Experiences with biogas plant modernization with ADA reactor

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Abstract

Anaerobic digestion is a commonly accepted way of organic wastes treatment connected with generation of renewable fuel - biogas. Nowadays more attention is paid to anaerobic digestion in Poland due to legal and economical support for renewable technologies. Basic knowledge of anaerobic digestion process and some operational problems in agricultural biogas plant were outlined in the paper. Anaerobic Digestion Accelerator technology, which significantly improves stability of the digestion process was also presented. Experiences from the first ADA implementation in Denmark confirm the positive influence of ADA on the anaerobic digestion process stability. ADA seems to be especially useful for protein-rich material degradation.

Streszczenie

Fermentacja beztlenowa jest powszechnie akceptowaną i uznaną metodą utylizacji odpadów pochodzenia organicznego, której towarzyszy produkcja biogazu. Obecnie w kraju nabiera ona coraz większego znaczenia ze względu na wsparcie prawne i finansowe dla technologii opartych na odnawialnych źródłach energii. W pracy przedstawiono podstawowe informacje o procesie fermentacji beztlenowej oraz zwrócono uwagę na wybrane typowe problemy eksploatacyjne biogazowni rolniczych. Zaprezentowana została technologia ADA, która znacząco wpływa na stabilizację procesu biodegradacji. Potwierdzeniem tej tezy są doświadczenia zebrane z pierwszego wdrożenia technologii ADA – modernizacji biogazowni w Danii. Technologia ta wydaje się być szczególnie użyteczna dla utylizacji odpadów o dużej zawartości protein.

1. Basis of anaerobic digestion

Anaerobic digestion (AD) is an acceptable process for the organic origin wastes treatment worldwide. One of the major advantages of this process is the generation of biogas – energy carrier from the renewable resource, which can be utilized in many ways, depending on local needs. Another benefit of the anaerobic digestion process is the usability of digestion residues applying them as soil conditioner or valuable fertilizer in organic farming. Recently knowledge of AD process has radically increased, however many of technical issues are still under development. Many different types of AD technologies are present on the market. Thinking of the agricultural biogas plants, they are mostly designed as low-rate, one-stage, wet, semi-continuous systems based on a continuously stirred tank reactor [1, 5, 7].

1.1 Stages of the process

The anaerobic degradation of organic substances to methane and carbon dioxide is a purely microbial process. The process is sequential and several different groups of bacteria are involved in its different stages, what is shown in Figure 1.1. The environmental conditions for each of these microbes can be different so it is difficult to define and achieve optimal process conditions. In general overall AD process can be divided into three stages: hydrolysis, acid-forming and methanogenesis. At the first stage complex insoluble compounds undergo enzymatic hydrolysis and it results in the formation of soluble simple sugars, fatty acids and amino acids. This stage can be slow and often determines the overall rate of anaerobic digestion process [2, 3]. The next stage – acid-forming and acetogenesis – results in the formation of organic acids, acetate, alcohols, carbon dioxide and hydrogen. The last step is caused by very sensitive and slowly growing bacteria called methanogens. They are some of the oldest microbes and are grouped in the domain Archaebacteria. In nature, methanogens can be found in decaying organic matter, deep-sea volcanic vents, deep sediment, black mud of lakes, swamps as well as in a digestive tract of humans and animals, particularly in a rumen of ruminants. It is worth mentioning that methane-forming bacteria are able to degrade only relatively small number of simple substrates, like acetate, carbon dioxide and monoxide, formate, hydrogen, methanol and methylamine. No species can utilize all those substrates, so for a successful and effective digestion a large number and a large diversity of methanogens are needed [3]. In a bioreactor ca. 70% methane is formed by acidotrophic methane bacteria from acetate and VFA. The remaining 30% is produced by hydrogenotrophic methanogens from H_2 and CO_2 [2, 3].

1.2 Important parameters of the AD process

The AD process as a complex biological process is influenced by several environmental factors among which the most important are temperature, pH, substrate composition and toxins. Achieving a correct range of those factors is realized by controlling such parameters like hydraulic retention time (HRT), organic loading rate (OLR) and bioreactor heating. Several other parameters, like gas production and gas composition, VFAs and ammonia concentration, oxygen reduction potential (ORP), pH and buffer capacity, are continuously or sequentially measured to assist biogas plant operation. Problems with controlling the process come from its sequential character with different optimal conditions for each stage. Other difficulties are due to lack of simple direct methods of measuring microbiological activity. Those facts, as well as high sensitivity of the process, causes necessity of applying complex monitoring and control systems in biogas plants to ensure balanced steady state with a stable and high yield of the biogas production.

Temperature is one of the most important factors affecting microbial activity in digester. It influences not only methanogens but also acid-forming bacteria. Most methanogens are active in two temperature ranges: 30 – 35°C (mesophilic) and 50 – 60°C (thermophilic). At higher temperature there is a faster degradation, higher rates of volumetric methane production per day and more effective pathogens destruction but thermophilic microbes are very sensitive to temperature fluctuations and their population size and diversity are less than mesophilic ones [1-3]. Daily changes of digester temperature should be no greater than 1°C for thermophiles and 2 – 3°C for mesophiles [3]. Acid-forming bacteria have an optimum temperature at about 30°C, so in practice mesophilic anaerobic digesters are more popular. Taking care of methane-forming bacteria, 32°C is the minimum temperature that should be maintained, and 35°C is the preferred temperature.

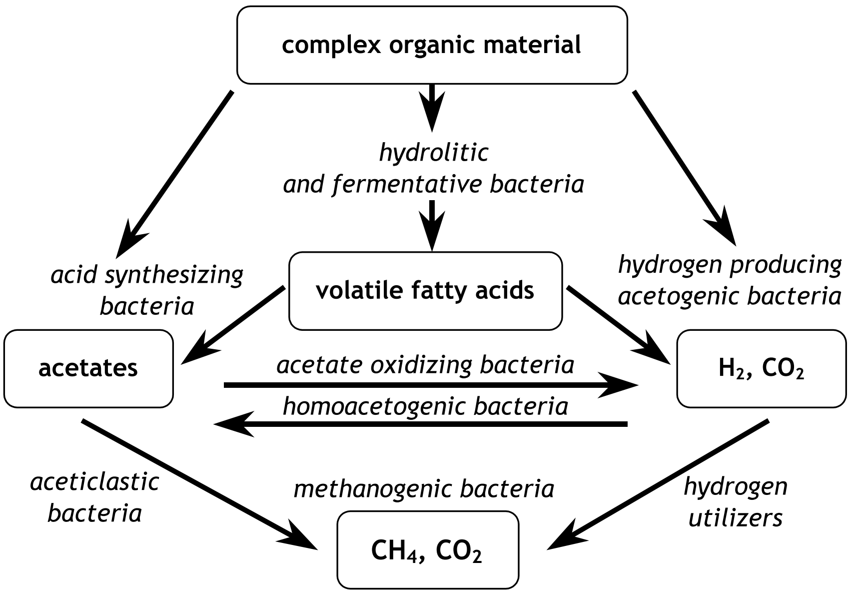

Figure 1.1. Model for the anaerobic digestion process [2]

Optimum pH conditions for methane-forming bacteria are within a range of 6.8 to 7.2. To prevent rapid changes in pH, high alkalinity is used as a buffer. If pH decreases below 6.2, the activity of methanogens is stopped and products of acid-forming bacteria accumulate in a digester. More information about pH influence can be found in subchapter 2.1, where theoretical aspects of ADA are described.

Proper substrate composition should ensure not too long time for hydrolysis and delivery of micro- and macronutrients needed for microbes to produce biogas. Correct ratio of COD:N:P and C / N between 25 and 32 in the feedstock is demanded as well as absence of toxins and process inhibitors. A common problem with the organic overload is often related to protein-rich feedstock, which degradation results in ammonia release. However nitrogen is needful nutrient for bacteria but only in soluble form as ammonical-nitrogen (NH_4^+ - N) and free ammonia is toxic for them [1, 3]. Overloading, too intensive mixing, temperature fluctuations or other operational conditions may result in a foaming problem in the digester. Foam also occurs as a result of scum breakdown on the surface. Problems associated with foam in the digester include reduced sludge feed pumping and inversion of digester solids profile (thick solids at the top and diluted at the bottom) [3].

Another operational problem in biogas plants can be hydraulic overload. Due to too short HRT the methane-forming bacteria cannot reproduce fast enough to avoid washout. Sometimes it is also related to washout of alkalinity, so buffer capacity decreases and process is more sensitive to pH fluctuations.

2. ADA technology

The Anaerobic Digestion Accelerator Technology (ADA) was developed by the Finnish company Preseco Oy. It seems to be a very good solution for improving the stability of the biodegradation process, related with the decrease of ammonia level in the reactor. The ADA technology is offered as a complete system in a newly designed biogas plant as well as a modernization of existing plant. The second case is presented in this paper.

2.1. Theoretical aspects of ADA

ADA technology allows efficient digestion of fats and proteins, which have high energy potential for biogas production. These substrates can cause problems with anaerobic digestion because of their degradation products. Anaerobic digestion of protein-rich wastes leads to high ammonia concentrations of the sludge and further to problems with the digestion process. Particularly soluble nitrogen in the form of free ammonia is toxic for microbes. When pH of the sludge increases over pH 8, more free ammonia is present in solution, because equilibrium between ammonia and ammonium is pH-dependent. The produced ammonia reacts with water, producing ammonium ions (NH_4^+) and hydroxide ions (OH^-), see scheme 2.1.1. The increased number of hydroxide ions is increasing the pH-value of the sludge.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad (2.1.1)$$

Variations in pH inhibit methanogenic bacteria reproduction slowing down the production of methane and consumption of methanogenic substrates (H_2, CO_2, acetate). Accumulation of these substrates can cause decrease in pH and a total failure of the digestion process.

In ADA technology, carbon dioxide of pressurized biogas dissolves to the sludge (pH~8) forming instable carbonic acid, which further reacts with hydroxide ions and forms hydrogen carbonates (i.e. bicarbonates) and carbonates (scheme 2.1.2). [4] This leads to higher buffer capacity of the sludge.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O \quad (2.1.2)$$

The decrease in the number of OH^- ions according to the reaction (2.1.2) results in a decrease of pH and also the number of free ammonia in the sludge. This further improves the conditions for anaerobic digestion. The conditions are becoming more stable and the methanogenic bacteria are working more efficiently. The formation of bicarbonate increases the alkalinity and buffer capacity of the sludge. The decreasing pH drives the equilibrium of ammonia (see reaction 2.1.1) from left to right producing ammonium ions (NH_4^+), which in turn are not as toxic as ammonia to the microbes. Ammonium is also tolerated in higher concentrations.

Ammonium and bicarbonate ions can form ion pairs in the sludge and behave as a buffer compound (scheme 2.1.3).

$$NH_4^+ + HCO_3^- \leftrightarrow NH_4HCO_3 \quad (2.1.3)$$

As described in the text above, the ability to form a buffer compound during ADA-treatment leads to an improvement of process stability. ADA allows digestion of sludge having high ammonia concentration by enhancing alkalinity and buffer capacity of the sludge. Higher buffer capacity stabilizes fluctuations in pH of the reactor, which is one of the most important parameters in controlling anaerobic digestion process. Buffer capacity is also able to stabilize acidic pH variations caused by the accumulation of VFA, unless the overload is too severe. [6]

2.2. Experiences with ADA implementation

2.2.1 Description of biogas plant and its enhancement

HP Energi biogas plant, which is the subject of interest, was built in 2001 near Ringkøbing in Denmark. The plant was designed as a modern wet thermophilic process to utilize pigs manure (94%) and fat (6%). The bioreactor volume is 800 m^3 and daily input of total solids is ca. 5.4 Mg. The bioreactor is equipped with mixing. Produced biogas is purified with microbiological H_2S filtration system. Purified biogas is used as a fuel for piston engine where heat and electrical energy are produced (CHP). Digestate is used as a fertilizer on plant owner's fields where the feed for swine is grown. Technical data of the plant are summarized in table 2.2.1.

Hydraulic retention time for this biogas plant is only 11 days, however the process of anaerobic digestion wasn't running correctly. The plant was suffering from a continuous overload of the reactor and a continuously instable process. As a result of these the biogas production was gone up and down and the average production was not achieved the desired level. The plant was also experienced problems with foam. There was also been a few total process stops due to high ammonia levels, especially during trying to feed the reactor with high protein material. It was noticed that the reactor cannot anticipate any extra proteins without significant process difficulties

Table 2.2.1. Design data of HP Energi biogas plant.

Feedstock:	
- pigs manure	20000 Mg per year
- fat	1450 Mg per year
Reactor volume	800 m^3
Process temperature	55 °C
Hydraulic retention time	11 days
Biogas production	1 200 000 m^3 per year
Biogas utilization	CHP engine, 290 kW_e and 600 kW_t

There was two targets when starting the ADA upgrade project: to decrease the existing plant operational problems mentioned above (high ammonia levels and foaming), and to replace fat with proteins and still keep the average biogas production at least at the same level. The reason of changing feedstock was only economical issue due to savings in production costs and possibility of selling fat.

Modernization of the biogas plant consisted in application of prefabricated ADA unit – pressure vessel with the size of about one to hundredth of the size of the bioreactor. Simple flow chart of the upgraded plant is presented in Figure 2.1.

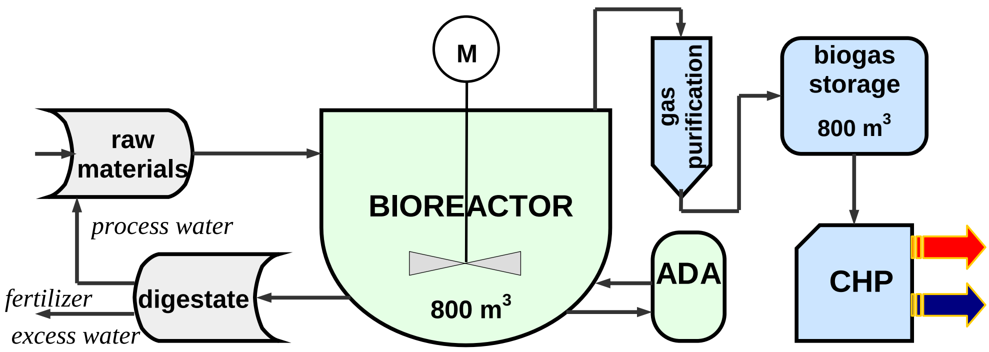

Figure 2.1 Simple flow chart of upgraded biogas plant

2.2.2. Some of ADA operating results

After technical installation the ADA-module the circulation of digestate through ADA was started. At this stage the feedstock mixture was not changed because the first aim was to stabilize the biogas reactor. Before ADA was started the free ammonia (NH_3) level in the reactor was 520 mg/dm^3 - 540 mg/dm^3. After 15 days of operation the free ammonia (NH_3) level settled to 300 mg/dm^3 – 350 mg/dm^3, what can be seen in Figure 2.2.

When the stabilization of the reactor was achieved (the reactor had never been running stable before), new substrate was introduced. The new substrate mixture contained protein (80% of VS) and fat (20% of VS) from pharmaceutical industry. Careful monitoring of the ADA and the biogas plant was continued during substrate change. An interesting side effect from the change was that during this time the floating layer that had been present in the reactor over two years broke up and got pumped out the normal way with the digestate.

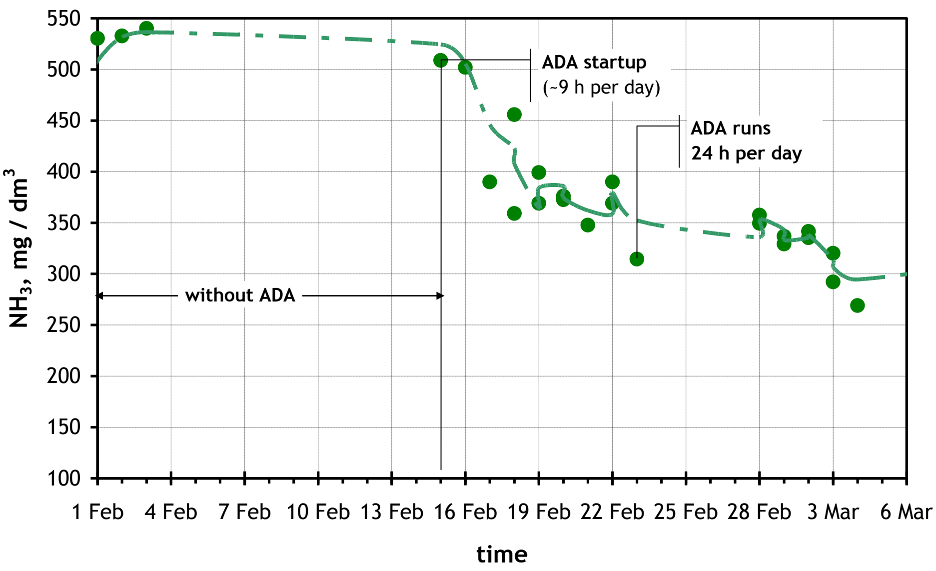

Figure 2.2. Decreasing ammonia level with ADA-treatment

Before protein feed it has not been possible to fill the reactor more than ~91% of the total volume. After changing the substrate mixture it was possible to fill the reactor up to 96%. This improved the use of the reactor volume and also helped with (too) short retention time.

The effect of ADA on the digestate was followed by analysing pH and free ammonia as a function of time from samples taken during ADA-treatment. The concentration of ammonia was measured with ammonia-selective electrode and pH was measured with pH-meter. Exemplary test's results, pH and ammonia concentration, are presented in Figure 2.3.

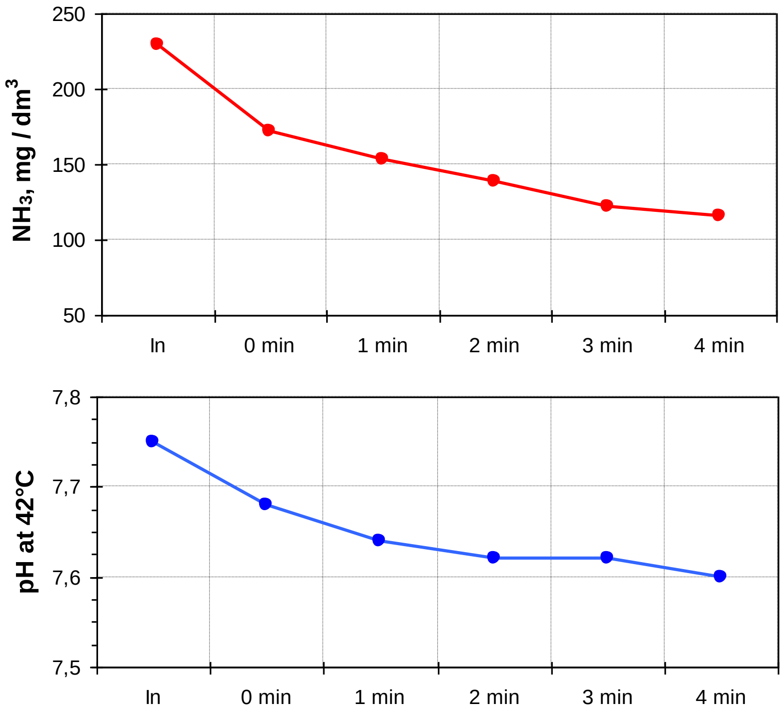

Figure 2.3 Effect of pressurized ADA-treatment on pH and the concentration of free ammonia

After reducing the amount of fat in substrate mixture and increasing the amount of protein in the mixture significant reductions of the free ammonia in the reactor have been achieved. As a result of this the process is more stable than ever, the fluctuations in biogas production are smaller and the average gas production is higher. Also the use of the reactor volume was improved a bit after floating layer from the reactor was removed with help of the protein feed; increasing filling rate from 91 % to 96 %. This improved the use of the effective reactor volume.

Direct benefits for HP Energi after ADA upgrade are savings in material costs (less fat needed), increased earnings in selling energy and less need for supervision at the biogas plant because process is running stable.

Compared to the HP Energi's biogas plant's own history it has never been running as well as it is today with the ADA. This shows also the function of ADA: ADA improves a biogas process in relation to its own history. Therefore it is impossible to give universal figures or promises of ADA's capability; each case has to be evaluated individually.

3. Conclusions

Anaerobic digestion seems to be the most environmentally friendly way of utilization of organic wastes. It is a result of its numerous merits, like efficient natural biological decay of organic matter, generation of renewable fuel – biogas, reduction of odors and pathogens, improvement in manuring effect due to using digestion residues to point out only a few. It is also worth to mention the avoided problems related to the uncontrolled greenhouse gasses emission, avoided air pollutant emission due to replacing of fossil fuels, reduced nutrient loading to surface and ground water.

Anaerobic digestion of some kinds of biowastes could cause serious operational problems. It particularly refers to protein-rich material, which often results in ammonia accumulation in a digester. As it was presented in the paper, applying of pressurized process with ADA reactor significantly improves the process stability by an increase in buffer capacity of sludge. ADA technology is a full scale commercial product and is especially recommended for feedstock which can cause troubles in a typical digestion technology. This type of material are e.g. slaughterhouses wastes. Experiences with the Danish agricultural biogas plant modernization with ADA reactor met investor's expectancy and confirmed the usability of this technology. The main advantage of ADA solution is its simplicity – the idea was taken from nature.

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