A Critical Overview of Development and Innovations in Biogas Upgrading

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Abstract. When organic matter decomposes in an anaerobic medium, it produces a gas mixture called biogas. This process is widespred in nature and occurs, for example, in swamps, lake beds, manure, and the rumen of ruminants. Organic material is almost completely converted into biogas by various microorganisms. In addition, certain amounts of energy (heat) and new biomass are produced. The formed gas mixture consists mainly of methane (50–75% by volume) and carbon dioxide (25–50% by volume). Biogas also contains small amounts of hydrogen sulfide, ammonia, siloxanes, nitrogen, oxygen, and moisture. Hydrogen sulfide, the main contaminant, is toxic and emits an unpleasant odor. The vapor contained in the biogas combines with hydrogen sulfide to form sulphuric acid. The acids attack the engines used in the upgrading of biogas, as well as the downstream components such as gas pipes and exhaust systems. Sulfur compounds also reduce the efficiency of downstream processing stages. For these reasons, agricultural biogas plants usually carry out desulphurization and drying of the biogas produced. The production of biogas and biomethane is important for the use of agricultural and industrial wastes and the replacement of non-renewable fossil fuels. This technical paper illustrates the production of biogas as a viable technological alternative to combat climate change and generate renewable energy. Analysis of the costs and applications of biogas is covered in this paper to understand the impact on the environment and world markets.

Keywords: Biogas · Biomethane · Hydrogen sulfide · Biomass

1 Introduction

The greatest global challenge in the fight against climate change is leading to an increasing use of renewable energy sources. In addition to environmental problems, the domination of fossil fuels is increasingly encountering obstacles such as price volatility and the tendency to reduce supply in the medium and long term [1].

In this context, biogas is emerging as one of the most sustainable alternatives, whose technology is at an advanced stage of industrial scaling. However, it is still in the early stages of a growth that could prove exponential [2].

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Biogas indeed offers exceptional conditions to reduce both organic methane (CH_4) and carbon dioxide (CO_2) released into the atmosphere. Its production involves circumscribed, controlled, and optimized processes that are commercially viable and produce a biofuel that can be used both in electricity generation and in vehicles as a substitute for diesel [1–3].

When biogas is burned, the methane is converted into CO_2 and water, which reduces the negative impact on the climate and makes the processing of waste profitable. Moreover, with some processing, it can be used as an alternative to natural gas in all its applications [2–4].

Agro-industrial waste accounts for three-quarters of the potential feedstock that can be explored for biogas production. Such a large potential leads to a more thorough consideration of the main issues in the development horizon [1–5].

Several issues currently arise for the further development of the sector, such as the cost of the technologies applied and the better use of subsidies and incentives to stimulate the market. Recently, the production of biogas has progressed on several fronts: improvement of solid waste and wastewater treatment processes, development of anaerobic digestion processes, production of heat and energy, purification of the product to make it compatible with existing uses of natural gas, and chemical extraction [6].

2 Fundamentals of Anaerobic Digestion

When organic matter decomposes in an anaerobic environment (without oxygen), it produces a gaseous mixture called biogas. This process is widespread in nature and occurs, for example, in swamps, at the bottom of lakes, in manure, and in the rumen of animals that chew the cud [5, 7]. Organic material is almost completely converted into biogas by various microorganisms. In addition, certain amounts of energy (heat) and new biomass are produced. The gas mixture formed consists mainly of methane (50–75% by volume) and carbon dioxide (25–50% by volume) [3, 8].

Biogas also contains small amounts of hydrogen sulfide, ammonia, siloxanes, nitrogen, oxygen, and moisture. Its composition is mainly influenced by the substrates used, the fermentation technique, and the different technologies used for plant construction. The process of biogas formation is divided into several stages. The first stage is hydrolysis, in which complex organic compounds such as carbohydrates, proteins, and lipids are broken down into less complex substances such as amino acids, sugars, and fatty acids [3, 9].

In this process, hydrolytic bacteria act and their released enzymes decompose the material through biochemical reactions. By means of acidogenic fermentative bacteria, the formed intermediates are then degraded to short-chain fatty acids (acetic, propionic, and butyric acids), carbon dioxide, and hydrogen in the so-called acidogenic phase (acidogenesis) [9]. In addition, small amounts of lactic acid and alcohols are also formed. The types of compounds formed in this phase depend on the concentration of intermediate hydrogen [8].

During acetogenesis, the process of acetic acid formation, these compounds are converted into biogas precursors (acetic acid, hydrogen, and carbon dioxide) by the acetogenic bacteria. At this point, the partial pressure of hydrogen is crucial. For energetic reasons, a very high hydrogen concentration prevents the conversion of intermediate products of acidogenesis [3, 9]. The consequence is the accumulation of organic acids that inhibit methanogenesis, such as propionic acid, isobutyric acid, isovaleric acid, and caproic acid, i.e. for this reason acetogenic (hydrogen-producing) bacteria must be closely associated with methanogenic archaea [5].

During the formation of methane, the archaea consume hydrogen and carbon dioxide (interspecific hydrogen transfer), creating the right environment for acetogenic bacteria. In the final phase of biogas formation, methanogenesis, the strictly anaerobic methanogenic archaea mainly convert acetic acid, hydrogen, and carbon dioxide into methane.

Hydrogenotrophic methanogens produce methane from hydrogen and carbon dioxide, and acetoclastic methanogens from the reduction of acetic acid. Under the conditions prevailing in agricultural biogas plants, the formation of methane occurs at higher organic load via the biochemical pathway using hydrogen, while methanogenesis by the reduction of acetic acid occurs only at relatively low organic load [2]. In general, the four stages of anaerobic decomposition occur in parallel in a one-step process. However, since the bacteria have different requirements for their habitat, such as pH and temperature, a middle ground must be found in terms of process technology. Since methanogenic microorganisms are the weakest link in the biocenosis and are most sensitive to disturbances due to their low growth rate, the conditions of the medium must be adapted to their needs [5].

However, in practice, any attempt to isolate hydrolysis and acidogenesis involves the partial formation of methane, despite the low pH in the hydrolysis phase (<6.5), so, the hydrolysis gas contains methane as well as carbon dioxide and hydrogen and must be consumed or treated to avoid safety risks and negative effects on the environment [2]. Depending on the construction and operation of the biogas plant, as well as the type and concentration of the fresh mass used as substrate, different conditions can be set for the medium in each stage of the fermentation in multistage processes. The environmental conditions in turn influence the composition and activity of the microbial biocenosis and thus have a direct impact on the metabolic products produced [5].

3 German Scenario of Biogas Production

Germany is a world reference in biogas production and upgrading. The current use of biogas in Germany is characterized by the decentralized conversion of raw gas into electricity at the point of production. Generators driven by internal combustion engines are usually used to produce electrical energy [5]. Biogas can also be used in micro gas turbines, fuel cells, and Stirling engines. Although these techniques are also initially used to convert biogas into electrical energy, to date they are rarely used for this purpose. Another possibility is to use the heat in suitable burners and boilers. In recent years, the option of upgrading biogas and then feeding it into the natural gas grid has also become established. As of August 2010, there were already 38 plants in Germany feeding upgraded biomethane into the natural gas grid. A large number of projects will be implemented in the coming years [7].

The German government's ambitious goal of replacing six billion cubic meters of natural gas per year with biogas by 2021 is remarkable. An alternative to feeding natural gas into the grid is the direct use of biomethane as a fuel, a practice that is not yet widespread in Germany and worldwide. It is generally not possible to use the raw biogas produced in a plant directly, as it contains certain substances such as hydrogen sulfide. For this reason, the biogas is subjected to several purification stages, which in different combinations are the prerequisite for the possibilities of use [5–7].

4 Brazilian Scenario of Biogas Production

The main sources of biogas production on a commercial scale in Brazil are the organic fraction of municipal solid waste, residues from the production of sugar and ethanol from sugar cane, such as vinasse and filter cake, and waste from pig farming. To a lesser extent, the following materials are also used: Residues from food production in general (cassava starch and orange juice are the most common examples), waste from restaurants, agroindustry waste, waste from cattle and poultry farming, and sanitary wastewater. Regardless of the feedstocks used, biogas production is a way to convert unwanted wastes into energy sources, raw materials for fertilizers, and other economically viable byproducts. In the Brazilian energy matrix, the share of biogas in effective production has generally increased from 0.01% in 2010 to 0.05% in 2016. In Brazil, biogas-derived energy has recently entered its maturity phase [7].

The inclusion of biogas in the electric energy expansion plan indicates that this energy is likely to become one of the main forms of renewable energy production in the coming years. As can be seen from the previous data, biogas is still in its early stages in terms of energy supply. Even if only biomass sources (8% of domestic supply) are considered, biogas represents only 1% of supply. However, the sector is developing rapidly: in 2015 there were 126 plants with a production of 1,373 thousand Nm^3/day. Most of these plants are located in the south (71) and southeast (41) of the country. Although the absolute numbers are small, the installed capacity of biogas for electricity generation has grown significantly. It increased from 20 MW in 2007 to 119 MW in 2016, using mainly municipal solid waste (MSW), a growth of 22%. As there are several substrate options for biogas generation, growth is expected to be even higher as specific technologies improve [7].

5 Biogas Purification

The long-term trend of conventional energy production presents a picture of progressive depletion of traditional sources (e.g. hydropower, coal, oil) and the emergence of new sources, especially renewables. Biogas production is part of the global carbon cycle. Between 590 million and 800 million tons of methane are released into the atmosphere annually through the natural biological decomposition of organic matter under anaerobic conditions [5]. Biogas utilization systems use these biochemical processes to decompose different types of biomass and use the released biogas as an energy source. In its raw form, biogas is completely saturated with water vapor and contains not only methane (CH_4) and carbon dioxide (CO_2) but also non-negligible amounts of hydrogen sulfide (H_2S) and other substances.

Hydrogen sulfide is poisonous and gives off an unpleasant rotten egg smell. The steam contained in the biogas combines with hydrogen sulfide to form sulfuric acid. The acids attack the engines used in biogas upgrading as well as downstream components such as gas pipelines and exhaust systems. Sulfur compounds also reduce the efficiency of downstream processing stages. For these reasons, agricultural biogas plants usually desulphurize and dry the biogas produced. However, depending on the accompanying substances contained in the biogas or the utilization technologies used (replacement of natural gas), it may be necessary to treat the gas additionally. CHP plant manufacturers set minimum quality standards for the properties of the fuel gasses used. These standards also apply to the use of biogas. The fuel gas quality requirements must be met to avoid shorter maintenance intervals or engine damage [7].

There are various processes for carrying out desulphurization. The processes are divided into biological, chemical, and physical processes. Depending on the application, a distinction is made between fine and coarse desulfurization. The selected process or combination of processes depends on the subsequent disposal of the biogas [5]. In addition to the gas composition, the flow rate of the biogas through the desulfurization unit also plays an important role. Depending on the progress of the process, the flow rate can vary considerably. Temporarily high biogas release rates and associated high flow rates can be observed after feeding the digester with fresh substrate and during the operation of the agitators. Currently, flow rates of 50% above average can occur. To ensure the efficiency of desulphurization, it is common to use oversized desulphurization units or to combine different techniques [7].

In order to avoid the above-mentioned disadvantages, biological desulphurization can also be carried out outside the biofilter using percolation filters. For this purpose, some companies offer biodesulfurization columns arranged in separate vessels [2]. In this way, the conditions necessary for desulfurization, such as the supply of air and oxygen, can be strictly controlled. To increase the fertilizing effect of the digested substrate, the precipitated sulfur can be added back to the digested substrate in the biofertilizer tank. The percolator filter process, in which hydrogen sulfide is absorbed using a scrubbing medium (regenerating the solution by adding atmospheric oxygen), achieves decomposition rates of up to 99%, which can result in residual gas concentrations of less than 50 ppm sulfur. Due to the high air input of about 6%, this method is not suitable for the treatment of biomethane. Unlike percolation filtration technology and internal desulfurization, the biological gas scrubber is the only biological method for treating natural gas quality [7].

The two-stage system consists of a packed scrubbing column (absorption of H_2S by dilute caustic soda), a biocleaner (regeneration of the scrubbing solution with atmospheric oxygen), and a sulfur separator (removal of elemental sulfur). The separate regeneration avoids the injection of air into the biogas. Although this technology allows the removal of large sulfur loads (up to 30,000 mg/m^3) with similar results to the percolator filter, it is only suitable for plants with large gas flows or high H_2S loads due to the high complexity of the equipment required. The main biogas purification processes are “water scrubbing”, “pressure swing adsorption (PSA)”, “membrane separation” and “amine scrubbing”.

5.1 Water-Washing Systems

Water-washing systems are a two-step process, similar to amine systems. The first step is a high-pressure reactor column that operates in countercurrent. Cooled water flows down and biogas flows up under high pressure (150 psi). Soluble gasses such as CO_2 dissolve in the water, similar to how CO_2 remains completely dissolved in a typical carbonated soft drink container. The second tower serves as a pressure relief tower where pressure is released from the solution and CO2 is degassed, similar to an open carbonated soft drink. Make-up water is added as needed. Blowdown water is flushed from the system to maintain the desired pH and water quality. This system is operated as a wet process, so pre-drying of the biogas is not formally required but is recommended. The H_2S contained in the biogas is adsorbed during the process. The H_2S is discharged from the system to the sewer system. However, some suppliers advocate H_2S removal before the system. As mentioned earlier, the operating temperature is approximately 16 °C and the operating pressure in the first reactor is 150 psi. Proper selection of components for this high-pressure system is critical to meet the long-term requirements of a high-pressure work environment. The water purification systems effectively meet stringent renewable natural gas (RNG) specifications. Methane levels in excess of 98% are easily achieved. Since O_2 and N_2 are not readily soluble in these systems, a polishing stage can be used when aggressive O_2 and N_2 specifications apply and elevated levels are detected in the feed gas [7].

5.2 Pressure Swing Adsorption (PSA)

Pressure Swing Adsorption is a batch process in which multiple vessels are operated in parallel under pressure. At the heart of the process, there is an adsorptive medium, similar to activated carbon, that separates gas molecules based on their molecular weight and size. Pre-drying of the gas prior to the adsorbers to about 5 °C is required to keep moisture out of the vessels and maximize their performance as dry adsorbers. Carbon dioxide is preferentially adsorbed on the media because it is a smaller molecule than methane and can penetrate more easily and deeply into the tiny pores of the carbon bed. The methane passes through the adsorber process columns relatively unaffected, while the CO_2 is retained in the media. The adsorption process is reversible, so the CO_2 is eliminated during the regeneration cycle [2]. When a vessel is saturated with contaminated gas, it is regenerated by lowering the pressure. At lower pressure, the compounds are removed from the medium and desorbed in a separate gas stream called “off-gas”. The usual cycle time to saturation is 2 to 4 min [5]. The off-gas is a low-grade gas stream that contains the previously adsorbed compounds such as CO_2, H_2S, and trace amounts of methane. Each vessel alternates between operating, depressurizing, regenerating, and finally depressurizing modes before switching back to operating mode. Manufacturers offer 4 to 10 adsorber vessels to optimize system performance and economics [7].

5.3 Membrane Separation

this technique uses polymer membranes to separate the CO_2 from the methane in the biogas under high pressure. The membranes are made of long, thin fibers with a hollow core. Typical fibers are about 0.5 to 1 mm in diameter. The compressed gas flows along with the fiber and the CO_2, which is a very ionically charged and smaller molecule, permeates through the porous membrane, while the methane resists permeation and remains in the core because it is larger and very nonpolar in its ionic charge [7].

5.4 Amine Scrubbing

The amine scrubbing system uses a two-step approach for biogas upgrading. The first step is adsorption, followed by a second step of stripping or desorption. The amine portion of the solvent molecule of the scrubbing reacts chemically with the CO_2 in the biogas to keep it in solution. A common chemical used as a scrubbing solvent is MDEA (mono-di-ethanol amine). The methane portion of the biogas passes through the fixed bed reactor without being touched by the scrubbing chemical. High methane purities can be achieved in the recovered natural gas (>99.9%). In the second step, the scrubbing solution is heated to boiling to reverse the chemical reaction. The CO_2 in the packed stripper tower is separated from the scrubbing solution and discharged. High CO_2 purities in the off-gas can be achieved to exploit the potential for CO_2 reuse. The regenerated amine wash solution is then cooled and recycled back to the scrubber tower in a closed-loop system. The systems operate at a relatively low operating pressure of about 0.5 to 3 psi. This low pressure provides equipment and operational savings compared to systems operating at high pressure. If the H_2S content in the raw biogas exceeds 300ppm, pretreatment with one of the desulfurization techniques is recommended [5–7].

6 Production Costs

The main commercial applications of biogas, after removal of CO_2 and pollutants, as a substitute for natural gas, are electricity generation and as fuel in motors (biomethane), especially for vehicles, and finally the use of waste as fertilizer for domestic use, especially in small and medium rural farms. Nowadays, the main use of biogas is for the production of thermal energy (heating) [7].

To obtain pure biogas, the most important parameter to consider in production is the price of electricity. The International Renewable Energy Agency estimates the cost of electricity for biogas to be between US$6 and US$14/kWh. The most important factor is the cost of feedstock. If this is cheap and abundant, such as industrial waste from agribusiness and/or garbage, the cost goes down, while it goes up if special plantations are used additional processing costs must be added [7].

In Brazil, there is clearly a competitive advantage in terms of the lower cost of crops and agro-industrial waste compared to other countries, and this advantage opens up opportunities to increase the scale of industrial biogas use in the country, especially in relation to agro-industrial waste [9]. Europe has excelled in the production of biogas. Between 2009 and 2015, the number of plants increased from 6,000 to about 17,000, and Germany in particular had about 10,800 production units in 2015. Despite the strong growth, biogas accounts for only 1.9% of total electricity generation in the European Union [7].

In relative terms, only a small percentage of biogas plants have been converted to produce biomethane - 0.3% of European gas consumption. A good example of how important government incentives for biomethane have been is the UK, where the introduction of carbon price support in 2013 and the feed-in tariff (FiT) per kWh of biomethane injected under the Renewable Heat Incentive led to twenty to thirty new plants per year between 2014 and 2016. It is worth highlighting the German experience in the European context. The first law to promote renewable energy was created in 1991, shortly after reunification. The Electricity Feed Act (Stromeinspeisungsgesetz, StrEG) ensured that electricity from all renewable energy sources was included in the feed-in and established a FiT11 tariff for twenty years. The number of biogas plants increased from about one hundred in 1990 to one thousand at the turn of the millennium, even if three-quarters of them were small plants with a capacity of less than 70 MW [2, 7].

In 2000, the Renewable Energy Sources Act (EEG) came into force, which was improved in 2004 and 2009. The law guaranteed a FiT tariff for renewable electricity and a reduction factor for this tariff between 1% p.a. and 1.5% p.a. to reflect the inclusion of technological improvements, in addition to a "biomass bonus" for biomass electricity generation. Finally, a waste heat incentive was also introduced to encourage more efficient plants that combine heat generation with electricity generation. This resulted in plants receiving, on average, a price more than four times higher than the spot wholesale electricity price and higher than the price paid by large industrial customers [7].

These mechanisms led to the construction of more than seven thousand biogas plants with a generation capacity of almost 3.5 GW and an average capacity of 500 MW per plant (OIES, 2017). This growth was triggered by the use of agricultural crops, particularly maize, which provides 75% of the feedstock for biogas plants. As a result, one million hectares or 8% of German arable land was used to grow crops for biogas production [9]. In 2012 and again in 2014, the incentives were abolished, which had a dramatic impact: while between 2009 and 2011 a thousand new plants were added annually, the new legislation reduced the number of new additions to a hundred plants in 2015. In any case, electricity generation from biogas still accounts for about 5% of the total energy demand of 600 TWh [7].

7 Conclusions

Due to growing environmental awareness, both to accelerate the replacement of fossil fuels and to improve and expand alternatives for organic waste treatment, biogas is the target of several development initiatives around the world, especially in countries such as Germany and the United States. Biogas has also experienced significant growth in Brazil.

In 2016, the country had an installed capacity of nearly 120 MW for biogas power generation. This is six times more than in 2007, and 95% of this figure was accounted for by plants using municipal solid waste (MSW). This shows that biogas from MSW is already a reality and is expected to grow further.

On the other hand, the potential of agro-industrial residues is still not sufficiently exploited, especially for large-scale biogas production. In fact, the potential of biogas is not limited to renewable electricity generation. The technological development of gas-powered tractors and trucks opens up an excellent opportunity to gradually replace diesel in agriculture, which represents 15% of national consumption, thus contributing to the reduction of CO_2 emissions and environmental sustainability.

However, for this potential to be fully exploited, public policies are needed that not only provide the necessary incentives for the development and introduction of biogas production technologies but also encourage the consumption of the product.

Thus, once a regulatory framework is in place that promotes greater inclusion, biogas will play a fundamental role in achieving the CO_2 emissions reduction targets set out in the Paris Agreement and in increasing the competitiveness and sustainability of the Brazilian agricultural sector.

References

1. Yousef, A.M., et al.: New approach for biogas purification using cryogenic separation and distillation process for CO2 capture. Energy **156**, 328–351 (2018)
2. Zhai, X., Chen, M., Lu, W.: Fuel ratio optimization of blast furnace based on data mining. ISIJ Int. **60**(11), 2471–2476 (2020)
3. Yao, X., et al.: The characteristics of syngas production from bio-oil dry reforming utilizing the waste heat of granulated blast furnace slag. Int. J. Hydrogen Energy **43**(49), 22108–22115 (2018)
4. Abd, A., et al.: Methane enrichment in biogas mixture using pressure swing adsorption: process fundamental and design parameters. Mater. Today Sustain. **11**, 100063 (2021)
5. Giwa, A., et al.: Prospects of China's biogas: fundamentals, challenges and considerations. Energy Rep. **6**, 2973–2987 (2020)
6. Khan, A., et al.: Metal–organic frameworks for biogas upgrading: recent advancements, challenges, and future recommendations. Appl. Mater. Today **22**, 100925 (2021)
7. Petersson, A., Wellinger, A.: Biogas upgrading technologies developments and inovations. IEA Bioenergy **20**, 1–19 (2019)
8. Santos, A.A.R., Castel, C., Favre, E.: Utilization of blast furnace flue gas: opportunities and challenges for polymeric membrane gas separation processes. J. Membrane Sci. **526**, 191–204 (2017)
9. Yousef, A.M., et al.: Upgrading biogas to biomethane and liquid CO2: a novel cryogenic process. Fuel **251**, 611–628 (2019)