensive.

In the GPP system from Gastreatment Services B.V. company biogas is first compressed to 17÷26 bar and then cooled to -25°C. In this step water, hydrogen sulphide, sulphur dioxide, halogens and siloxanes are removed from the gas. The gas is then passed through a coalescing filter, and the catalyst, which removes any remaining impurities.

Carbon dioxide is removed in two subsequent stages. In the first stage the gas is cooled to a temperature of (-50)÷(-59)°C. In these conditions, is removed approximately 30÷40% carbon dioxide. During the second stage the remaining amount of carbon dioxide is removed in solid form. Because gas at this stage is solid for the proper conduct of the process is needs an additional column, which is used during unfreezing and removing carbon dioxide from the first column.

Gastreatment Services B.V. Company is developing the GPP plus system which in addition to upgrading biogas will produce liquid methane as an end-product. This system is in the research phase and a pilot plant has been in operations in the Netherlands since the beginning of 2009. By decreasing the temperature enough to produce liquid methane, it is also possible to separate nitrogen, which is an advantage when upgrading landfill gas.

9.2 In situ methane enrichment

During upgrading biogas with methane enrichment using in situ technique (Fig. 4.), sludge from digester, in the first stage, is referred to the desorption column, and then back to the digester. In the desorption column, carbon dioxide is desorbed by passing air dose through the sludge. Continuous process of removing CO₂ from the sludge leads to an increase methane concentration in the biogas, leaving the fermentation chamber.

Process simulations have shown that it may be possible to reach a biogas quality of 95% methane with a methane loss below 2%. Cost estimations have show that for a raw gas flow of below 100 Nm³/h, the cost can be one third of the cost of conventional techniques. The first installations connecting biogas purification process with a simultaneous enrichment of methane using in situ method have been functioning since 2006.

In experiments where different sludge and air flows were tested the highest methane content obtained was 87% with 2% nitrogen and a methane loss of 8% in the off-gas from the desorption column. In situ technology is relatively simple and there is no need for much auxiliary equipment such as pressurized tanks. Therefore, it has a potential for a lower upgrading cost compared to other techniques. However, the process is dedicated to smaller plants where a high methane concentration (>95%) is not needed.

Conclusions

Biogas is currently used as an energy carrier, primarily for electricity generation, and on the occasion on this process to generate heat. Process heat is usually used to supply installation and maintenance facilities. In many landfills only partial of biogas is use as an energy sources; rest is burning in flares. Regardless of technical difficulties resulting from the complexity of connecting local energy sources to the electricity networks, we know that every process of energy conversion is a process which cause losses, also by summing up for each stage of processing, entropy component.

Combustion engine supplied by biogas power and driving a generator, electric current flow and re-power the electric motor by the current, or another receiver contents much higher losses than the direct supplying of engines by the biogas purified into biomethane as a fuel. Regardless of the source connection of biogas supplied to the purity of natural gas, or biomethane, the gas network does not pose any technical problems. Hence, the use of biomethane as a direct energy source is much better and should be preferred as it promoted.

Beside the current use of biogas mainly to produce electricity and heat, biogas should be use in following applications:
- as fuel for internal combustion engines with internal circulation, traction
- as fuel for internal combustion engines with external Stirling circulation
- to supply gas microturbines
- for applications in fuel cells
- as fuel in polygeneration systems
- as a carrier of energy in industrial and municipal gas network.

Biomethane as a second-generation biofuel is taken into account in the current strategy for the future development of biofuels. Therefore, scientific research to develop the most effective technology for cleaning biogas to the quality of natural gas is leading. Poland in 2008 at the WIREC 2008 conference in Washington indicated its intention of building up to 2020 about 2,500 biogas plants. Therefore, regarding to the establishment of the European Research Strategy on biofuels, and the Biofuels Road Map for Transport, it is necessary to work on the development of optimal technology for cleaning biogas to biomethane and implement these technologies in construction plant or planned to build.

Literature

Krzysztof BIERNAT- Ph.D. (Mech.Eng.) - an adiunct in the Automotive Industry Institute, acting as Coordinator of Polish Technology Platform for Biofuels. He was a member of the Scientific Council Institute for Fuels and Renewable Energy last term. He is a representative of Poland in European Technology Platform as a member of “Mirror Group” and he represent Platform in American Council On Renewable Energy “ACORE”. He is a member of “ACORE”. K. Biernat is a member of “Advisory Board” BIOPOL Project „Assessment of BIOrefinery Concept and the Implication for Agriculture and Forestry POLicy”, member of “Working Group” BITES Project, “Biofuels Technologies European Showcase”, an expert in Organization States of America and Operational Programmes: Infrastructure and Environment, Innovation Economy and Human Capital. He is also the Deputy Director of Institute of Ecology and Bioethics on public University Cardinal Stefan Wyszynski in Warsaw. He specializes in chemical thermodynamics of environmental processes as well as obtaining technologies, quality evaluation and use of exploitative liquids, including biofuels, and bioraftinary systems. He has many national and foreign distinctions, decoration and orders for scientific and pro-innovative activities. He has been a member of International Jury, World-wide Showroom of Scientific Progress and Inventiveness “Brussel’s Eureka” for twenty years. He is an author of above 200 publications in area of properties and exploitative conditionings of fuels, biofuels and other exploitative liquids as well as environmental protection. He promoted a few dozen of master’s and engineering thesis’s in this area. K. Biernat has expert licence in the field of fuel and energy economy. He is also an examined lecturer of Polish Economic Society and Polish Federation of Engineering Associations. Last, but not least, he is a member of national and foreign educational societies and General Secretary of Polish Sociology Society including American Chemical Society and American Association for the Advancement of Science.

Izabela SAMSON-BRĘK - M.Sc., graduate toward the environment at the University of Cardinal Stefan Wyszynski University in Warsaw, and since 2008, a doctoral student. In 2010, completed postgraduate studies in the field of “environmental management, environmental protection adviser in the European Institute of Education. She is certified by the Internal Auditor of Quality Management Systems and Environmental Management System according to PN-EN ISO 19011 and the Waste Management Supervisor. Since 2008 she works at the Institute for Fuels and Renewable Energy (from 01.2011 on Automotive Industry Institute) as a specialist team of renewable energy resources. Expert Institute for Fuels and Renewable Energy - conducting classes in the project “Bioenergy for the Region - Manager of Renewable Energy” in the prediction of the energy needs of municipalities and businesses. PARP Trainer (training in environmental management). The author and co-author of numerous publications on second generation biofuels and environmental management. She is co-founder of the Polish Association of Scientific Recycling.

SUNNY CHEMISTRY - the initiative of the Program Council of the monthly magazine CHEMIK and the Polish Association of Chemical Engineers, is supposed to change awareness and formulate a new way of thinking about chemistry in the society and science, technique and economy.

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