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Biogas as Renewable Energy Resource

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Introduction

How are renewable energy resourses exploited? This covers a wide range of topics. Water, wind and geothermal energy up to plants growing – this all is caused by the sun, the greatest source of renewable energy [1]. Bioenergy is one of the forms of renewable energy. This energy is considered to be an important source of renewable energy for the future time, because fossil fuels are running out [16]. This essay is confined to biogas production. Biomass can be defined as the different materials of biological origin, that can be used as a primary source of energy [2]. The final aim in these days is to obtain heat, electricity and fuels. Sources for biomass energy include plants in general and besides animal and agricultural wastes, forestry wastes and crops. Historical ways to exploit biomass is wood burning and making paper from forestry wastes. By anaerobic digestion of biomass, methane can be turned out, which is later used for generating electricity, heat and as fuels in engines.

Biological processes

The biological process includes anaerobic digestion. Biogas arises from a natural process of biomass conversion to gaseous fuel. Rich in methane, but nonnegligible amounts of sulfur are also produced. Organically bound materials are mineralized to methane and carbon dioxide [2].

One fundamental of methanogenesis is the biogeochemical carbon cycle [3]. During anarobic conditions, the carbon that has been fixed through photosynthesis, is converted to methane by microbial processes. Methane is naturally formed from sediments of oceans, lakes, rivers, swamps, marshes, animal intestinal tracts and other anaerobic habitats. Also aerobic habitats release methane to the atmosphere. Oxidising, aerobic bacteria may reoxidise CH_4 to CO_2. Methane reaching the stratosphere, is reoxidised to CO_2 through reaction products of the ozone cycle. Carbon dioxide can again be assimilated by green plants, closing the biogeochemical carbon cycle.
About 70% of methane is built from acetate. The remaining 30% is formed by reduction of CO_2 through H_2.
The formation of biogas occurs usually in a three-stage process [5]: hydrolysis, acidification and methanogenesis. Specific bacteria break down the materials to biogas, which is a mixture of CH_4, CO_2 and trace gases [6].
The first step is hydrolysis of polysaccharides, proteins and fats into oligosaccharides, sugars, fatty acids and glycerol. The hydrolytic liquefaction is mediated by a microbial community of fermentative bacteria which comprises both strictly and facultative anaerobic bacteria. Microorganisms involved in the hydrolytic and thermophilic process are mostly still unknown. Due to enzymes located on the outer side of the bacterial cell wall or released by the bacteria in the outer medium, the solid crop residue is broken down [11]. Followed by fermentation into mainly organic acids like acetic, propionic and butyric acid and carbon dioxide and hydrogen. The second step is the acetogenesis, which concentrates the material to acetic acid and carbon dioxide. Here are involved the so-called transitional bacteria [8]. It is the role of a number of strictly anaerobic bacterial species belonging either to the obligate hydrogen producing acetogens or to the sulphate reducers to metabolize these products into acetate [11]. Some bacteria like *Clostridium* are distinctive in producing H_2 as the final product [13].

As last step follows methanogenesis with up to 70% methane and 30% carbon dioxide. Two types of methanogenic bacteria take over. The first, called acetoclastic, dismutates acetate into methane and bicarbonate [11]. The second, called hydrogenotrophic, reduces bicarbonate through dihydrogen to methane. Methanogens are the main producers of methane. Important strains that have been isolated are *Methanosarcina* or *Methanobacterium* [5]. Methanogens differ from other microbes in the lack of peptidoglycan in their cell walls. The fatty acid esters in their membranes are replaced by phytanyl ethers. Their choice of substrates is limited to acetic acid, hydrogen and C1-compounds.

There is a competition for hydrogen during methanogenesis, depending on the substrate composition [3]. Sulfate-reducing bacteria (e.g. *Desulfovibrio desulfuricans*) reduce sulfate with hydrogen to form hydrogen sulphide. Acetogenic bacteria, that are involved in methanogenesis, reduce inorganic carbon with hydrogen to produce acetate. For thermodynamic reasons, sulfate-reducing bacteria obtain hydrogen and acetate more easily than methane-forming bacteria under low-acetate concentrations. With a high sulfur concentration follows a high H_2S synthesis during methanogenesis. Increasing sulfur levels may inhibit bacterial reactions[3].

Feedstocks for biogas production

The first anaerobic digester studies (at Penn State) used cow manure [2], which is also useful for inoculation. Feedstock can come from other farm animals such as pigs, chicken and horses. There are vegetable oils, pure carbohydrates like sugar and starch and heterogeneous “woody” materials, which is lignocellulose. Sugar crops are often used for ethanol production. Even organic waste from hospitals containing paper and cotton, municipal sewage sludge, waste from agriculture or food production, organic-rich industrial waste water etc. can be used as substrate. Energy crops are often especially grown for biogas production and can be fed purely into the fermenter. These plants can be maize, clover, grass, young poplar and willow [4]. To ensure a constant quality of substrates and minimize the carbon loss throughout the year, green plant material is stored as silage.

The economics and general benefit of biogas are always most favourable when the digester is placed in a flow of waste already present. Examples are sewage systems, piggery washings, cattle shed slurries, abattoir wastes, food processing residues and municipal refuse landfill dumps [13].

To choose the right combination of feed as the case may be community waste, can provide all nutrient requirements. For example, combining municipal solid waste low in nitrogen and sulfur with sewage sludge high in both can be a smart decision [8].
Bjorndal and Moore [12] investigated several feedstocks and classified those in terms of fermentability. This gives an idea of suitability of feedstocks for biogas production. Another value they used is the CWC (cell wall constituents), because many potential feedstock consist of cell walls in high percentage. Brassicas, sweet potatoes and emergent aquatics were found to have a high digestibility. It has to be mentioned that fermentability not only varies between the different species but also within the species. Within species, the variation is primarily due to stage of maturity, differential distribution of plant parts and planting, harvesting and storage techniques [12].

Biogas from distillery waste as feedstock yields a very high rate of methane (>0.69 m^3/kg of volatile solids) [9]. The average methane yield is about 0.38m^3/kg. With the generated biogas, it is possible to substitute up to 90% of the process energy (heat and electricity) of the distillery by using in-house production residues.

Conditions

Conditions can be considered as physical, like water, temperature, retention time, loading rate, mixing and particle surface area, and as chemical like substrates, anaerobic conditions, nutrients and pH [8]. Cellulose is known to be the major substrate. One chemical condition is the sufficient concentration of organisms in the digester and at the same time a substrate concentration that allows the microbes to generate the required rate of gas production. For the growth of the microorganisms, a slowly increasing feed concentration until equilibrium is recommended.

Nitrogen should be present at 10% by mass of dry input and phosphorus at 2%. If there is too much nitrogen in the substrate biomass, the latter accumulates as ammonia in the methane digestion liquor to amounts which become toxic for the methanogenic bacteria [11].

Perfectly anaerobic conditions are not possible to achieve, but facultative anaerobes lower the oxygen level [8]. The oxygen in the system arises from oxygen dissolved in added water or from the feed stream. If there is oxygen present, it can act on the one hand as electron acceptor forming water instead of methane. On the other hand, oxygen in the end product gas is a contaminant and a potential safety hazard.

The water environment is often overlooked as a primary need for microbial function in the digester. Water is required for transport of nutrients and substrates to and waste products from the bacteria. It is also responsible for heat transfer. Traditionally, a higher water content was taken, because it is easier to handle in terms of mixing and pumping.

The rate of methane production is found to be higher at temperatures like 55-60°C (thermophilic) compared to standard mesophilic operation (35-40°C). Therefore the system must be insulated properly for avoiding heat losses. Digesters with lower temperatures are more stable and normally require less process energy, but due to lower reaction rates, it can require larger reactor volumes [3].

The methane forming bacteria are sensitive to pH, and conditions should be mildly acidic (pH 6.6-7.0) and certainly not below pH 6.2 [13]. The oxidation state of carbon in carbohydrates is such that the gas produced by fermentation is 50% carbon dioxide [8]. This high partial pressure of CO_2 in the gas phase will depress digester pH and require a higher level of alkalinity to maintain neutral pH. An economical source of basic ions needed to maintain alkalinity is lime.

Mixing is not necessary for the methanogenic biology to take place. It does not greatly modify production rate and yield or biogas composition. But it achieves a uniform temperature in the digester and reduces scum formation and settlement inside the reactor [11].

Biogas Processing

From the engineering point of view, biomethanation is a relatively simple reaction [3]. Advantages of processing biomass via anaerobic digestion are the ability to use non-sterile reaction vessels, automatic product separation by outgassing and relatively simple equipment and operations [6]. The technical biomethanation process comprises four steps [3]: 1. feedstock delivery, pre-treatment and storage, 2. digestion, 3. digestate use and 4. energy recovery from biogas. The extent of pre-treatment depends on the substrate and can include sieving, wind sorting or cyclones. Next, the purified waste stream enters the digester, where several kinds of bacteria do their job to convert the biomass into methane. In most cases, the effluent leaving the digester undergoes a second digestion step in the post digester. The final digestate storage tank is designed for storing periods of many months. The digestate is further treated by dewatering and composting of the solid fraction. The liquid fraction can be directly used as fertilizer. The methane released during the digestion is collected in both digestion steps and stored in gas tanks. It undergoes purification steps like desulphurisation.

The biogas plants are run as a single- or two-stage process with a secondary fermentation in large storage tanks. Most tanks are liquid fermenters with more than 12% dry mass (dry fermentation) or less (liquid fermentation).

The yield of methane with 70% is quite low. To increase the amount of methane, the hydrolysis process must be improved. Instead of mesophilic processes, thermophilic processes are used more and more to speed up the reactions. During anaerobic digestion there are two effluent streams produced: biogas and sludge. Depending on the employed feedstock the biogas is between 55% and 75% methane by volume. Anaerobic digesters can be either singletank reactors, which are operated in batch, intermittent or continuous mode, or two-tank reactors.

In a batch mode the reactor is once loaded and only gas is removed during the process. The reactor is non-steady in its operation.

The intermittent mode adds periodically feedstock, while drawing off an equal volume. In this kind of reactor are found different layers: stabilized solids at the bottom, the layer of actively digesting solids in the middle and the supernatant with a scum layer at the top. The challenge in an intermittent reactor is to retain the sludge until it is fully digested. The continuous mode offers a higher digestion rate and a lower retention time. Two-tank reactors are employed, because methanogenesis appears to be the rate-limiting step in anaerobic digestion. Thus, each process, acid-formation and methane-formation can take place under optimal conditions. The produced biogas is richer in methane.

The end product biogas is used for stationary power generation. Alternatively, the gas can be compressed after purification and enrichment and then fed into the gas grid or used as fuel in combustion engines or cars [4]. The digested solids can be applied as fertilizers, for animal bedding or even for animal feed. Thermal combustion seems to be the easiest way to use methane for heating purposes. The use of biogas in engines of combined heat and power plants [3] transfers the chemical energy of methane into electrical power (about 1/3) and heat (about 2/3).

Problems with biogas

The biogas produced containes usually 60% methane, 32-34% carbon dioxide, 6-8% nitrogen and trace amounts of hydrogen sulphide. In history, there occured the problem of hydrogen sulphide which is an end product of anaerobic digestion. It is an unpleasant trace component in biogas [14]. It is explosive in contact with air and is known as one of the most dangerous materials in general technical use, because it can cause headaches up to collapses and death.

Hydrogen sulphide leads to corrosion of pipes and engines [6]. The hydrogen sulphide concentration affects the rate and extent of corrosion. But it is also dependent on the humidity in the reactor, length of exposure and metal composition. It is important to employ corrosion resistant metals (steel) or coated metal.

There are several H_2S removal processes [14], but it must be considered whether such a treatment is economically, because the cost of treatment in a farm digester can be readily greater than the value of the gas per cubic metre. These removal processes like “Girbitol” or “Vacuum Carbonate”, that use absorption and reaction, have been developed for large industrial scale. For smaller plants the iron oxide box, based on reaction of H_2S with Fe_2O_3, is more suitable. Another problem in terms of hydrogen sulphide treatment is the lack of commercial market for it.

Scrubbing is an operation that removes H_2S from biogas [15]. It forms sulphurous acids with other components in biogas, which causes heavy corrosion. One way to get rid of it is to give it something else to corrode, e.g. steel wool, so that the equipment is prevented to be corroded. Hydrogen sulphide is converted into black iron sulphide by the steel wool. After some time, the steel wool must be renewed. Another scrubbing method is a gas-liquid-contactor [10] which uses a liquid reduction/oxidation process. In this case, hydrogen sulphide is converted to elemental sulphur and water. The process is highly efficient (up to 99% removal) and unexpensive. A very common method for biogas scrubbing is dry oxidation process [7]. During this process a small amount of oxygen is introduced into the anaerobic system which makes the hydrogen sulphide possible to be oxidized into sulphur and water. The danger with this method is that methane is explosive with air.

Hydrogen sulphide can be further removed with the help of adsorption on activated carbon.

Adsorption of H_2S using iron oxide leads to sulphur and water. For this procedure, iron oxide pellets

are employed. This method is sensitive to water and the sulphur-covered pellets have to be removed for regeneration.
Liquid phase oxidation offers an opportunity to remove low concentrations of H_2S. In physical absorption hydrogen sulphide can be absorbed by solvents like water enriched with sodium hydroxide. Chemical absorption can take place with iron salt solutions to form insoluble precipitates and is very effective for high H_2S concentrations.

The storage of biogas may also be a problem, as it is always with gaseous products. Biogas could not be stored easily, as it does not liquefy under pressure at ambient temperature [7]. Its critical temperature and pressure are -82.5°C and 47.5bar. Compressing the biogas reduces the storage requirements, offers a concentrated energy content and gives pressure to overcome the resistance to gas flow. Most commonly used biogas storage options are in propane or butane tanks and commercial gas zylinders up to 200bar. Depending on the application of biogas (e.g. vehicle fuel, domestic cooking) the storage facilities vary.

To consider the greenhouse effect of methane as a product, it has been estimated, that about 0.55-1.3 billion tons of CH_4 is released annually to the atmosphere [3]. Compared to CO_2, the greenhouse effect of CH_4 is rough CH_4 7 times higher. Thus a proper use of generated CH_4 must be assured.

Conclusion

The dramatic increase of fossil energy costs made biogas a more attractive, alternative renewable energy source. The number of energy crop digestion plants for instance doubled in Germany within 2 years from 1,500 (2002) to more than 3,000 (2004) applications [3]. The big advantage of biogas production is its wide range of feedstock. Disadvantages in terms of production of biogas such as slow reaction rates, production of toxic and corrosive hydrogen sulphide and low methane yields should be mentioned.

Digestion of biomass is a promising alternative for supplementing the world´s energy needs [2]. Waste which is already present, can be applied usefully [16]. The economic benefits are that input material does not have to be specially collected, waste disposal is improved and uses are likely to be available for the biogas [13]. Biogas generation is suitable for small to large scale operation. It is particularly attractive for integrated farming, where the aim is to emulate a full ecological cycle on the single farm.

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